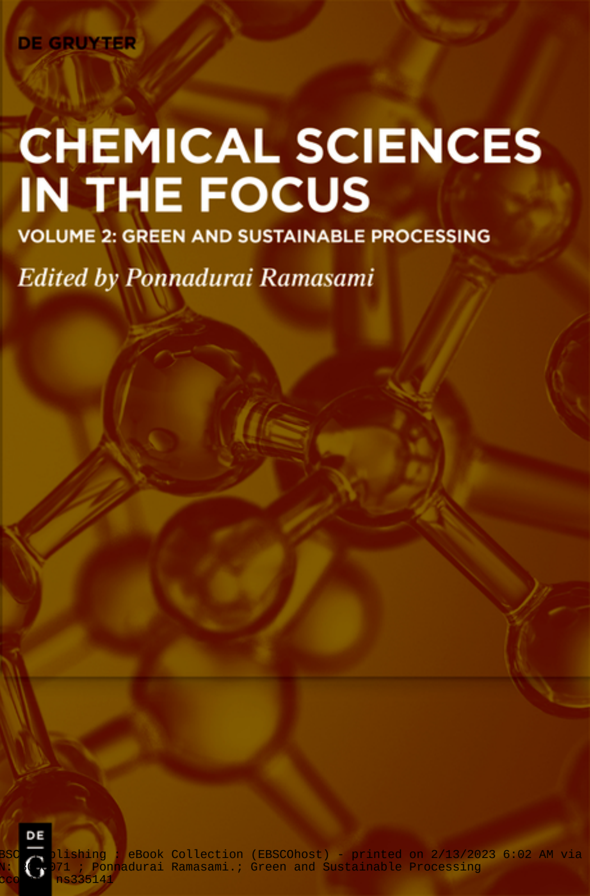


DE GRUYTER

CHEMICAL SCIENCES IN THE FOCUS

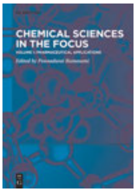
VOLUME 2: GREEN AND SUSTAINABLE PROCESSING

Edited by Ponnadurai Ramasami

Ponnadurai Ramasami (Ed.)

Chemical Sciences in the Focus

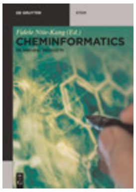
Also of interest



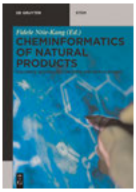
Chemical Sciences in the Focus
Volume 1: Pharmaceutical Applications
Ponnadurai Ramasami (Ed.), 2021
ISBN 978-3-11-071072-4, e-ISBN 978-3-11-072659-6

Chemical Sciences in the Focus
Volume 3: Theoretical and Computational Chemistry Aspects
Ponnadurai Ramasami (Ed.), 2021
ISBN 978-3-11-073974-9, e-ISBN 978-3-11-073976-3

Computational Chemistry Methods.
Applications
Ponnadurai Ramasami (Ed.), 2020
ISBN 978-3-11-062906-4, e-ISBN 978-3-11-063162-3



Chemoinformatics of Natural Products
Volume 1: Fundamental Concepts
Fidele Ntie-Kang (Ed.), 2020
ISBN 978-3-11-057933-8, e-ISBN 978-3-11-057935-2



Chemoinformatics of Natural Products
Volume 2: Advanced Concepts and Applications
Fidele Ntie-Kang (Ed.), 2021
ISBN 978-3-11-066888-9, e-ISBN 978-3-11-066889-6

Physical Sciences Reviews.
e-ISSN 2365-659X

Chemical Sciences in the Focus

Volume 2: Green and Sustainable Processing

Edited by
Ponnadurai Ramasami

DE GRUYTER

Editor
Prof. Dr. Ponnadurai Ramasami
Computational Chemistry Group,
Department of Chemistry, Faculty of Science,
University of Mauritius,
Reduit 80837,
Mauritius

Department of Chemistry,
College of Science, Engineering and Technology,
University of South Africa,
P.O. Box 392, Pretoria 0003,
South Africa
E-mail address: p.ramasami@uom.ac.mu

ISBN 978-3-11-072659-6
e-ISBN (PDF) 978-3-11-072614-5
e-ISBN (EPUB) 978-3-11-072618-3

Library of Congress Control Number: 2021940634

Bibliographic information published by the Deutsche Nationalbibliothek
The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at http://dnb.dnb.de.

Cover image: BlackJack3D/E+/Getty Images
Typesetting: TNQ Technologies Pvt. Ltd.
Printing and binding: CPI books GmbH, Leck

www.degruyter.com

Preface of the Book of Proceedings of the Virtual Conference on Chemistry and its Applications (VCCA-2020)

A virtual conference on chemistry and its applications (VCCA-2020) was organized online from 1st to 31st August 2020. The theme of the virtual conference was “Research and Innovations in Chemical Sciences: Paving the Way Forward”.

There were 190 presentations for the virtual conference with 300 participants from 50 countries. A secured platform was used for virtual interactions of the participants. After the virtual conference, there was a call for full papers to be considered for publication in the conference proceedings. Manuscripts were received and they were processed and reviewed as per the policy of De Gruyter.

This book, volume 2, is a collection of the eleven accepted manuscripts covering green and sustainable processing.

Ittibenjapong et al reported on *Catunaregam tomentosa* fruit extracts and AgNPs synthesized from these extracts. Omokpariola and Omokpariola evaluated the health and exposure risk assessment of heavy metals from the usage of rainwater from inhabitants of four oil producing area of Rivers State, Nigeria. Chinda and Chinda investigated the awareness level of social media and how it is used for learning in an era of Corona virus by Chemistry students in tertiary institutions in Rivers State Nigeria. Adeniyi and Giwa determined the concentration of cadmium, calcium, iron, lead, manganese and zinc in the groundwater sources in selected locations in Aboru, Igando, Akesanand Obadore, Lagos, Nigeria. Narod and Narrainsawmy focused on a detailed analysis of the feedback obtained from educators regarding the evaluation of the chemistry curriculum. Lowe and Canal shared their experience in including Polymer science modules to the curriculum at two neighbouring post-secondary institutes and emphasized on educating post-secondary students from different disciplines with polymer science. Constance and Amadou reported on the Influence of calcium oxide on low temperature attack two types of bauxite namely gibbsite and boehmite from Guinea. Odukoya et al studied the volatile components generated from fresh egg, adult female and male of *Pestarella tyrrhena* and these were assessed using a two-dimensional gas chromatography coupled to time-of-flight mass spectrometry to understand their contribution to odour production. Hernández-Mendoza et al compared the quadrupole inductively coupled plasma mass spectrometry (ICP-QMS) detection and the sector field ICP-MS (ICP-SFMS) for the quantification of elements such as arsenic, cadmium, copper, lead, zinc and uranium in drinking water. Lawrence et al studied the decontamination of laboratory wastewater with an activated carbon derived from maize cob, an agricultural waste, to ascertain its adsorption effectiveness for water treatment. Ejeromedoghene et al presented on the progress in the preparation

https://doi.org/10.1515/9783110726145-201

of polymeric ionic liquids via different polymerization reactions and highlight the advances in the fabrications of polymeric ionic liquids based on smart polymeric materials.

I hope that these chapters of this volume 2 will add to literature and they will be useful references for researchers.

To conclude, VCCA-2020 was a successful event and I would like to thank all those who have contributed. I would also like to thank the Organising and International Advisory committee members, the participants and the reviewers.

Prof. Ponnadurai Ramasami

Contents

List of contributing authors

Adeleke Adeniyi
Lagos State University
Chemistry
Ojo, Lagos
Nigeria
lekeadeniyi@yahoo.com

Sheriff Adewuyi
Federal University of Agriculture Abeokuta
Department of Chemistry
Abeokuta, Ogun
Nigeria
adewuyis@funaab.edu.ng

Lawrence Olusegun Ajala
Akanu Ibiam Federal Polytechnic
Unwana Nigeria
Department of Science Laboratory Technology
Afikpo, Ebonyi
Nigeria
loajala@akanuibiampoly.edu.ng

Ewa Ezeali Ali
Akanu Ibiam Federal Polytechnic
Unwana Nigeria
Department of Science Laboratory Technology
Afikpo, Ebonyi
Nigeria
aliwas5000@gmail.com

Nancy Lara Almazán
Instituto Nacional de Investigaciones Nucleares
Laboratorio de Investigación en Forense Nuclear
Ocoyoacac, Mexico
Mexico
nancy.lara@inin.gob.mx

Marie Constance Béavogui
Laboratoire de Recherche Appliquée en
Géoscience et Environnement
Institut Supérieur des Mines et Géologie de Boké,
BP 84, Republic of Guinea - Metallurgy
Boke
Guinea
beavoguimarie11@gmail.com

John P. Canal
Simon Fraser University - Chemistry
8888 University Drive, Burnaby, British Columbia
V5A 1S6
Canada
jcanal@sfu.ca

Punnita Chaichamni
Mahidol Wittayanusorn School
Nakhon Pathom
Thailand
s6107721@mwit.ac.th

Sekou Amadou Conde
RUSAL
Department of Chemistry Rusal Guinea(Fria)
FRIA
Guinea
sekou.conde@rusal.com

Abraham Kuri Cruz
Instituto Nacional de Investigaciones Nucleares
Ocoyoacac, Mexico
Mexico
abraham.kuricruz@nist.gov

Onome Ejeromedoghene
Southeast University
School of Chemistry and Chemical Engineering
Nanjing 210096
China
armstrong4onomsky@yahoo.com

Olayiwola Giwa
CESSED
Ojo
Nigeria
rafiugiwaofficial@gmail.com

Inocent Gouado
University of Douala Faculty of Sciences
Laboratory of Food Sciences and Nutrition
Douala
Cameroon
gouadoi@yahoo.fr

https://doi.org/10.1515/9783110726145-202

Elizabeth Teresita Guzmán
Instituto Nacional de Investigaciones Nucleares
Ocoyoacac, Mexico
Mexico
elizabeth.romero@inin.gob.mx

Monisola Ikhile
University of Johannesburg - Doornfontein Campus
Department of Chemical Sciences
Doornfontein, Gauteng
South Africa
mikhile@uj.ac.za

Chanyapat Ittibenjapong
Mahidol Wittayanusorn School
Nakhon Pathom
Thailand
S6107717@mwit.ac.th

Prit Kanjanahitanon
Mahidol Wittayanusorn School
Nakhon Pathom
Thailand
s6107733@mwit.ac.th

Eugenie Kayitesi
University of Pretoria
Department of Food and Consumer Science
Pretoria, Gauteng
South Africa
eugenie.kayitesi@up.ac.za

Ahmed Amara Konaté
Laboratoire de Recherche Appliquée en Géoscience et Environnement, Institut Supérieur des Mines et Géologie de Boké, BP 84, Republic of Guinea - Géologie
BOKE
Guinea
konateahmed@hotmail.com

Jimmy Lowe
British Columbia Institute of Technology
Chemistry
Burnaby, British Columbia
Canada
Jimmy_Lowe@bcit.ca

María Judith Rios Lugo
Universidad Autonoma de San Luis Potosi
San Luis Potosi, San Luis Potosi
Mexico
judith.rios@uaslp.mx

Héctor Hernández Mendoza
Universidad Autonoma de San Luis Potosi
San Luis Potosi, San Luis Potosi
Mexico
hector.mendoza@uaslp.mx

Mokgadi Precious Mphahlele
University of Johannesburg - Doornfontein Campus
Department of Chemical Sciences
Doornfontein, Gauteng
South Africa
mokgadimphahlele25@gmail.com

Fawzia Bibi Narod
Mauritius Institute of Education
Science Education
Reduit, Moka
Mauritius
f.narod@mie.ac.mu

Vickren Narrainsawmy
Mauritius Institute of Education
Science Education
Reduit, Moka
Mauritius
vickren.narrainsawmy@mie.ac.mu

Derek Tantoh Ndinteh
University of Johannesburg - Doornfontein Campus
Department of Chemical Sciences
Doornfontein, Gauteng
South Africa
dndinteh@uj.ac.za

Jean Michel Njinkoue
University of Douala Faculty of Sciences
Laboratory of Food Sciences and Nutrition
Douala
Cameroon
jmnjinkoue@yahoo.fr

Emmanuel Okewe Nnachi
Akanu Ibiam Federal Polytechnic Unwana Nigeria
Department of Science Laboratory Technology
Afikpo, Ebonyi
Nigeria
okewetic@yahoo.co.uk

Olayinka Oderinde
Southeast University
School of Chemistry and Chemical Engineering
Nanjing 210096
China
yinkaoderinde@yahoo.com

Johnson Oluwaseun Odukoya
University of Johannesburg - Doornfontein Campus
Department of Chemical Sciences
Doornfontein, Gauteng
South Africa
Federal University of Technology Akure
Department of Chemistry
Akure, Ondo
Nigeria
joodukoya@futa.edu.ng

Patrick Leonard Omokpariola
National Agency for Food and Drug Administration and Control - Chemical Regulation and Regulation Directorate
Ikeja, Lagos
Nigeria
olaleo06@yahoo.com

Daniel Omeodisemi Omokpariola
Nnamdi Azikiwe University
Pure and Industrial Chemistry
Awka, Anambra
Nigeria
omeodisemi@gmail.com

Valentine Ifenna Onwukeme
Nnamdi Azikiwe University Faculty of Natural Sciences
Department of Chemistry
Awka, Anambra
Nigeria
valentineifenna@yahoo.com

Sirirat Panich
Mahidol Wittayanusorn School
Nakhon Pathom
Thailand
sirirat.pan@rmutp.ac.th

Nuchutha Thamsumet
Mahidol Wittayanusorn School
Nakhon Pathom
Thailand
nuchutha.tha@mwit.ac.th

Loginova Irina Viktorovna
Ural Federal University, Yekaterinburg, Russia - Metallurgy
Yekaterinburg, Russia
Russian Federation
loginova_irina@mail.ru

Chinda Worokwu
Ignatius Ajuru University of Education
Chemistry
Port Harcourt, Rivers
Nigeria
wororolly@gmail.com

Chanyapat Ittibenjapong, Prit Kanjanahitanon,
Punnita Chaichamni, Sirirat Panich and Nuchutha Thamsumet*

1 Green synthesis of silver nanoparticles from *Catunaregam tomentosa* extract

Abstract: Silver nanoparticles (AgNPs) have been widely used in many fields (e.g., sensors, medical supplies, food, cosmetics, medicines, etc.) due to their unique properties such as optical property, antibacterial property, and high conductivity. AgNPs are normally synthesized by chemical, physical, or biological methods. Among these methods, biological synthesis or green synthesis of AgNPs has drawn much attention since it is an easy and environmental-friendly method. Herein, AgNPs synthesized using *Catunaregam tomentosa* extracts were studied. The extracts obtained from different *C. tomentosa* fruit were found to be blue, green, and brown. It was found from the foam test and IR spectra that all extracts (blue, green, and brown extracts) contained saponins. According to the DPPH assay, the blue and the green extracts had the antioxidant activities of 84.47 ± 12.13 and 47.66 ± 2.86 mg ascorbic acid equivalent/g of *C. tomentosa* powder, respectively. This showed that the blue and the green extracts could act as reducing agents in AgNPs synthesis. The successfully synthesized AgNPs using *C. tomentosa* extracts showed the surface plasmon resonance peak at 400 nm corresponding to literatures. The particle sizes and zeta potential values measured by dynamic light scattering also indicated the size stability of the synthesized AgNPs during seven-day period with no significant difference ($P > 0.05$).

Keywords: antioxidant; *Catunaregam tomentosa*; green synthesis; plant extract; silver nanoparticles.

1.1 Introduction

Silver nanoparticles (AgNPs) have been extensively used in medical area, healthcare products, cosmetics, food industry, pharmaceutical industry, drug delivery, engineering, mechanics, optical sensors, and chemical industries [1, 2]. These are due to their unique properties including antibacterial [3, 4], antiviral [5], antifungal [6, 7], anti-inflammatory

---

***Corresponding author: Nuchutha Thamsumet**, Mahidol Wittayanusorn School, Nakhon Pathom, Thailand, E-mail: nuchutha.tha@mwit.ac.th. https://orcid.org/0000-0001-5451-9850
Chanyapat Ittibenjapong, Prit Kanjanahitanon and Punnita Chaichamni, Mahidol Wittayanusorn School, Nakhon Pathom, Thailand
Sirirat Panich, Faculty of Science and Technology, Rajamangala University of Technology Phra Nakhon, Bangkok, Thailand

This article has previously been published in the journal Physical Sciences Reviews. Please cite as: C. Ittibenjapong, P. Kanjanahitanon, P. Chaichamni, S. Panich, and N. Thamsumet "Green synthesis of silver nanoparticles from *Catunaregam tomentosa* extract" *Physical Sciences Reviews* [Online] 2021, 6. DOI: 10.1515/psr-2020-0094 | https://doi.org/10.1515/9783110726145-001

[1, 8], catalytic, optical, and electrical properties [1, 2]. However, these properties, especially biological or pharmacological activity, are found to depend on the characteristics of nanoparticles such as size, shape, morphology, surface chemistry, size distribution, and aggregation [2]. Therefore, synthesized nanoparticles are usually characterized by these techniques including UV–Vis spectroscopy, dynamic light scattering (DLS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffractometry (XRD), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and localized surface plasmon resonance (LSPR) to achieve highest potential of their properties [2]. Typically, physical and chemical methods (e.g., evaporation-condensation, spark discharging, pyrolysis, laser ablation, electrochemical reduction, thermal decomposition, sono-decomposition, chemical reduction, etc.) are employed to synthesize AgNPs [2]. Although no hazardous chemicals are used in physical methods, high energy requirement, imperfection of nanoparticle surfaces, and nonuniform properties are major drawbacks of these methods. Chemical methods provide ease of production with higher yield compared to physical methods, but hazardous and toxic by-products are generated during syntheses [1, 2]. These might cause a serious safety issue when AgNPs are used in consumer products. Therefore, environmental-friendly approaches of AgNPs syntheses or ‘green syntheses’ are needed. Many researchers reported the use of microorganisms, biomolecules, and plants as reducing and capping agents for AgNPs syntheses. Not only are there nontoxic residues after syntheses, but green syntheses also provide cost-effective and simple way to produce well-defined size, shape and distribution of AgNPs [1, 2]. Among these green reagents, plant extracts seem to be the promising choice for industrial-scale production of metal nanoparticles since they provide single-step and low-cost upscaling syntheses [1, 9]. To date, several plant extracts from different parts including leaf, bark, stem, root, flower, fruit, peel, and seed used for AgNPs syntheses are reported in literatures [1, 10, 11]. Biomolecules found in plant extracts such as alkaloids, phenolic compounds, terpenoids, tannins, saponins, flavones, quinones, proteins, enzymes and polysaccharides are responsible for Ag^+ reduction and are potentially capping and stabilizing agents [1, 10, 11].

Fruit extracts are one of the plant parts that have been widely studied for AgNPs syntheses as listed in Table 1.1. Not only are being local fruit chosen for AgNPs syntheses, but there are also many reasons underpinning this. For example, Cashew apple (*Anacardium occidentale* L.) was chosen due to being a low-cost by-product from cashew nut industry and potential antibacterial agents [12]. *Annona reticulata* L. fruit or custard apple [13], *Averrhoa bilimbi* L. Fruit [14], *Momordica cymbalaria* fruit [15], *Quercus infectoria* fruit or oak [16], *Sambucus nigra* fruit or European black elderberry [17], *Tanacetum vulgare* fruit or tansy [18], and *Tribulus terrestris* L. fruit [19] have long been employed in traditional medicine for various treatments and are found to exhibit antioxidant activity. *Catunaregam tomentosa* (Blume ex DC) Tirveng (Figure 1.1), a medium height tree, cream white flowers, and berry fruits with yellow hairs, is found in many countries in Southeast Asia including Burma, Vietnam, Malaysia, and also Thailand [20]. Indigenous knowledge indicated that its extract has been used as a

Table 1.1: Green synthesis of silver nanoparticles using fruit extracts.

Plants	AgNPs synthesis conditions	Size, λ_{max}, shape, and stability of AgNPs	Antioxidant of extract	References
Anacardium occidentale L. fruit	1 drop of extract/ 1 mL of 1 mM $AgNO_3$	39–56 nm with 45 nm in average (SEM), λ_{max} 405 nm, spherical	N/A	[12]
Annona reticulata L. fruit	Extract:0.01 M $AgNO_3$ (1:9 ratio)	12.72 nm (XRD), λ_{max} 482 nm, spherical	N/A	[13]
Averrhoa bilimbi L. fruit	0.1 mL extract/5 mL of 1 mM $AgNO_3$	50–175 nm, λ_{max} 420 nm, hexagonal or rhomboidal	N/A	[14]
Averrhoa carambola fruit	10 mL of 5% w/v extract/4 mM $AgNO_3$	10–40 nm with 20 nm in average (TEM), λ_{max} 448 nm, spherical	N/A	[23]
Lantana camara fruit	10 mL extract/ 90 mL of 1 mM $AgNO_3$	12.55–12.99 nm (TEM), λ_{max} 439 nm, spherical	N/A	[24]
Momordica charantia fruit	1 mL extract/50 mL of 5 mM $AgNO_3$	16 nm (TEM), λ_{max} 460 nm	N/A	[25]
Momordica cymbalaria fruit	10 mL extract/ 90 mL of 1 M $AgNO_3$	15.5 nm, λ_{max} 450 nm, spherical (AFM, SEM)	60.4% free radical scavenging activity (DPPH assay)	[15]
Piper longum fruit	10 mL extract/ 50 mL of 1 mM $AgNO_3$	15–200 nm, average 46 nm (DLS), λ_{max} 430 ± 6 nm, spherical	216 ± 0.7 mg GA/g sample	[26]
Quercus infectoria fruit	40 mL of 10% w/v extract/10 mL of 1 mM $AgNO_3$	40 nm (DLS), spherical, −25.3 mV	N/A	[16]
Sambucus nigra fruit	16.6 mL extract/ 200 mL of 0.03% $AgNO_3$	20–80 nm (TEM), λ_{max} 426 nm, spherical, −20.9 mV	N/A	[17]
Tanacetum vulgare fruit	1.8 mL extract/ 50 mL of 1 mM $AgNO_3$	10–40 nm, λ_{max} 452 nm, −26 mV	N/A	[18]
Tribulus terrestris L. fruit	100 mL extract/ 1 mM $AgNO_3$	22 nm (TEM), λ_{max} 435 nm, spherical	N/A	[19]
Vitis Vinifera fruit	5 mL extract/95 mL of 1 mM $AgNO_3$	30–40 nm (SEM), λ_{max} 450–470 nm, spherical	N/A	[27]
Vitis Vinifera fruit	10 mL extract/ 10 mL of 20 mM $AgNO_3$	2–40 nm with19 nm in average (DLS), λ_{max} 450 nm, spherical	N/A	[28]

laundry detergent, body wash, and even an ingredient in traditional medicine formula in Thailand [21, 22]. Its fruit and leaf extracts also showed the significant antibacterial activity against Gram-positive bacteria, i.e., *Bacillus subtilis* and *Staphylococcus aureus* [22]. Since *C. tomentosa* fruit contains saponins [20], its extract could be employed to

Figure 1.1: *Catunaregam tomentosa* fruit and tree.

synthesize AgNPs. In this work, *C. tomentosa* fruit extracts and AgNPs synthesized from these extracts were studied.

1.2 Materials and methods

1.2.1 Chemicals and plant samples

Silver nitrate ($AgNO_3$) was purchased from POCH S.A. (Gliwice, Poland). 2,2-Diphenyl-1-picrylhydrazine (DPPH) and sodium borohydride ($NaBH_4$) were obtained from Sigma Aldrich (St. Louis, MO, USA). An analytical grade ascorbic acid was purchased from POCH S.A. (Gliwice, Poland). Methanol 95% was purchased from Fisher Chemical (Pittsburgh, PA, USA). Deionized water used in this work was generated by water purification system from Elga Purelab (Hyde Wycombe, UK). *C. tomentosa* fruit was collected from Ubon Ratchathani province, Thailand.

1.2.2 Characterization of *C. tomentosa* powder

Each color of *C. tomentosa* powder was characterized using Fourier Transform Infrared (FTIR) Spectrophotometer (PerkinElmer, Waltham, MA, USA) in the range of 450–4000 cm^{-1}.

1.2.3 Preparation and characterization of *C. tomentosa* extracts

Each dried *C. tomentosa* fruit was ground, and its powder was kept separately in a container since each fruit yielded different colors (blue, green, or brown). To prepare each of 1% w/v aqueous extract, 0.185 g of the *C. tomentosa* powder was weighed and mixed with 18.5 mL of deionized water. The mixture was stirred using a magnetic stirrer at room temperature for 20 min. It was then centrifuged using a benchtop centrifuge (Hettich EBA 20, Beverly, CA, USA) at 6000 rpm at 25 °C for 15 min and was filtered using a filter paper (Whatman Inc., Clifton, NJ, USA). Each 1% w/v extract was then diluted with deionized water to the concentrations of 0.05, 0.1, and 0.2% w/v. The absorption spectra of the extracts were recorded as a function of wavelength using a UV–Vis spectrophotometer (AquaMate 8000, Thermo Scientific, Waltham, MA, USA). The extracts were also characterized for particle sizes by dynamic light scattering (Zetasizer Nano-ZS, Malvern Panalytical, Malvern, UK).

1.2.4 Determination of saponins using foam test

Each *C. tomentosa* extract was tested for the presence of saponins using foam test by boiling 5 mL of 1.0% w/v extract in a test tube. The extract was cooled down, filtered, and diluted by adding 2 mL of distilled water. It was then shaken vigorously and observed for the development of stable foam indicating the presence of saponins.

1.2.5 Evaluation of antioxidant activity by DPPH assay

The antioxidant activity of each extract was evaluated using DPPH assay [29]. Briefly, 0.3 mL of standard solutions or samples was added to 2.7 mL of 0.10 mM DPPH dissolved in 80% v/v methanol/water. The solutions were mixed and kept in the dark for 30 min. Ascorbic acid solutions with the concentrations in the range of 0–50 ppm were used as standard solutions for constructing a calibration. The antioxidant activities were reported as mg ascorbic acid equivalent per gram of *C. tomentosa* powder.

1.2.6 Chemical synthesis of silver nanoparticles

2.00 mL of 1 mM $AgNO_3$ was added dropwise at the rate of 1 drop/s into 30 mL of 2 mM $NaBH_4$. The mixture was stirred on a magnetic stirrer at 5 °C until the addition of $AgNO_3$ solution was complete.

1.2.7 Green synthesis of silver nanoparticles

Briefly, 2.00 mL of 1 mM $AgNO_3$ was added dropwise at the rate of 1 drop/s into 30 mL of each *C. tomentosa* fruit extract. The mixture was stirred on a magnetic stirrer at room temperature until the addition of $AgNO_3$ solution was complete. Biosyntheses of AgNPs were performed using 0.05, 0.1, and 0.2% w/v blue and green extracts.

1.2.8 Characterization of silver nanoparticles

The absorption spectra of the synthesized AgNPs were obtained using the UV–Vis spectrophotometer (AquaMate 8000, Thermo Scientific, Waltham, MA, USA). Size and zeta potential were measured by dynamic light scattering (Zetasizer Nano-ZS, Malvern Panalytical, Malvern, UK).

1.3 Results and discussion

1.3.1 Characterization of *C. tomentosa* fruit powder and extracts

Three batches of *C. tomentosa* fruit powder obtained from three different fruits were found to be brown, green, and blue ranging from young to old fruit age, respectively. FTIR absorption spectra of brown, green, and blue powder depicted in Figure 1.2 showed characteristics frequencies similar to those of saponins [30, 31] and polyphenols [26]. The strong bands from 3280 to 3290 cm^{-1} belonged to O-H stretching from hydroxyl groups, which might be responsible for Ag^+ reduction [19, 23, 32]. The C–H and C=C bonds were observed at 2925 and 1634 cm^{-1}, respectively. The small shoulder of C=O at around 1715 cm^{-1} and the peak corresponding to C–O at 1032 cm^{-1} were observed in all samples. The existence of saponins was also confirmed by foam (froth) test in which all extracts yielded stable foam after shaking as shown in the inset picture in Figure 1.3.

The extracts were tested for antioxidant activities using DPPH assay. It was found that the blue and the green extracts had the antioxidant activities of 84.47 ± 12.13 and 47.66 ± 2.86 mg ascorbic acid equivalent per gram of *C. tomentosa* powder, respectively. Meanwhile, the antioxidant activity of the brown extract was not detected. The blue and the green extracts could act as reducing agents for AgNPs syntheses although % inhibition of DPPH of both extracts (15.16% for blue and 9.16% for green) were much lower than that was reported for *M. cymbalaria* fruit extract (60.4% inhibition of DPPH) [15].

According to the absorption spectra in Figure 1.3, the blue extract had the highest absorbance at 600 nm following by the green and the brown extracts, respectively. The absorbance values at 600 nm and the antioxidant activities of these extracts showed the similar trends. This could be implied that some phytochemical species in the extracts absorbing light at this wavelength acted as antioxidants or reducing agents.

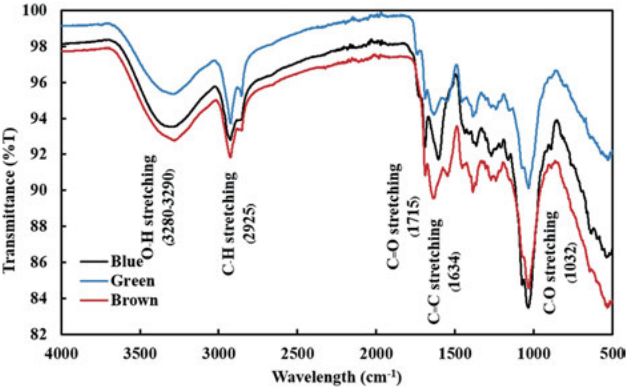


Figure 1.2: FTIR spectra of blue, green, and brown *Catunaregam tomentosa* fruit powder.

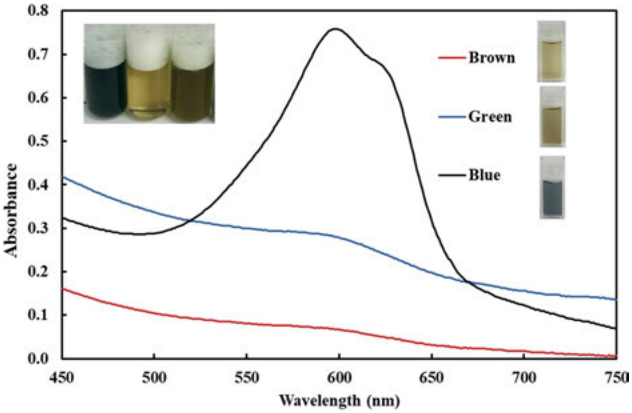


Figure 1.3: UV–Vis spectroscopy absorption spectra of the three different colors of *Catunaregam tomentosa* extracts.

The results also showed that the older age of the fruit was, the higher antioxidant capacity was obtained.

1.3.2 Characterization of AgNPs synthesized using *C. tomentosa* fruit extracts

According to the antioxidant activity result, only the blue and the green extracts of *C. tomentosa* fruit exhibited satisfied antioxidant capacity and were used for biosyntheses in this experiment. The UV-visible absorption spectra of AgNPs synthesized using 0.1% w/v blue extract illustrated in Figure 1.4 revealed the absorption peaks of the blue extract at around 600 nm and the strong surface plasmon resonance (SPR) absorption bands belonging to AgNPs at around 400 nm [32]. This value of SPR peak was in accordance with AgNPs synthesized by other fruit extracts (405–482 nm), as shown in Table 1.1. The single SPR band also indicates spherical silver nanoparticles according to Mie theory [14]. The similar pattern was also observed for the synthesized AgNPs employing the green extract. As the concentrations of both extracts were higher, the amount of AgNPs indicated by the absorbance at 400 nm increased, as shown in Figure 1.5a and 1.5b for the blue and the green extract-mediated AgNPs syntheses, respectively. It was also found that the rates of AgNPs formation using the blue extract was higher than that of the green one, which also corresponded to the antioxidant activity result mentioned earlier. When comparing between chemical synthesis (Ag^+ was reduced using $NaBH_4$) and biosynthesis using the blue extract on Day 1, it was found that no SPR band at 400 nm was observed for the biosynthesis (Figure 1.4) indicating the lower rate of AgNPs formation.

The stability of nanoparticles is often defined in terms of the certain size over a long period of time. Herein, the hydrodynamic size of AgNPs was monitored for more than

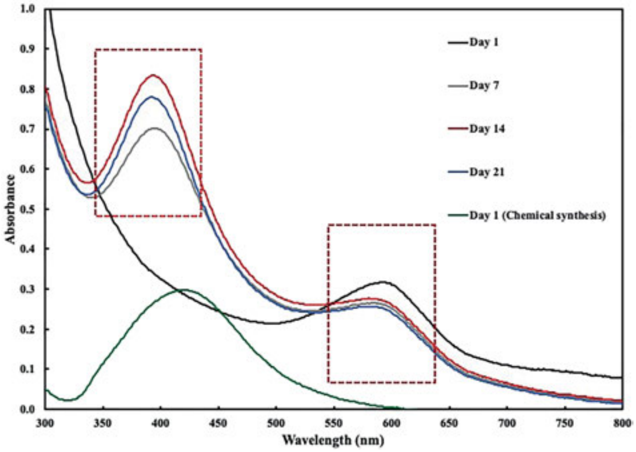


Figure 1.4: UV–Vis spectroscopy absorption spectra of AgNPs synthesized by the blue extract and by chemical synthesis ($NaBH_4$).

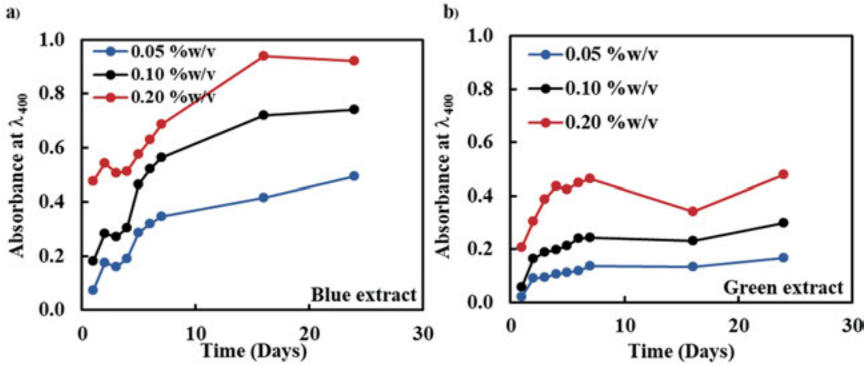


Figure 1.5: Absorption at λ_{max} for various concentrations of the (a) blue and (b) green extracts.

three weeks using dynamic light-scattering (DLS) technique. The size distribution of the synthesized AgNPs exhibited intense major peaks in which the peak responsible for the AgNPs could be clearly distinguished from those of the extracts. The measured AgNPs sizes over three weeks after syntheses using various concentrations of both extracts were depicted in Figure 1.6. First, the synthesized AgNPs with either blue or green extract were found to be stable during the observation period of time from day 1 until day 7 with no significant difference ($P > 0.05$). Secondly, the results indicated that lower concentrations of both extracts yielded smaller nanoparticle sizes. In particular, the blue extracts always resulted in smaller sizes of AgNPs when comparing the same concentrations of the blue and the green extracts. Thirdly, there was no significant difference ($P > 0.05$) between AgNPs sizes synthesized using 0.05% w/v and 0.10% w/v blue extracts. However, AgNPs size obtained by using 0.20% w/v blue extract was significantly different ($P < 0.05$) from those of the other two concentrations. It was also found that all concentrations of the green extracts provided significant difference in AgNPs sizes ($P < 0.05$). The nanoparticle sizes obtained from all concentrations of the blue extract were ranging from 69.0 to 127.6 nm corresponding to AgNPs synthesized from *A. bilimbi* L. fruit extract [14] and *Piper longum* fruit extract [26]. Meanwhile, the nanoparticles obtained from the green extract were in the range of 99.1–249.8 nm in which most of them were larger than those reported in the literatures [12–19, 23–28]. In addition, AgNPs from biosynthesis in this work were found to be much larger than that of the chemical synthesis, which have the average size of 37.2 nm.

The long-term stability of nanoparticle colloids was monitored not only by the particle size but also the zeta potential value (ζ), which were observed by dynamic light scattering. The measurement of the electrostatic charge magnitude indicates the change of the surface charge on nanoparticles in a given environment over a period of time. A large positive or negative zeta potential value indicates high repulsive force, which prevents colloidal particles from agglomerating. This parameter can therefore be used to predict the stability of particles. The zeta potential values of the synthesized AgNPs employing the blue and the green extracts at the concentration of 0.2% w/v were −19.37 ± 1.10 and −27.73 ± 1.35 mV, respectively. These values were similar to the synthesized AgNPs using *Q. infectoria* fruit [16], *S. nigra* fruit [17], and *T. vulgare* fruit [18]. Moreover, the zeta potential values of these two colloidal solutions were found to be consistent up to 7 days. The negative zeta potential value indicated that the surface of the synthesized nanoparticles was negatively charged. Meanwhile, the magnitude of the zeta potential suggested the stability of the nanoparticles, which possibly arose from the use of the extracts acting as capping or stabilizing agent [33, 34].

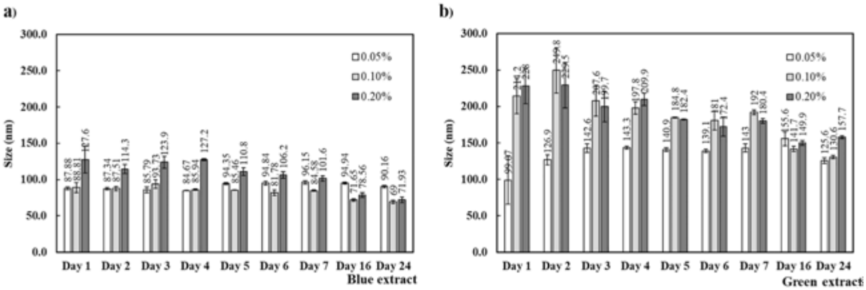


Figure 1.6: Particle size measurement of synthesized AgNPs using (a) the blue extract and (b) the green extract from *Catunaregam tomentosa* fruit powder.

1.4 Conclusions

Simple ecofriendly one-step AgNPs syntheses using *C. tomentosa* fruit extracts were successfully carried out in this work. Herein, both extracts (blue and green) containing saponins and other phytochemical species acted as reducing agents in Ag^+ reduction. Interestingly, all concentrations of the blue extracts were found to yield significantly smaller sizes of AgNPs than that of the green ones. The sizes of AgNPs obtained from all concentrations of the blue extract were in the same range as those of fruit extracts in the literatures. Although both extracts yielded larger sizes of AgNPs than that of the chemical synthesis, the biosynthesized AgNPs were found to be stable longer. The sizes of AgNPs obtained from either the blue or the green extracts were not statistically different during 7-day period after syntheses indicating the stability of the synthesized AgNPs. The extracts were not only responsible for reducing Ag^+ to Ag, but also stabilizing the AgNPs. The *C. tomentosa* fruit was therefore a promising choice for cost-effective, green, and efficient AgNPs syntheses that might be useful for various applications including healthcare and medicine.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.
Research funding: This work was supported by Mahidol Wittayanusorn School, Thailand.
Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Ahmed S, Ahmad M, Swami BL, Ikram S. A review on plants extract mediated synthesis of silver nanoparticles for antimicrobial applications: a green expertise. J Adv Res 2016;7:17–28.
2. Zhang XF, Liu ZG, Shen W, Gurunathan S. Silver nanoparticles: synthesis, characterization, properties, applications, and therapeutic approaches. Int J Mol Sci 2016;17:1–34.
3. Tang S, Zheng J. Antibacterial activity of silver nanoparticles: structural effects. Adv Health Mater 2018;7:1–10.
4. Salomoni R, Leo P, Montemor A, Rinaldi B, Rodrigues M. Antibacterial effect of silver nanoparticles in Pseudomonas aeruginosa. Nanotechnol Sci Appl 2017;10:115–21.
5. Salleh A, Naomi R, Utami ND, Mohammad AW, Mahmoudi E, Mustafa N, et al. The potential of silver nanoparticles for antiviral and antibacterial applications: a mechanism of action. Nanomaterials 2020;10:2–20.
6. Khatami M, Mortazavi SM, Kishani-Farahani Z, Amini A, Amini E, Heli H. Biosynthesis of silver nanoparticles using pine pollen and evaluation of the antifungal efficiency. Iran J Biotechnol 2017; 15:95–101.
7. Nadhe SB, Singh R, Wadhwani SA, Chopade BA. Acinetobacter sp. mediated synthesis of AgNPs, its optimization, characterization and synergistic antifungal activity against C. albicans. J Appl Microbiol 2019;27:445–58.

8. Ahmad S, Munir S, Zeb N, Ullah A, Khan B, Ali J, et al. Green nanotechnology: a review on green synthesis of silver nanoparticles—an ecofriendly approach. Int J Nanomed 2019;2019:5087–107.
9. Alsammarraie FK, Wang W, Zhou P, Mustapha A, Lin M. Green synthesis of silver nanoparticles using turmeric extracts and investigation of their antibacterial activities. Colloids Surf B Biointerfaces 2018;171:398–405.
10. Rajeshkumar S, Bharath LV. Mechanism of plant-mediated synthesis of silver nanoparticles – a review on biomolecules involved, characterisation and antibacterial activity. Chem Biol Interact 2017;273:219–27.
11. Kulkarni N, Muddapur U. Biosynthesis of metal nanoparticles: a review. J Nanotechnol 2014;2014: 1–8.
12. Mukunthan KS, Balaji S. Cashew apple juice (*Anacardium occidentale* L.) speeds up the synthesis of silver nanoparticles. Int J Green Nanotechnol 2012;4:71–9.
13. Ghotekar S. Biosynthesis of silver nanoparticles using unripe fruit extract of *Annona reticulata* L. and its characterization. World J Pharm Pharmaceut Sci 2015;4:1304–12.
14. Isaac RSR, Sakthivel G, Murthy C. Green synthesis of gold and silver nanoparticles using *Averrhoa bilimbi* fruit extract. J Nanotechnol 2013;2013:1–6.
15. Swamy MK, Akhtar MS, Mohanty SK, Sinniah UR. Synthesis and characterization of silver nanoparticles using fruit extract of *Momordica cymbalaria* and assessment of their in vitro antimicrobial, antioxidant and cytotoxicity activities. Spectrochim Acta 2015;151:939–44.
16. Heydari R, Rashidipour M. Green synthesis of silver nanoparticles using extract of oak fruit hull (jaft): synthesis and in vitro cytotoxic effect on MCF-7 cells. Int J Breast Cancer 2015;2015: 846743–6.
17. David L, Moldovan B, Vulcu A, Olenic L, Perde-Schrepler M, Fischer-Fodor E, et al. Green synthesis, characterization and anti-inflammatory activity of silver nanoparticles using European black elderberry fruits extract. Colloids Surf B Biointerfaces 2014;122:767–77.
18. Dubey SP, Lahtinen M, Sillanpaa M. Tansy fruit mediated greener synthesis of silver and gold nanoparticles. Process Biochem 2010;45:1065–71.
19. Gopinath V, MubarakAli D, Priyadarshini S, Priyadharsshini NM, Thajuddin N, Velusamy P. Biosynthesis of silver nanoparticles from *Tribulus terrestris* and its antimicrobial activity: a novel biological approach. Colloids Surf B Biointerfaces 2012;96:69–74.
20. Catunaregam tomentosa. Pharmacognosy plants herbal herb traditional medicine alternative botany; 2020. Available from: http://www.epharmacognosy.com/2020/06/catunaregam-tomentosa.html [Accessed 23 Oct 2020].
21. Junlatat J, Thorajak P, Peng-ngummuang K. Anti-inflammatory effect of *Catunaregam tomentosa* fruit extract. J Tradit Thai Med Res 2018;4:58–65.
22. Thimabut K, Keawkumpai A, Permpoonpattana P, Klaiklay S, Chumkaew P, Kongrit D, et al. Anti bacterial potential of extracts of various parts of *Catunaregam tomentosa* (Blume ex DC) Tirveng and their effects on bacterial granularity and membrane integrity. Trop J Pharmaceut Res 2018;17: 875–82.
23. Gavade SJM, Nikam GH, Dhabbe RS, Sabale SR, Tamhankar BV, Mulik GN. Green synthesis of silver nanoparticles by using carambola fruit extract and their antibacterial activity. Adv Nat Sci Nanosci Nanotechnol 2015;6:045015–6.
24. Sivakumar P, Nethradevi C, Renganathan S. Synthesis of silver nanoparticles using *Lantana camara* fruit extract and its effect on pathogens. Asian J Pharmaceut Clin Res 2012;5:97–101.
25. Malaikozhundan B, Vaseeharan B, Vijayakumar S, Sudhakaran R, Gobi N, Shanthini G. Antibacterial and antibiofilm assessment of *Momordica charantia* fruit extract coated silver nanoparticle. Biocatal Agric Biotechnol 2016;8:189–96.

26. Reddy NJ, Nagoor D, Rani VM, Rani SS. Evaluation of antioxidant, antibacterial and cytotoxic effects of green synthesized silver nanoparticles by *Piper longum* fruit. Mater Sci Eng C Mater Biol Appl 2014;34:115–22.
27. Gnanajobitha G, Paulkumar K, Vanaja M, Rajeshkumar S, Malarkodi C, Annadurai G, et al. Fruit-mediated synthesis of silver nanoparticles using *Vitis vinifera* and evaluation of their antimicrobial efficacy. J Nanostruct Chem 2013;3:1–6.
28. Roy K, Biswas S, Banerjee PC. Green synthesis of silver nanoparticles by using grape (*Vitis vinifera*) fruit extract: characterization of the particles and study of antibacterial activity. Res J Pharm Biol 2013;4:1271–8.
29. Kim DO, Lee KW, Lee HJ, Lee CY. Vitamin C equivalent antioxidant capacity (VCEAC) of phenolic phytochemicals. J Agric Food Chem 2002;50:3713–7.
30. Almutairi MS, Ali M. Direct detection of saponins in crude extracts of soapnuts by FTIR. Nat Prod Res 2015;29:1271–5.
31. Mondal MH, Malik S, Garain A, Mandal S, Saha B. Extraction of natural surfactant saponin from soapnut (*Sapindus mukorossi*) and its utilization in the remediation of hexavalent chromium from contaminated water. Tenside Surfactants Deterg 2017;54:519–29.
32. Sharma M, Yadav S, Srivastava MM, Ganesh N, Srivastava S. Promising anti-inflammatory bio-efficacy of saponin loaded silver nanoparticles prepared from the plant *Madhuca longifolia*. Asian J Nanosci 2018;4:244–61.
33. Saeb ATM, Alshammari AS, Al-Brahim H, Al-Rubeaan KA. Production of silver nanoparticles with strong and stable anti microbial activity against highly pathogenic and multidrug resistant bacteria. Sci World J 2014;2014:1–9.
34. Ranjani S, Tamanna K, Hemalatha S. Triphala green nano colloids: synthesis, characterization and screening biomarkers. Appl Nanosci 2020;10:1269–79.

Daniel Omeodisemi Omokpariola* and
Patrick Leonard Omokpariola

2 Health and exposure risk assessment of heavy metals in rainwater samples from selected locations in Rivers State, Nigeria

Abstract: Rainwater has being getting popularity in use due to lack of portable water sources in Nigeria. The study seeks to evaluate the health and exposure risk assessment of heavy metals from the usage of rainwater from inhabitants of four oil producing area of Rivers State, Nigeria. A total of 32 rainwater samples were collected from different sampling surfaces (ambient, zinc, aluminium, asbestos and stone-coated) to analyse for arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), lead (Pb) and zinc (Zn) using inductively coupled plasma – optical emission spectrophotometer. Analysed concentration (mg/L) showed varying results across different sampling surfaces converted to average concentration (mg/kg) was below WHO/FAO recommended guideline with no issue associated. Health and Exposure risk assessment were performed on analysed results from rainwater samples as non-carcinogenic risk assessment showed that HI value is less than 1.0 indicating no risk to population who consumes rainwater across different roofing surfaces in Rivers state. Carcinogenic risk assessment showed that chromium-VI were found to be the highest contributor to cancer risk across all sampling surfaces. Special treatment and regulations should be taken into consideration especially on stone-coated roof before administering to children, as they are prone to health issues due to developing immunity compared to adults.

Keywords: average daily intake, heavy metals concentration, Nigeria, Rivers State, risk assessment

2.1 Methodology

Rainwater remains a potential source of clean water compared to other water sources [1], however, atmospheric contamination from an array of natural and industrial activities, mode of rainwater collection and storage influence human health and wellbeing from consumption [2, 3]. These contaminants includes gaseous release from carbon oxides, sulphur oxides, nitrogen oxides, ammonia, methane, aerosols, that are chemical precursor for reaction (hydration, polymerization, redox, and

---

***Corresponding author: Daniel Omeodisemi Omokpariola**, Department of Pure and Industrial Chemistry, Nnamdi Azikiwe University, Awka, Nigeria, E-mail: omeodisemi@gmail.com. https://orcid.org/0000-0003-1360-4340

Patrick Leonard Omokpariola, Directorate of Chemical Evaluation and Regulation, National Agency for Food, Drug Administration and Control, Lagos, Nigeria, E-mail: olaleo06@yahoo.com

This article has previously been published in the journal Physical Sciences Reviews. Please cite as:
D. O. Omokpariola and P. L. Omokpariola "Health and exposure risk assessment of heavy metals in rainwater samples from selected locations in Rivers State, Nigeria" *Physical Sciences Reviews* [Online] 2021, 7.
DOI: 10.1515/psr-2020-0090 | https://doi.org/10.1515/9783110726145-002

hydrolysis) with other pollutants such as metals that transforms soluble metallic ions in different mediums thus leading to increased risk for exposure and toxicity in humans [4–8].

USEPA [5] classified metals based on health effects – nutritionally essential such as Co, Cr (III), Cu, Fe, Mn, Mo, Se, Zn, non-essential with possible beneficial effect such as B, Ni, Si, Vn and non-essential with no beneficial effect such as Al, Sb, As, Ba, Be, Cd, Pb, Hg, Ag, which are under debate by WHO and other critics. Several physiochemical studies has being conducted on rainwater samples in Nigeria and beyond without due cause to the health and exposure risk assessment in human from usage of rainwater [9–13].

The purpose of this study was to identify sampling surfaces available for rainwater collection across locations in Rivers State, determine heavy metal content analytically, conduct its level with WHO/FAO standards for drinking water and determine potential health and exposure risk by cumulative carcinogenic and non-carcinogenic risk for children and adults. Finally to assist environmental and health protection agency in decision-making process in Nigeria.

2.2 Methodology

2.2.1 Sampling site and methodology

Rivers State lies between latitude 4.8581°N and longitude, 6.9209°E covering total area of 11,077 km^2 bounded on the South by the Atlantic Ocean, to the North by Imo State and Abia State, to the East by Akwa Ibom State, and to the West by Bayelsa State. It is located in south-south Nigeria with multilingual and diverse culture, which has existed due to economic importance since it was a route for transporting palm produces, fishing and different agricultural activities during the British conquest in Nigeria [14]. Since the discovery of crude in Southern Nigeria, Rivers state has created economic relief to Nigeria's Gross Domestic Product of over $500 Billion, which has brought multinational companies and social amenities thus increased population of over seven million [15].

The sampling location was Ogale, Eleme (4.79°N, 7.12°E), Rumuodomaya/Rumuodome, Obio-Akpor (4.88°N, 7.02°E), Diobu, Port-Harcourt (4.77°N, 6.99°E) and Chokocho, Etche (4.99°N, 7.05°E) in Rivers State. Figure 2.1 shows the map of study area. The sampling period was from April to October 2019 in three regiments: Early rain (April–June), mid rain (July–August) and late rain (September–October). Rainwater samples were harvested above 1 m using a precleared bowl and transferred into four different 500 mL pre-treated polyethylene bottle from different sampling surfaces: ambient and different roof materials: zinc, aluminium, asbestos, and stone-coated. The samples were well labelled, packaged in a black cellophane and taken to the lab within 24 h of collection and kept in a refrigerator until analysed. Sample preparation and handling were carried out according to APHA [16].

2.2.2 Analytical method

Heavy metals were analysed by digesting 100 mL rainwater samples with 5 mL of concentrated nitric acid (HNO_3) for 10 min at 165–170 °C. The samples were cooled, made up 100 mL deionized water in a volumetric flask. Eight heavy metals (As, Cd, Cr, Cu, Fe, Hg, Pb, and Zn) were determined in triplicate using Agilent Inductively Coupled Plasma – Optical Emission Spectrophotometer (ICP-OES) 280FS AA Instrument with plasma touch using air–acetylene flame and auto sampler [17–19].

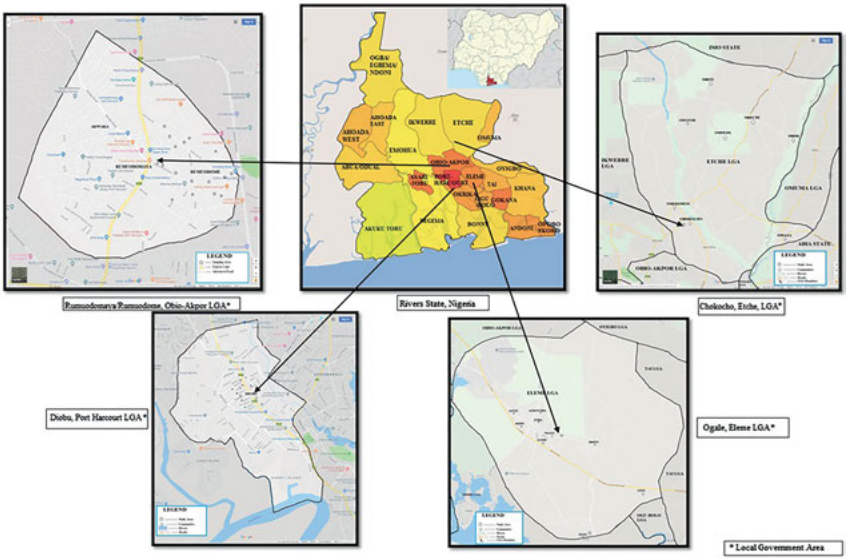


Figure 2.1: Map indicating sampling location.

The analytical results from ICP–OES instrument were converted from mg/L to mg/kg for risk assessment using the formula:

$$\text{mg/kg} = \frac{\text{mg/L (volume of sample (L))}}{\text{sample weight (kg)}} \tag{2.1}$$

2.2.3 Health and exposure risk assessment

Risk assessment is used to estimate the health effect that is associated from exposure to carcinogenic and non-carcinogenic chemicals [5, 20]. The heavy metal species (iron, lead, cadmium, arsenic, mercury, zinc, copper, and chromium-VI) were taken into considerations for both adults and children by measuring the average daily intake (ADI) of heavy metals in the study area. Health and exposure risk assessment was conducted using USEPA risk models by using rainwater average daily intake (dermal contact and ingestion) across different sampling surfaces for adults and children to ascertain cumulative carcinogenic and non-carcinogenic risk [3, 5, 7, 20, 21].

$$\text{ADI}_{\text{dermal}} = \frac{C_w \times \text{SAF} \times A_{\text{skin}} \times \text{DAF} \times F_{\text{exp}} \times T_{\text{exp}} \times 10^{-6}}{\text{ABW} \times T_{\text{avg}}} \tag{2.2}$$

$$\text{ADI}_{\text{ingestion}} = \frac{C_w \times R_{\text{ing}} \times F_{\text{exp}} \times \text{IAF} \times T_{\text{exp}} \times 10^{-6}}{\text{ABW} \times T_{\text{avg}}} \tag{2.3}$$

where ADI is average daily intake (mg/kg day),
- C_w is concentration of heavy metal in water (mg/kg),
- SAF is skin adherence factor; (0.2 mg/cm^2 for adults and children)
- A_{skin} is skin area; (5800 cm^2 for adults and 2800 cm^2 for children),

- DAF is dermal absorption factor (unitless) (0.001 for adults and children),
- F_{exp} is exposure frequency (350-day/year),
- T_{exp} is exposure duration (24 years for adults and 6 years for children),
- ABW is body weight (70 kg for adults and 15 kg for children)
- T_{avg} is average time for non-carcinogens = $T_{\text{exp}} \times 365$ days; carcinogen = 70×365,
- R_{ing} is ingestion rate (100 mg/day for adults and 200 mg/day for children),
- IAF is ingested fraction (unitless); (0.80 for adults and children).

2.2.3.1 Carcinogenic risk assessment: Carcinogenic risk assessment is the estimated probability for exposure to potential carcinogens, which can develop into total cancer risk via a pathway from dermal and ingestion of rainwater using the formula:

$$\text{Risk}_{\text{total}} = \text{Risk}_{\text{dermal}} + \text{Risk}_{\text{Ingestion}} = \sum_{k=1}^{n} \text{ADI}\,(E)_k \text{CSF}_k \tag{2.4}$$

where Risk is a unit-less probability of an individual developing cancer over a lifetime,

- ADI (E) is average daily intake (exposure).
- CSF: Cancer slope factor of heavy metal (mg/kg/day).

2.2.3.2 Non-carcinogenic risk assessment: Non-carcinogenic risk assessment is the sum total of hazard index from different exposure pathway from dermal and ingestion of rainwater that expresses the probability of adverse health effect using the formula:

$$\text{HI} = \sum_{k=1}^{n} \text{HQ}_k = \sum_{k=1}^{n} \frac{\text{ADI}\,(E)_k}{\text{RfD}} \tag{2.5}$$

where HI > 1, the exposed population is unlikely to experience adverse health effect.

- HI < 1, then there may be concern of potential non-carcinogenic effect.
- HQ: hazard quotient for dermal and ingestion.
- ADI (E) is average daily intake (exposure).
- RfD is reference dose of heavy metal (mg/kg/day).

2.3 Results and discussion

2.3.1 Heavy metal concentration of rainwater

Figure 2.2 shows the concentration of heavy metal from different sampling locations and surfaces. Arsenic values obtained ranged from ND – 1E-04 mg/L; ND – 0.124 mg/L; ND – 0.001 mg/L and ND – 0.0041 mg/L for different sampling surfaces in Ogale, Rumuodomaya/Rumudome, Diobu and Chokocho respectively. Arsenic concentration were below detection limit for sampling period and surfaces, which is considered extremely toxic to human as it leads to skin, bladder and lung cancer, vascular disease and hyper or hypo-pigmentation with exposure period of five years [22, 23].

Cadmium values obtained ranged from ND – 0.0091 mg ND – 0.21 mg/L; ND – 0.002 mg/L; and ND – 0.013 mg/L for different sampling surfaces in Ogale, Rumuodomaya/Rumudome, Diobu and Chokocho respectively. In decreasing order based

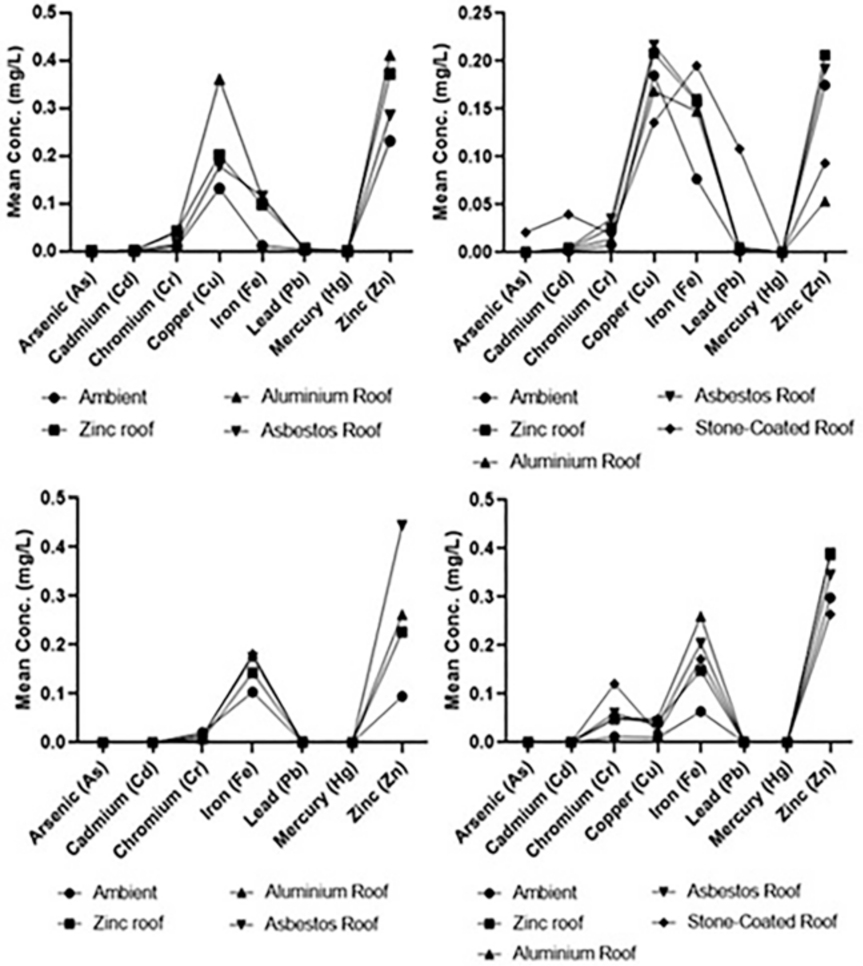


Figure 2.2: a–d Mean concentration line plot of Ogale; Rumudomaya/Rumuodome; Diobu and Chokocho across different sampling surfaces.

on locations: Rumuodomaya/Rumuodome > Ogale > Chokocho > Diobu which can be attributed to presence of dust particles from rock weathering industrial emission which deposits on different sampling surfaces [24–26]. Zinc is used as a detoxifying agent from cadmium poisoning [26].

The values of chromium ranged from ND – 0.20 mg/L; ND – 0.13 mg/L; ND – 0.95 mg/L and 0.001–0.93 mg/L for different sampling surfaces in Ogale, Rumuodomaya/Rumudome, Diobu and Chokocho respectively. There is strong correlation between zinc and cadmium as it accumulates in the kidney causing health issues like reproductive defects, enzyme interference and has a biological half-life of 10–35 years;

which is also a carcinogenic to human [24, 25]. Chromium (III) is an essential dietary requirement in human but Chromium (VI) is a carcinogen since it has potential to cause tumour, lung cancer in human [27, 28].

The values of copper ranged from 1E–04 to 1.91 mg/L; 9E–04 to 1.45 mg/L; ND to 0.31 mg/L and ND to 0.27 mg/L for different sampling surfaces in Ogale, Rumuodomaya/Rumudome, Diobu and Chokocho respectively. Copper gets into environmental matrices by rock weathering and industrial emission that impacts on water hardness, increase in dissolved carbonate species in rainwater [27, 29, 30].

Iron values obtained ranged from 0.017 to 0.28 mg/L; 0.004 to 0.65 mg/L; 0.005 to 0.55 mg/L and 0.02 to 0.94 mg/L for different sampling surfaces in Ogale, Rumuodomaya/Rumudome, Diobu and Chokocho respectively. The relative iron concentration varied significantly across different location with Chokocho having the highest iron content, followed by Diobu, Rumudomaya/Rumuodome and Ogale respectively. Iron influences taste, colour and turbidity of water, which is attributes to corrosion and dissolution in water sources [31, 32].

Lead values obtained ranged from 2E–05 to 0.015 mg/L; ND to 0.659 mg/L ND to 0.093 and ND to 0.03 mg/L for different sampling surfaces in Ogale, Rumuodomaya/Rumudome, Diobu and Chokocho respectively. In terms of decreasing lead concentration in sampling locations, Rumuodomaya/Rumuodome was high due to stone-coated roof followed by Ogale, Chokocho and Diobu which can be attributed to leaded paint dust and industrial emissions which is influenced by temperature, pH and presence of dissolved carbonate in water. Exposure leads to neurological effects, increased mortality, impaired renal function, hypertension and low IQ [30, 33].

Mercury values ranged from ND to 0.0001 mg/L; ND to 0.0021 mg/L; ND to 0.0005 mg/L and ND to 0.0003 mg/L for different sampling surfaces in Ogale, Rumuodomaya/Rumudome, Diobu and Chokocho respectively. Mercury concentration were below detection limit for some sampling period and surfaces which was influence of environmental matrices. Mercury affects humans health both short and long-term such as kidney failure, skin cancer, acute oral poisoning from haemorrhages and colitis [27, 33].

Zinc values ranged from 6E–04 to 1.57 mg/L; 9E–04 to 0.86 mg/L; 2E–04 to 2.40 mg/L and 0.001 to 2.05 mg/L for different sampling surfaces in Ogale, Rumuodomaya/Rumudome, Diobu and Chokocho respectively. Zinc was relatively high across different location for zinc roof, aluminium roof, asbestos roof, ambient and stone-coated roof, which is attributed to dissolution of zinc mineral by increase in pH and total inorganic carbon in rainwater samples [34, 35].

2.3.2 Average concentration of heavy metal in rainwater

Table 2.1 shows the average concentration of heavy metals in mg/kg of rainwater across the four locations for different sampling surfaces. The results presented showed that

Table 2.1: Average concentration of heavy metal in rainwater across different sampling surfaces (mg/kg).

Sampling surfaces		As (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Fe (mg/kg)	Hg (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
Ambient	Average	0.002	0.007	0.13	0.93	0.64	0.001	0.02	1.99
	Minimum	0.00	0.00	0.008	0.01	0.04	0.00	0.00	0.03
	Maximum	0.022	0.04	0.60	5.50	1.79	0.002	0.10	7.30
Zinc roof	Average	0.004	0.012	0.31	1.38	1.37	0.002	0.03	2.99
	Minimum	0.00	0.00	0.00	0.01	0.12	0.00	0.002	0.04
	Maximum	0.016	0.10	1.30	5.90	3.10	0.01	0.10	11.00
Aluminium roof	Average	0.002	0.02	0.29	1.63	1.76	0.002	0.03	2.79
	Minimum	0.00	0.0001	0.04	0.01	0.42	0.00	0.001	0.03
	Maximum	0.01	0.10	1.40	9.90	4.00	0.006	0.10	10.70
Asbestos roof	Average	0.004	0.01	0.31	1.20	1.64	0.002	0.03	3.17
	Minimum	0.00	0.00	0.01	0.014	0.10	0.00	0.00	0.05
	Maximum	0.021	0.13	1.60	5.60	4.60	0.003	0.10	12.20
Stone-coated roof	Average	0.11	0.20	0.70	0.78	1.83	0.002	0.55	1.79
	Minimum	0.001	0.00	0.04	0.00	0.15	0.00	0.00	0.10
	Maximum	0.62	1.10	3.50	3.90	3.90	0.004	2.20	7.00
WHO/FAO guidelines [27]		3	20	n. a.	100	100	n. a.	300	100

n. a.: not available.

across different sampling surfaces varied significantly. Comparing with recommended maximum allowable limit using WHO/FAO guidelines shows that heavy metals were all below thus, there is no significant health risk to rainwater users [17].

2.3.3 Carcinogenic risk assessment

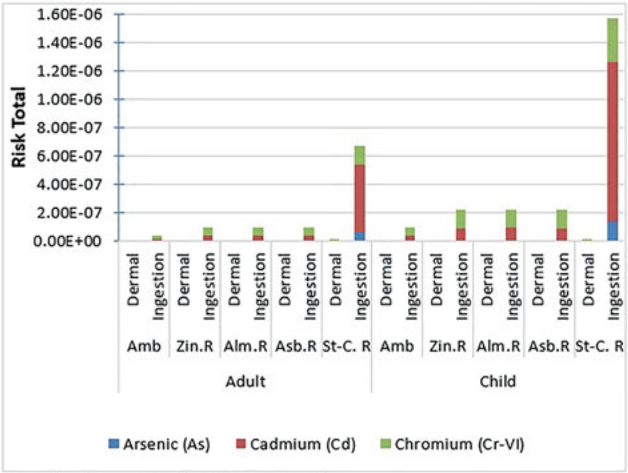
The average daily intake for carcinogenic risk for adults and children as calculated and presented in Table 2.2. The ADI values was used to calculate the carcinogenic risk using cancer slope factor (CSF) for arsenic (Ar), cadmium (Cd) and chromium (Cr^{6-}) presented in Figure 2.3.

For adults and children, cadmium was found to be the highest contributor to cancer risk across all sampling surfaces and locations followed by chromium and arsenic the less contributor. The USEPA considers acceptable cancer risk in range of 1.0E−06 to 1.0E−04 thus both adult and child are not at risk though children are more at risk are from rainwater consumption from cadmium, chromium and arsenic poisoning, followed by dermal contact of rainwater compared to adults [17, 36, 37].

Table 2.2: Average daily intake (ADI) values for adults and children from different sampling surfaces for carcinogenic risk.

Pathway			Average daily intake (ADI) of heavy metals (mg/kg day)							
			As	Cd	Cr-VI	Cu	Fe	Pb	Hg	Zn
Adult	Amb	Dermal	1.34×10^{-11}	3.71×10^{-11}	6.84×10^{-10}	5.08×10^{-09}	3.48×10^{-09}	9.03×10^{-11}	3.16×10^{-12}	1.08×10^{-08}
		Ingestion	9.27×10^{-10}	2.56×10^{-09}	4.71×10^{-08}	3.50×10^{-07}	2.40×10^{-07}	6.22×10^{-09}	2.17×10^{-10}	7.51×10^{-07}
	Zin.R	Dermal	1.99×10^{-11}	8.07×10^{-11}	1.68×10^{-09}	7.51×10^{-09}	7.45×10^{-09}	1.56×10^{-10}	1.02×10^{-11}	1.63×10^{-08}
		Ingestion	1.37×10^{-09}	5.56×10^{-09}	1.16×10^{-07}	5.18×10^{-07}	5.14×10^{-07}	1.07×10^{-08}	7.09×10^{-10}	1.12×10^{-06}
	Alm.R	Dermal	1.17×10^{-11}	8.97×10^{-11}	1.59×10^{-09}	8.88×10^{-09}	9.56×10^{-09}	1.59×10^{-10}	9.76×10^{-12}	1.51×10^{-08}
		Ingestion	8.11×10^{-10}	6.19×10^{-09}	1.10×10^{-07}	6.12×10^{-07}	6.59×10^{-07}	1.10×10^{-08}	6.73×10^{-10}	1.04×10^{-06}
	Asb.R	Dermal	2.36×10^{-11}	8.15×10^{-11}	1.70×10^{-09}	6.55×10^{-09}	8.91×10^{-09}	1.40×10^{-10}	8.53×10^{-12}	1.72×10^{-08}
		Ingestion	1.63×10^{-09}	5.62×10^{-09}	1.17×10^{-07}	4.52×10^{-07}	6.14×10^{-07}	9.66×10^{-09}	5.88×10^{-10}	1.18×10^{-06}
	St-C.R	Dermal	5.80×10^{-10}	1.09×10^{-09}	3.81×10^{-09}	4.25×10^{-09}	9.99×10^{-09}	2.99×10^{-09}	1.09×10^{-11}	9.74×10^{-09}
		Ingestion	4.00×10^{-08}	7.57×10^{-08}	2.63×10^{-07}	2.93×10^{-07}	6.89×10^{-07}	2.06×10^{-07}	7.57×10^{-10}	6.72×10^{-07}
Child	Amb	Dermal	7.56×10^{-12}	2.09×10^{-11}	3.85×10^{-10}	2.86×10^{-09}	1.96×10^{-09}	5.08×10^{-11}	1.77×10^{-12}	6.13×10^{-09}
		Ingestion	2.16×10^{-09}	5.97×10^{-09}	1.10×10^{-07}	8.17×10^{-07}	5.60×10^{-07}	1.45×10^{-08}	5.07×10^{-10}	1.75×10^{-06}
	Zin.R	Dermal	1.12×10^{-11}	4.54×10^{-11}	9.49×10^{-10}	4.23×10^{-09}	4.19×10^{-09}	8.76×10^{-11}	5.79×10^{-12}	9.16×10^{-09}
		Ingestion	3.20×10^{-09}	1.29×10^{-08}	2.71×10^{-07}	1.21×10^{-06}	1.19×10^{-06}	2.50×10^{-08}	1.65×10^{-09}	2.62×10^{-06}
	Alm.R	Dermal	6.62×10^{-12}	5.05×10^{-11}	9.00×10^{-10}	5.00×10^{-09}	5.38×10^{-09}	8.99×10^{-11}	5.49×10^{-12}	8.55×10^{-09}
		Ingestion	1.89×10^{-09}	1.44×10^{-08}	2.57×10^{-07}	1.42×10^{-06}	1.54×10^{-06}	2.57×10^{-08}	1.57×10^{-09}	2.44×10^{-06}
	Asb.R	Dermal	1.32×10^{-11}	4.59×10^{-11}	9.61×10^{-10}	3.69×10^{-09}	5.02×10^{-09}	7.89×10^{-11}	4.80×10^{-12}	9.72×10^{-09}
		Ingestion	3.79×10^{-09}	1.31×10^{-08}	2.74×10^{-07}	1.05×10^{-06}	1.43×10^{-06}	2.25×10^{-08}	1.37×10^{-09}	2.77×10^{-06}
	St-C.R	Dermal	3.27×10^{-10}	6.18×10^{-10}	2.15×10^{-09}	2.39×10^{-09}	5.63×10^{-09}	1.68×10^{-09}	6.18×10^{-12}	5.48×10^{-09}
		Ingestion	9.35×10^{-08}	1.77×10^{-07}	6.14×10^{-07}	6.84×10^{-07}	1.61×10^{-06}	4.81×10^{-07}	1.77×10^{-09}	1.57×10^{-06}

N.B.: Amb, ambient; Zin.R, zinc roof; Alm.R, aluminium roof; St-C.R, stone-coated roof.



CSF values (As: 1.50, Cd: 6.30, Cr-VI: 0.50)

Figure 2.3: Risk total of heavy metal for adult and child in rainwater samples.

2.3.4 Non-carcinogenic risk assessment

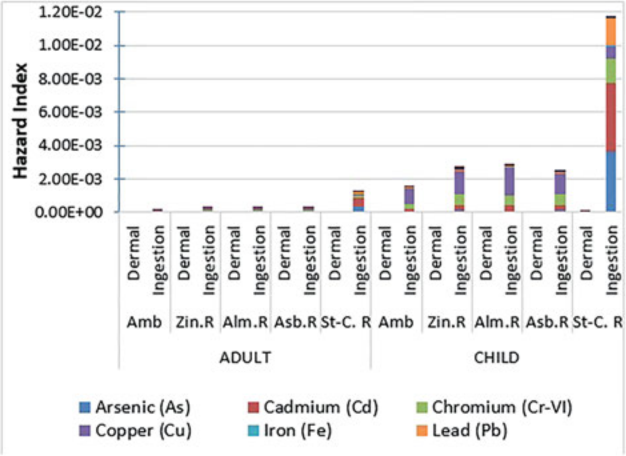
Non-carcinogenic risk for adults and children were calculated to determine average daily intake (ADI) from dermal and ingestion pathway presented in Table 2.3. The ADI values was used to determine hazard index (HI) using reference dose (RfD) presented in Figure 2.4 as they are less than 1 indicating no risk to population who consumes rainwater from different roofing surfaces in Rivers state.

Cadmium, chromium-VI and copper was predominant across all sampling surfaces, which can accumulate over time leading to increased toxicity and impact health of adults and children [36, 38]. Cadmium, chromium (VI), arsenic, lead and mercury are potentially toxic metals, which are non-beneficial to humans as they affect gastrointestinal, liver, kidney, central nervous system of children, reduce IQ and interfere with reproductive organs over a long period of bioaccumulations [5, 39, 40]. The results indicates that children are most at risk compared to adults from ingesting rainwater containing these heavy metals while dermal contact is least contributor to non-carcinogenic risk.

Table 2.3: Average daily intake (ADI) values for adults and children from different sampling surfaces for non-carcinogenic risk.

Pathway			**Average daily intake (ADI) of heavy metals (mg/kg day)**							
			As	**Cd**	**Cr-VI**	**Cu**	**Fe**	**Pb**	**Hg**	**Zn**
Adult	Amb	Dermal	3.92×10^{-11}	1.08×10^{-10}	1.99×10^{-09}	1.48×10^{-08}	1.02×10^{-08}	2.63×10^{-10}	1.02×10^{-08}	3.17×10^{-08}
		Ingestion	2.70×10^{-09}	7.46×10^{-09}	1.38×10^{-07}	1.02×10^{-06}	7.00×10^{-07}	1.82×10^{-08}	7.00×10^{-07}	2.19×10^{-06}
	Zin.R	Dermal	5.81×10^{-11}	2.35×10^{-10}	4.91×10^{-09}	2.19×10^{-08}	2.17×10^{-08}	4.54×10^{-10}	2.17×10^{-08}	4.74×10^{-08}
		Ingestion	4.00×10^{-09}	1.62×10^{-08}	3.39×10^{-07}	1.51×10^{-06}	1.50×10^{-06}	3.13×10^{-08}	1.50×10^{-06}	3.27×10^{-06}
	Alm.R	Dermal	3.43×10^{-11}	2.62×10^{-10}	4.66×10^{-09}	2.59×10^{-08}	2.79×10^{-08}	4.65×10^{-10}	2.79×10^{-08}	4.43×10^{-08}
		Ingestion	2.37×10^{-09}	1.80×10^{-08}	3.21×10^{-07}	1.79×10^{-06}	1.92×10^{-06}	3.21×10^{-08}	1.92×10^{-06}	3.05×10^{-06}
	Asb.R	Dermal	6.89×10^{-11}	2.39×10^{-10}	4.98×10^{-09}	1.91×10^{-08}	2.60×10^{-08}	4.08×10^{-10}	2.60×10^{-08}	5.03×10^{-08}
		Ingestion	4.75×10^{-09}	1.64×10^{-08}	3.43×10^{-07}	1.32×10^{-06}	1.79×10^{-06}	2.82×10^{-08}	1.79×10^{-06}	3.47×10^{-06}
	St-C.R	Dermal	1.69×10^{-09}	3.20×10^{-09}	1.11×10^{-08}	1.24×10^{-08}	2.91×10^{-08}	8.72×10^{-09}	2.91×10^{-08}	2.84×10^{-08}
		Ingestion	1.17×10^{-07}	2.21×10^{-07}	7.67×10^{-07}	8.55×10^{-07}	2.01×10^{-06}	6.01×10^{-07}	2.01×10^{-06}	1.96×10^{-06}
Child	Amb	Dermal	8.83×10^{-11}	2.44×10^{-10}	4.49×10^{-09}	3.34×10^{-08}	2.29×10^{-08}	5.93×10^{-10}	2.29×10^{-08}	7.16×10^{-08}
		Ingestion	2.52×10^{-08}	6.96×10^{-08}	1.28×10^{-06}	9.54×10^{-06}	6.54×10^{-06}	1.69×10^{-07}	6.54×10^{-06}	2.04×10^{-05}
	Zin.R	Dermal	1.31×10^{-10}	5.30×10^{-10}	1.11×10^{-08}	4.94×10^{-08}	4.90×10^{-08}	1.02×10^{-09}	4.90×10^{-08}	1.07×10^{-07}
		Ingestion	3.74×10^{-08}	1.51×10^{-07}	3.16×10^{-06}	1.41×10^{-05}	1.40×10^{-05}	2.92×10^{-07}	1.40×10^{-05}	3.05×10^{-05}
	Alm.R	Dermal	7.73×10^{-11}	5.89×10^{-10}	1.05×10^{-08}	5.83×10^{-08}	6.28×10^{-08}	1.05×10^{-09}	6.28×10^{-08}	9.97×10^{-08}
		Ingestion	2.21×10^{-08}	1.68×10^{-07}	3.00×10^{-06}	1.67×10^{-05}	1.80×10^{-05}	2.99×10^{-07}	1.80×10^{-05}	2.85×10^{-05}
	Asb.R	Dermal	1.55×10^{-10}	5.36×10^{-10}	1.12×10^{-08}	4.31×10^{-08}	5.85×10^{-08}	9.20×10^{-10}	5.85×10^{-08}	1.13×10^{-07}
		Ingestion	4.43×10^{-08}	1.53×10^{-07}	3.20×10^{-06}	1.23×10^{-05}	1.67×10^{-05}	2.63×10^{-07}	1.67×10^{-05}	3.24×10^{-05}
	St-C.R	Dermal	3.82×10^{-09}	7.21×10^{-09}	2.51×10^{-08}	2.79×10^{-08}	6.56×10^{-08}	1.96×10^{-08}	6.56×10^{-08}	6.40×10^{-08}
		Ingestion	1.09×10^{-06}	2.06×10^{-06}	7.16×10^{-06}	7.98×10^{-06}	1.88×10^{-05}	5.61×10^{-06}	1.88×10^{-05}	1.83×10^{-05}

N.B.: Amb, ambient; Zin.R, zinc roof; Alm.R, aluminium roof; St-C.R, stone-coated roof.



RfD values (As: 0.0004, Cd: 0.0005, Cr-VI: 0.005, Cu: 0.20, Fe: 0.70, Pb: 0.0035, Hg: 0.0003, Zn: 0.30)

Figure 2.4: Hazard index of heavy metals for adult and child in rainwater samples.

2.4 Conclusions

The study assessed concentration of heavy metal of rainwater from different sampling locations and surfaces, which varied significantly. Comparing with WHO/FAO recommended guidelines showed that the average concentrations were below thus, there is no health issues associated. Carcinogenic and non-carcinogenic risk assessment showed that rainwater ingestion is a major route pathway contributor compared to dermal contact, which was least for both adults and children respectively. Children are more prone to have health related issues from consumption of contaminated and untreated rainwater. Based on the results, one can draw that rainwater from different roofing materials particularly rainwater consumption from stone-coated roofs should not be utilized or further treatment be done to meet water demand in Rivers State, Nigeria. Thus, further regulations needs to put in place to prevent industrial pollution and protect residents especially children who are susceptible to health related illness and create environmental sustainability

Acknowledgements: We are thankful to Professor Ponnadurai Ramasami and other anonymous reviewers for their assistance. This research work was self-funded, as the authors declare no conflict of interest.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: None declared.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Mendez CB, Klenzendorf JB, Afshar BR, Simmon MT, Barret ME, Kinney KA, et al. The effect of roofing material on the quality of harvested rainwater. Water Res 2011;45:2049–59.
2. Gikas DG, Tsihrintzis AV. Assessment of water quality of first-flush roof runoff and harvested rainwater. J Hydrol 2012;446-447:115–26.
3. Živković N, Takić L, Djordjević L, Djordjević A, Mladenović-Ranisavljević I, Golubović T, et al. Concentrations of heavy metal cations and a health risk assessment of sediments and river surface water: a case study from a Serbian mine. Pol J Environ Stud 2019;28:2009–20.
4. Spiridonov V, Curic M. Atmospheric chemistry. In: Fundamentals of metrology. Cham: Springer; 2021, 327–47pp. https://doi.org/10.1007/978-3-030-52655-9_22.
5. USEPA. Risk assessment guidance for superfund, volume I: human health evaluation manual (Part E, supplemental guidance for dermal risk assessment). Washington, DC, USA: USEPA; 2004.
6. USEPA. Framework for metals risk assessment. Washington, DC 20460, USA: USEPA. EPA 120/R-07/001; 2007.
7. Jaishankar M, Anbalagan TTN, Mathew BB, Beeregowda KN. Toxicity, mechanism and health effects of some heavy metals. Interdispl Toxicol 2014;7:60–72.
8. Giripunje MD, Fulke AB, Meshram PU. Remediation techniques for heavy metals contamination in lakes: a mini review. CLEAN Soil Air Water 2015;43:1350–4.
9. Gav BL, Vesuwe RN, Ijeomah AO, Okoko EE, Tor PN, Tsaviv JN. Determination of heavy metal concentrations of rainwater harvested from different roofing sheets in outskirt of Makurdi, Benue State, Nigeria. Asian J Chem Sci 2018;4:1–6.
10. Ebong G, Joseph E, Cyril E, Samuel E. Levels of inorganic contaminants in rainwater samples harvested from different rooftops in Uyo metropolis, Akwa Ibom state, Nigeria. Int J 2012;3:152–7.
11. Ahammed F. A review of water-sensitive urban design technologies and practices for sustainable stormwater management. Sustain Water Res Manag 2017;3:269–82.
12. Abdulla F, Abdulla C, Eslamian S. Concept and technology of rainwater harvesting. In: *Handbook of water harvesting and conservation: basic concepts and fundamentals*. Wiley Online Library; 2021, 1–16pp.
13. Sanjeeva A, Puttaswamiah SG. Influence of atmospheric deposition and roof materials on harvested rainwater quality. J Environ Eng 2018;144:04018121.
14. Kirkpatrick A. The Routledge handbook of world Englishes. Rouledge; 2020. http://vulms.vu.edu.pk/Courses/ENG506/Downloads/Andy.Kirkpatrick.The.Routledge.Handbook.of.World.Englishes.(Routledge.Handbook.in.Application.Linguistics).2010.pdf.
15. UNESCO. Action plan Nigeria (PDF); 2012. http://www.unesco.org/fileadmin/MULTIMEDIA/HQ/ED/pdf/Nigeria.pdf [Accessed 03 May 2019].
16. Braid RN, Eaton AD, Rice EW, Bridgewater L. Standard methods for the examination of water and wastewater, 23rd ed. Washington, DC. United States: Water Environment Federation. American Water Works Association; 2017.
17. Kamunda C, Mathuthu M, Madhuku M. Health risk assessment of heavy metals in soil from witwaters-rand gold mining basin, South Africa. Int J Environ Res Publ Health 2016;13:1–11.
18. USEPA. Determination of metals by inductively coupled plasma (ICP) methods. United States Environmental Protection Agency (EPA) Methods SW846/3015/3050B/6010B. United States: National Environmental Laboratory Accreditation Committee (NELAC); 2006.

19. Mohammed R, Zainudin BH, Yaakob AS. Method validation and determination of heavy metals in cocoa beans and cocoa products by microwave assisted digestion techniques with inductively coupled plasma mass spectrometry. Food Chem 2020;303:125392.
20. United States Environmental Protection Agency (US EPA). Guidelines for carcinogen risk assessment [EPA report]. Washington, DC: U.S. Environmental Protection Agency, Risk Assessment Forum; 2005a (EPA/630/P-03/001F). http://www2.epa.gov/osa/guidelines-carcinogen-risk-assessment.
21. United States Environmental Protection Agency (US EPA). Supplemental guidance for assessing susceptibility from early-life exposure to carcinogens. Washington, DC: U.S. Environmental Protection Agency, Risk Assessment Forum; 2005b. EPA/630/R-03/003F https://www3.epa.gov/airtoxics/childrens_supplement_final.pdf.
22. Nurchi VM, Djordjevic AB, Crisponi G, Alexander J, Bjorklund G, Aaseth J. Arsenic toxicity: molecular targets and therapeutics agents. Biomolecules 2020;10:235.
23. Hare V, Chowdhary P, Kumar B, Sharma DC, Baghel VS. Arsenic toxicity and its remediation strategies for fighting the environmental threat. In: Bharagava R, Chowdhary P, editors. Emerging and eco-friendly approaches for waste management. Singapore: Springer; 2019, 143–70pp. https://doi.org/10.1007/978-981-10-8669-4_8.
24. Lai YH, Ahmad Y, Yusoff I, Bong CW, Kong SY. Effects of roof pitch gradient and material to harvested rainwater quality. IOP Conf Ser Mater Sci Eng 2018;401:012011.
25. Lestari E, Sofyan M, Pamuji B. Utilization of roof garden installation to reduce rainwater runoff in urban residential. IOP Conf Ser Mater Sci Eng 2020;852:012029.
26. Shamelashvili K, Ostrovska S, Shatorna V. The toxic effect of cadmium on living organism and its detoxification by zinc ions. Modern Sci 2020;3:150–7.
27. WHO. Guidelines for drinking water quality. Recommendation, 4th ed. New Delhi: AUBS Publishers; 2011b.
28. WHO. Chromium in drinking water. Background document for development of WHO Guidelines for drinking water quality. Geneva: World Health Organization; 2020. WHO/HEP/ECH/WSH/2020.3.
29. Nkwunonwo UC, Odika PO, Onyia NI. A review of the health implication of heavy metals in food chain in Nigeria. Sci World J 2020;2020:1–11.
30. Ali H, Khan E. Assessment of potential toxic heavy metals and health risk in water, sediment and different fish species of River Kabul, Pakistan. Hum Ecol Risk Assess 2018;24:2101–18.
31. Sun H, Shi B, Yang F, Wang D. Effects of sulfate on heavy metal release from iron corrosion scales in drinking water distribution system. Water Res 2017;114:69–77.
32. Xu X, Shuming L, Smith K, Ciu Y, Wang Z. An overview on corrosion of iron and steel components in reclaiming water supply systems and the mechanism involved. J Clean Prod 2020;276:124079.
33. Rana MN, Tangpong J, Rahman MM. Toxicodynamics of lead, cadmium, mercury and arsenic-induced kidney toxicity and treatment strategy: a mini review. Toxicol Rep 2018;5:704–13.
34. Kasozi KI, Namubiru S, Kamugisha R, Eze ED, Tayebwa DS, Ssempijja F, et al. Safety of drinking water from primary water sources and implications for the general public in Uganda. J Environ Public Health 2019;2019:1–13.
35. Chiroma TM, Ebewele RO, Hymore K. Comparative assessment of heavy metal levels in soil, vegetables and urban grey waste water used for irrigation in Yola and Kano. Int Ref J Eng Sci 2014;3:1–9.
36. Williams PL, James RC, Roberts SM. Principles of toxicology environmental and industrial applications, 2nd ed. United States: Wiley-Interscience Publishers; 2014:1–495 pp.
37. Al-Khatib IA, Arafeh GA, Al-Qutob M, Jodeh S, Hasan A, Jodeh D, et al. Health risk associated with some trace and some heavy metals content of harvested rainwater in Yatta area, Palestine. Water 2019;11:238.

38. Osarenotor O, Imarhiagbe EE. Health risk and quality assessment of non-roof harvested rainwater from oil producing community in Nigeria. Environ Monit Assess 2020;192:169.
39. Balamurugan P, Kumar P, Shankar K, Nagavinothini R, Vijayasurya K. Non-carcinogenic risk assessment of groundwater in southern part of Salem district in Tamilnadu, India. J Chil Chem Soc 2020;65:4697–707.
40. Abdallah MAM. Bioaccumulation of heavy metals in mollusca species and assessment of potential risks to human health. Bull Environ Contam Toxicol 2013;90:552–7.

Chinda Worokwu* and Kechinyere Chinda

3 Social media and learning in an era of coronavirus among chemistry students in tertiary institutions in Rivers State

Abstract: The study examined the awareness level of social networking site and how it is applied for learning in an era of coronavirus by Chemistry students in tertiary institutions in Rivers State Nigeria. Three research questions and two hypotheses guided the study. The study adopted the analytic descriptive survey design. One hundred and sixty undergraduate students from Ignatius Ajuru University of Education (IAUE) and Rivers State University (RSU) were randomly selected for the study. The instrument for data collection was a researcher made questionnaire titled social media awareness and application for learning in COVID-19. The consistency coefficient of the instrument was determined by Pearson product moment as a measure of its stability over time. The reliability coefficient of the instruments was 0.95. The instrument was administered to the students online via their numerous class social media platforms. Mean, standard deviation and *t*-test were the statistical tools used for data analysis. The result reveals that students are aware of social media for learning such as Zoom, WhatsApp, Facebook etc. A second outcome of this investigation showed that there is poor application or used of social networking site for learning among Chemistry students in Rivers State owned universities, it was also found out that finance, travel restriction, assessment and evaluation, poor internet reception, availability of electricity and others were identified as challenges while mental health of student, lack of pre-class preparation and associating with real friends were not considered to be challenges to the use of social media for learning. Furthermore, there was no significant difference in the level of awareness between IAUE students and those of RSU in the use of social network site for learning. The extent to which students apply social media for learning does not depend on university type. Based on the above results, it was recommended among others that universities in Rivers State should endeavor to engage their students in training that will avail them the opportunity to apply or utilize effectively social media in their learning activities.

Keywords: chemistry; era; learning and coronavirus; social media.

***Corresponding author: Chinda Worokwu**, Department of Chemistry, Faculty of Natural and Applied Sciences, Ignatius Ajuru University of Education, P.M.B 5047 Rumuolumeni, Port Harcourt, Rivers State, Nigeria, E-mail: wororolly@gmail.com

Kechinyere Chinda, Department of Educational Foundation, Faculty of Education, Rivers State University, Nkpolu Oroworukwo, Port Harcourt, Rivers State, Nigeria

This article has previously been published in the journal Physical Sciences Reviews. Please cite as: C. Worokwu and K. Chinda “Social media and learning in an era of coronavirus among chemistry students in tertiary institutions in Rivers State” *Physical Sciences Reviews* [Online] 2021, 6. DOI: 10.1515/psr-2020-0093 | https://doi.org/10.1515/9783110726145-003

3.1 Introduction

Coronavirus disease 2019 also known as the (COVID-19) was started in Wuhan city of China in December 2019 [1]. Corona disease (COVID-19) is a contagious infection triggered by a newly revealed coronavirus of SARS CoV transmitted from civet cats to humans in China [2]. Coronavirus disease 2019 (COVID-19) is defined as the illness caused by a new coronavirus now called severe acute breathing syndrome coronavirus 2 (SARS-CoV-2) formerly called 2019 NCoV. These viruses are known as source to illness ranging from common cold to more severe diseases such as Middle East respiratory syndrome (MERS) and severe acute breathing syndromes (SARS) [3].

On 30th January 2020, WHO declared the novel coronavirus a Universal health emergency, it recommended certain standards to reduce the spread of the disease such as continuing simple hand and respirational hygiene and safe food cultural practice and preventing of close contact with any person having symptoms of breathing illness such as coughing and sneezing. The disease spread to over 177 countries in February thereby causing WHO on 11th of March, 2020 to declare COVID-19 a universal pandemic [2]. As at March 2020, it has infected over 722,435 persons resulting to about 722,435 deaths [4].

In order to contain the spread of the disease many countries introduced travel restrictions, ban on religious and social gathering, closure of bars gyms, and other public places. In addition, this development also led to the closure of schools in many countries. On 20th of March 2020, the Nigeria University Commission (NUC) issued circulars to Vice Chancellors to close university for a period of one-month effect from March 30, 2020. This directive was adhered to strictly on 21st March, 2020 by the Senate of Ignatius Ajuru University of Education (IAUE) and Rivers State University (RSU). They suspended all academic activities and school were closed down all students vacated the universities. The outbreak of COVID-19 has challenged the notion of two state owned Ivory tower in Rivers State preventing it from using the school timetable as planned by their senate. With disruption of academic calendar, the universities transitioned numerous courses and programs from face-to-face to virtual delivery mode through the use of social media site.

Outbreak of COVID-19 has posed a challenge to learning globally. The closure of schools has disengaged students from learning process and other skill, values attitude and potentials associated with learning. There are also the challenges of finance where students who engage in small medium scale business on campus to support themselves are suffering both academic and financial deficiencies. The closure of schools has taken most youths to social vices, such as prostitution, cybercrime and cultism to collaborate with the statement that an idle mind is devil workshop. All these and other challenges can be minimized if learning was taking place.

Learning is a relatively permanent change in behavior due to again knowledge understanding or skill accomplished through experience, which may comprise study, instruction, observation or training [5]. For learning to take place there must be a change in behavior. The change must be through experience or practice (only adaptive changes and not necessary changes due to growth, maturation and disease). The change must be relatively permanent that is it must last for a fairly long time.

3.2 Types of learning

I. Physical-sensory learning

This can be referred to as psychomotor or sensory perceptive learning. It involves the development of skills, and those insights that lead to the efficient performance of physical activity. Other components of this type of learning include skill, know-how, and economic performance of activity, e.g., reaction time and speed safety measures and efficient alternatives.

II. Intellectual/cognitive learning

This refers to the acquisition of new information and understanding. The components of cognitive learning include assembling and analysis of facts and opinions. It also includes developing problem solving techniques or approaches.

III. Affective learning

This relates to the development of attitudes, emotions, feelings, as well as qualities of character and conscience, values, interest and appreciations that are internally consistent.

The inter-relatedness of these three domains of learning is significant in the execution of an educational program. The teacher as a resource person provides the pupils with the opportunity to use their sensory, cognitive and affective processes to adjust adequately to a learning process.

For effective learning to take place Ikegbunam [5] listed seven essential conditions necessary for effective learning to take place

(i) Readiness—There has to be the mental maturity and appropriate background experience for the learning experience being undertaken.

(ii) Motivation—Motivation is crucial to learning because it arouses, withstands, guides and controls the strength of learning effort. Some of the best motivational techniques are to provide for the learner's desire for practical activities and creative use of his talents.

(iii) Self-discovery and problem solving—Self-discovery may be accompanied by explaining, demonstrating, correcting the learner's provisional trials; by organizing learning sequences and leading questions/cues which aid self-discovery learning.

(iv) Perception of effects—Knowledge of result of each goal-directed trial is essential for improvement and mastery. Through perception of effects, one is able to identify and correct his mistakes and at the same time confirm his correct knowledge.

(v) Practice—Appropriate and well distributed practice improve memory and practical skills. Practice conditions should be made to resemble as much as possible the situation in which the skill or knowledge is required to be demonstrated.

(vi) Transfer—Ability to apply previous learning to new problems is indicative of effective learning. Student should be aided to discover similarity of concepts in order to facilitate transfer, generalization, application, and integration of new learning with previous knowledge.

(vii) Mental health—Effective learning is fostered under conditions of good mental health, emotional and social adjustment. The student who feels insecure or rejected either by his teacher, parents or classmates may develop neurotic anxiety and emotional maladjustment.

In the center of this COVID-19 crisis, we are sure that fellow educators, like us, are pondering what we need to be organizing our students for effective learning to take place. Though students being able to gain information, and even study a practical skill, through a few connects on their phones, tablets and computers. We will need to reexamine the role of the educationalist in the lecture hall. This may mean that the part of educationalists will move to helping young people's progress as contributing members of society through use of social media sites.

Social media also known as social networking service (SNS) is a virtual platform that persons use to build united relation with other people who share similar personal or career interest activities, background or real life connection [6].

It also a form of electronic communication (such as websites for social networking and microblogging through which users create virtual communities to share information, concepts, private messages, and other content (such as videos). Similarly, social media is a catch-all term for a variety of interest presentations that allow users to interact with each other. It is internet based applications that help users to communicate freely with people of like minds. They believe that social network is possible in person especially in work place, universities, high schools and most popular online [7].

Social network site can be divided into three namely [8]

1. Entertaining social network services used primarily for meet people with existing friends (e.g., Facebook).
2. Interacting social network used primarily for nonsocial relational communication (e.g., a profession and occupation oriented site.
3. Social direction-finding network sites used principally for helping users to find specific material or educational resources (e.g., good reads for books).

In another development, Farema in Akainwor [9] divided social media into 10 namely:

1. Social relationship network—connect with people
2. Mass media sharing networks—share photos, videos and other media
3. Conversation forum—where news and ideas are shared
4. Book marking and content duration networks. It is used to learn, save and grant new content
5. Customer assessment network—find and assess businesses
6. Blogging and dissemination networks—print content online
7. Attention-based networks—share interest and leisure
8. Shopping networks—shop virtual
9. Business network—trade, goods and services
10. Secret social networks—communicate secretly

The first recognizable social network site was created in 1997 [10]. It was used to transfer an information and make friends with other users. In 1999, the first blogging site became widespread creating a social media awareness that is still known. The six degree moved the internet into the era of blogging and instant messages. By the year 2000, more than 100 million people had access to the internet it became an avenue to chat, make friends, dating and discuss topics of interest. In 2003, the first social media surge LinkedIn was created, it was geared toward professionals who want to network with one another.

During 2004–2006, a great revolution was made with social networking service (SNS) when Mark Zuckerberg in 2004 launched the Facebook a number one social media website that is currently used by billions of people. The face.com that was launched for just Harvard students was widely patronize thus Mark Zuckerberg released it to the whole world. Other social media that marked this era was Twitter created by Jack Dorsey, and Co. This has allowed over 500 million users to send tweets to other users. In 2010 and beyond, dozens of website was develop to provide social media services. Social media services such as Flickr, Foursquare, Instagram, Google buzz, Lopp, Blippy Groupon etc. were invented in the era. The major happening in this era was that social media became widely used and widespread as a means of commerce (marketing).

Social media today consist of thousands of media platform all serving the same purpose of communication but slightly different in purpose. A user of social media platform decides on the purpose for use and the platform that will serve that purpose. Notwithstanding the popularity of social media sites for private use there are a small ratio of students who use them for educational purpose [14]. The use of social media for educational aim such as helping by undergraduate students with course work. The use of social media for teaching and learning such as blog provide students with more participating role in learning process therefore by the integration of blog for educational purpose should be adopted by lecturers.

There are plethora of social network with various feature meant to suit different people. They include WhatsApp, Facebook QQ, we chat Qzone, Tumblr, Instagram, Pinterest, LinkedIn, Telegram, Reddit, Tagged Four square, Renten, Tagged, Badoo, My space, stumble upon, THE-DAYS, Kiwibox.com skyrock snapfish, flixster, care2, YouTube, class mates, my Heritage flickr Wikipedia etc. The various social network sites are used by millions of people on daily bases.

These various social networks are patronized by mostly students and youths.

Social media has introduced new method of teaching and conducting research and have brought into educational facilities for online learning and research collaboration [9]. Cassidy et al. [11] asserts that social network sites seize the attention of the students and then distract it towards nonacademic and wrong action including unnecessary conversation. Social media platforms have benefits for student for developing ideas opinion, share information, ask question and get feedbacks.

A study conducted by Barikpe [12] revealed that undergraduate students use social media platforms for online publishing that creates opportunities for producing knowledge sharing, research building social networks and developing professional interaction with minimum difficulty. In the same vein Halie et al. [13] assert that social media is an academic platform utilize by instructors and students to build creative thinking, collaborate by posting ideas, sharing essay to peers.

Therefore social platform allows undergraduate students to post class time, rules, assignment notification, suggested reading, and exercises, uses for class discussions, organizing seminars and to provide summaries of reading, write ideas to be based on merit, rather than origin, and ideas that are of quality fitter across the internet 'viral-like' and across the blogosphere.

Social media are interactive networks which provide information and communication technology (ICTs) to the modern society through the instrumentality of the internet and telecommunication gadgets. These international network (internet) its makes the network to expand and increase the possibilities for communicating with wider users across the globe. According to Omekwu et al. [14], it was about 38 years for radio to spread 50 million consumers, 13 years before television attracted the same number and four years for the internet to do so, but took Facebook only 12 months to gain 200 million users

3.2.1 Factors militating the use of social media in teaching and learning during the (COVID-19)

These are some of the problems universities faced in using social media sites in teaching and learning during to the COVID-19 pandemic.

3.2.2 Shift from classroom learning to virtual learning

The change from classroom learning due to the coronavirus pandemic has so many challenges ranging from one nation to another. Virtual learning is new strategy in teaching and learning in most universities in Nigeria. Most schools do not have adequate structure or resources to enable virtual teaching with instant effect. Functioning at home was a difficult task for the lecturers as most of them do not have internet facilities. Courses such practical, music and art could not be taught online as we do not have the expertise to do so. The home front was another challenge especially the female folks who have to guide their children and perform other house chores, this made it difficult for us function effectively in the virtual teaching. Undergraduates who do not have access to computers and at home-based internet services were not part of virtual learning. There is a higher disconnection of students with learning needs (educational, economical, students with special learning needs) or person who special needs who may study without the assistance of their fellow students [15].

3.3 Finance

Students from low income family find it difficult to participate in the online teaching due to financial constraint. Kakuchi [16] reported that many students in Japan have drop out of university studies for financial motives, after the country's coronavirus crisis and restrictions due to the loss of job and problems with personal incomes. The scholars were faced with the challenges of laptop, android phones and internet facilities in order to join the online learning. The university also faced a lot of unexpected, expenses from the outbreak of the COVID-19 by bearing the cost of increase technology cost associated with moving to online classes [17].

3.4 Mental health

COVID-19 pandemic has disturbed the life of several family around the globe with the death total of over 70,000,000 people, this has caused a lot of stress and anxiety which has led to harsh effect on knowledge and Mental health of students [18]. Undergraduates staying far from the home are not only concerned about their health care and learning but are also concerned about their families well-being [19]. The study carried out by www.a.zurem.com revealed that the amount of time spent online has health implication on the students. The use of social media for a long term decides the way the genes operate in the body and weaken body system and hormone levels, it also has affect the psychological health of students.

3.5 Assessment and evaluation

Feedback inform of assessment and evaluation are motivators in education. knowledge of result enhances the performance of student. With the outbreak of COVID-19 many universities are unable to assess or evaluate their students. The two state owned Universities used in this study suspended their semester examination, teaching practice and industrial training due to the challenges of online learning. Laboratory practical, test, gymnastics and performance test cannot be conducted online [20]. Students who cannot access to internet facilities were disadvantaged in the assessment procedure and this will affect their performance [21].

3.5.1 Review of empirical literature

Williams and Adesope [22] investigated students' attitude towards the use of social media sites for educational purpose. The study was carried out in Rivers State Nigeria. The research design was a descriptive research design; the sample size was 300 undergraduate students from three faculties in University of Port Harcourt. The instrument for data collection is a structured questionnaire titled undergraduate attitudes towards the use of social media site for learning process (UATUSMLP). The data obtained were analyzed using mean, ANOVA, Z-test and Scheffe's model. The result showed that social media site are used for learning purposes in terms of fast development in awareness and evidence.

Oye et al. [23] conducted a study on the awareness adoption and acceptance of ICT innovation in higher education institutions. The study was carried out in Jos Plateau State Nigeria. The sample size is 100 undergraduate students (57 males and 43 females). The instrument for data collection is a questionnaire titled UTAUT. The data collected were analyzed using simple percentage, Pearson moment correlation. The result of the studies shows that university ICT makes task more easily accomplished

Fatokun [24] investigated the effect of social media sites on learner achievement and awareness in chemistry in the North–central geopolitical zone of Nigeria. The study adopted a cross-sectional survey design with 240 chemistry learners as the sample size, the result revealed that 60.8% of the students engage in social media for academic purposes. The respondents also revealed that social media has helps in increasing their achievement. The findings further reveal that Facebook is most frequently used among the respondents. The result of the disclose that students did not see social media site as an effective studying instrument and that has made most of the not adopting to modern technology and are not proficient on it usage. The attention of 67.5% respondents are enhanced when using social media site for educational purposes. The findings also reveal that addiction, poor time management and health issues as problem facing the usage of social media site in learning

In the same Vein Omachonu and Akanya [25] asserts that most students using social media sites, spend much time to displace their learning period thereby affecting them negatively. Similarly Asemah, Okpanachi and Edegoh [26] found that social media has adverse effects on the educational achievement of chemistry undergraduates and the Facebook is the mostly frequently used social media.

Priti-Bajpai [27] reveal that university students extensively used WhatsApp, Instagram, LinkedIn, Snapchat Google plus or YouTube for academic purpose and socializing. He further encourages university students to strike a place between the both purposes.

3.6 Statement of the problem

In the era of coronavirus called COVID-19 learning has become difficult if not impossible among students of various institutions due to the closure or shutdown of school. That is face-to-face learning and teaching which is the primary mode of teaching and learning in various institutions have been hindered due to COVID-19. However, social media has been seen as an alternative means of transmitting knowledge skills and values into students without necessarily coming in contact with the students. The question remains that despite the importance of social media in aiding learning and teaching are students aware of this advantage social media has over face-to-face learning a pandemic situation like COVID-19. If the answer to this question is yes for instance another question due arise and that is the level of presentation of social media for learning by students. Also what could be the possible challenges of the use of social network site for learning in coronavirus era forms crux of this investigation hence the problem of the study is to determine the level of awareness and application of social media for learning by undergraduates students in tertiary institutions in Rivers State as well as the possible challenges associated with the aforementioned activities.

3.7 Aim of the study

The purpose of this study was to determine the awareness and application of social media for learning in tertiary institutions in Rivers State. Specifically, the study seeks to:

1. determine the extent to which students are aware of social media for learning in Rivers State owned tertiary institutions.
2. determine the extent to which students apply social media for learning in Rivers State owned tertiary institutions.
3. determine the challenges of students' in the use of social media sites for learning in Rivers State owned universities.

3.8 Research questions

The following research questions guided the study.

1. To what extent are students aware of social media for learning for Rivers State owned Universities?
2. To what extent do students apply social media for learning for Rivers State owned Universities?
3. What are the challenges of students' in the use of social media site in learning in Rivers State Universities?

3.9 Hypotheses

The following null hypotheses were formulated and tested at 0.05 level of significance.

1. There is no significant difference in the level of awareness between RSU students and those of IAUE in the use of social media for learning.
2. The extent to which students apply social media does not significantly depend on university types.

3.10 Methodology

The study adopted the analytic descriptive design. Nwankwo [28] defines descriptive survey design as that study in which the researcher collects data from a great sample taken from a given people and designates certain structures of the sample as they are at the time of the investigation which are of interest to the investigator, though, without controlling any independent variables of the study. One hundred and 60 year two undergraduate Chemistry students of Ignatius Ajuru University of Education (IAUE) and Rivers State University (RSU) both in Rivers State, Nigeria, were randomly selected Three research questions and two null hypotheses guided the study. The instrument for data collection was a researcher made questionnaire named Social Media Awareness and Application for Learning in COVID-19 (SMAALC). To ensure validity, the instrument was given to three experts in the field of science education, educational technology and educational measurement and evaluation. The topic, aims, hypotheses were also presented to the experts for them to indicate the relevance of items in the instrument with stated objectives. Observations and comments made by the professionals were used to modify and correct the items where necessary. The reliability coefficient of the instrument was determined by Pearson product moment as a measure of its stability over time. The consistency coefficient of the instruments was 0.95. The instrument was administered to the students online via their various class social media platforms. Mean, standard deviation and *t*-test were the statistical tool used for data scrutiny

3.11 Results

Research question 3.1: To what extent are students aware of social media for learning for Rivers State owned universities?

Table 3.1 show a grand mean of 2.90 which is higher than the criterion means of 2.50. The result is that student are aware of social media for learning in Rivers State owned universities. This means that the level of consciousness of social media among Chemistry students at tertiary institutions in Rivers State can be described as high.

Research question 3.2: To what extent do students apply social media for learning in Rivers State owned universities**?**

The results in Table 3.2 showed that the grand mean was found to be 2.01, which is less than the benchmark mean of 2.50. Consequently, the application or use of social media for learning in Rivers State owned universities is said to be low.

Table 3.1: Mean rating of responses on the awareness of social media by students.

SN	Social media items	Mean	SD	Remark
1.	Zoom	3.63	0.486	High
2.	Instagram	3.75	0.434	High
3.	WhatsApp	4.00	0.000	High
4.	Skype	3.75	0.434	High
5.	Blog	1.81	0.392	Low
6.	YouTube	3.25	0.434	High
7.	Snapchat	2.75	0.434	High
8.	Imo	1.75	0.434	Low
9.	LinkedIn	3.81	0.392	High
10.	Wikipedia	3.31	0.465	High
11.	My space	2.69	0.585	High
12.	Facebook	4.00	0.000	High
13.	Duo	1.81	0.392	Low
14.	Google classroom	2.81	0.392	High
15.	Twitter	3.81	0.392	Low
16.	Flicky	1.81	0.392	High
17.	E-mail	3.88	0.332	High
18.	2go	3.06	0.430	High
19.	Google	1.13	0.323	Low
20.	Viber	1.00	0.000	Low
21.	Xender	3.13	0.332	High
	Grand mean	**2.90**		**High**

Table 3.2: Mean rating of responses on the use of social media for learning by students.

SN	Item statements remark	Mean	SD	
1.	I use social media for my education purposes	1.50	0.502	Low
2.	I can exchange ideas with the use of social media	2.38	0.698	Low
3.	I watch experiments in YouTube	1.81	0.810	Low
4.	Social media encourages me to meet with other researchers	2.13	0.486	Low
5.	I use social media for online learning	1.50	0.502	Low
6.	Social media helps me to do my assignments and other	2.44	0.498	Low
7.	I share and get information from my class mates and university group via social media	1.81	0.528	Low
8.	I use social media in sending instructional video to my peers outside class time	1.50	0.502	Low
9.	The posting of instructional video and audio clips and images on blogs increase my motivation for social network	2.00	0.869	Low
10.	Social media makes online learning easier during lockdown periods	1.75	0.664	Low
	Grand mean	**2.01**		**Low**

Research question 3.3: What are the challenges of students' in the use for social media for learning in Rivers State universities?

Table 3.3 is the results on the issue of challenges students perceive to the confronting the usage of social media for learning at Rivers State owned universities. The data on the Table revealed that items 1, 3, 4, 5, 6, 7, 8, 9, 10, 12, 13, 14, 15, 16, 17, 18 and 20 all had mean values greater or equal to the criterion mean of 2.50, hence were considered to be some of the challenges students in tertiary institutions in Rivers State owned universities face in the usage of social media site for learning. While, items 2, 11, and 19 had mean values lower than 2.50, therefore, were not considered to be challenges.

Hypothesis 3.1: There is no significant difference in the level of awareness between RSU students and those of IAUE in the use of social media for learning.

Table 3.4, shows that the mean and standard deviation values for IAUE is 61.00 and 2.379, respectively, while those of RSU were 60.90 and 2.368. On further analysis with independent *t*-test, the calculated $t_{(158)} = 0.258$, at $df = 158$, $p\ (0.797) > 0.05$ level of significance, i.e., not significant. Hence, the stated null hypothesis is accepted. The result is that there is no significant difference in the level of awareness between RSU students and those of IAUE in the use of social media for learning.

Hypothesis 3.2: The extent to which students apply social media does not significantly depend on university types

Table 3.3: Mean rating of responses on the challenges of social media for learning by students.

SN	Challenges	Mean	SD	Remark
1.	Finance	3.63	0.486	Agree
2.	Mental health	1.89	0.700	Disagree
3.	Travel restrictions	3.88	0.459	Agree
4.	Poor interest reception	3.75	0.434	Agree
5.	Assessment and evaluation	3.86	0.432	Agree
6.	Lack of immediate responses to students' questions	3.25	0.434	Agree
7.	Home front	2.75	0.434	Agree
8.	Electricity	3.50	0.718	Agree
9.	Audio problems	3.81	0.392	Agree
10.	Poor voice quality	3.31	0.465	Agree
11.	Lack of pre-class preparation	1.89	0.700	Disagree
12.	Less control over online teaching	3.75	0.434	Agree
13.	Lack of trained assistant to support online education platform	3.94	0.231	Agree
14.	Inability to connect to class	3.75	0.434	Agree
15.	Lack of computer literacy	3.89	0.388	Agree
16.	Limited number of people to connect	3.25	0.434	Agree
17.	Location of the student	2.75	0.434	Agree
18.	Lack of privacy	3.89	0.419	Agree
19.	Real friendship	1.78	0.660	Disagree
20.	I am addicted to social media and this is a challenge	3.31	0.465	Agree

That affects my academic life.

Table 3.5, shows that the mean and standard deviation values for IAUE is 22.08 and 2.173, respectively, while, those of RSU were 22.15 and 2.105. On further analysis and independent *t*-test, the calculated $t_{(158)} = 0.192$, and $df = 158$, $p^{(0.848)} > 0.05$ level of significance, i.e., not significant. Hence, the stated null hypothesis is accepted. The result is that the extent to which students apply social media for learning does not significantly depend on university types.

3.12 Discussion

The results of the study from Table 3.1 show that the students are aware of social media for learning in Rivers State owned universities. The level of awareness of social

Table 3.4: Independent *t*-test analysis on the level of awareness of social media by students.

University	*n*	Mean	SD	T	*df*	Sig	Decision type
IAUE	60	61.00	2.379	0.258	158	0.797	NS
RSU	100	60.90	2.368				

NS, not significant, $p > 0.05$ level of significance; IAUE, Ignatius Ajuru University of Education; RSU, Rivers State University.

Table 3.5: Independent *t*-test analysis on the use of social media for learning by students.

University	*n*	Mean	Sd	T	*df*	sig	Decision type
IAUE	60	22.08	2.173	0.192	158	0.848	NS
RSU	100	22.15	2.105				

NS, not significant, $p > 0.05$ level of significance; IAUE, Ignatius Ajuru University of Education; RSU, Rivers State University.

media among chemistry students in tertiary institution in Rivers State can be describe as high based on grand mean of 2.90. The students since they are youths will like to exert their energy on new technologies in other to be abreast with the time they found themselves. The result of this study is in agreement with Barikpe [12] that undergraduate students are aware of social media platforms and use them for online publishing that create opportunities for producing knowledge sharing, research building social networks and developing professional interactions with minimum difficulty. Similarly, William and Adesope [22], Oye, Aiahad and Abraham [23] affirms that students are aware of social media and it is use for educational purpose makes them to accomplish educational task easily.

Results in Table 3.2 show that the level of usage of social media for learning at state owned universities is low with a grand mean of 2.01. The low level of attributed to what Omachonu and Akanya [25] asserts that most students use social media site and spend much period in which displace their learning time thereby affecting them negatively The result of the study disagrees with Oye et al. [23] affirms that students are aware of social media and it is use for educational purpose makes them to accomplish educational task easily.

The results in Table 3.3 reveal that students are faced with enormous challenges in the use of social media site. The challenges namely finance, travel restriction, privacy, assessment and evaluation, poor internet reception addiction, home front, poor voice quality among others. The result agrees with Omekwu et al. [14] , Fatokun [24], Smalley [17], Sahu [20] and Alruwise et al. [21] that students and universities are face with a lot of unexpected challenges to cope with learning in this era of coronavirus. The result of the study disagree with Al-Rabiahab et al. [18], Zhai and Du [19] that sees mental health as one of the challenge in the use of social network site in the era of coronavirus pandemic.

Furthermore, Table 3.4 also shows that there no significant difference in the level of awareness between RSU students and those of IAUE in use of social network site for learning. The no significant result is because students in the university in this era of coronavirus are faced with socials media as the only option that can be used for learning since the face-to-face learning is not available. Smalley [17] and Sahu [20] asserts the novel coronavirus has reposition the university education system there by transitioning to online platform. Online instruction as the only option for instruction for this era has increased the students' awareness of various social media platforms. The no significant difference in the results is also attributed to the educational benefits of these social media platforms as observed by Barikpe [12] that student Mahe use of the benefit of social media especially to deal with the unexpected incident of online education due to coronavirus.

In Table 3.5 the extent to which students apply social media for learning does not significantly depend on university types. The students in the both university have low level of application for social media. This is due to inability of students to make use of social network site for learning. The result of the study is in agreement with Fatokun [24] affirms that most students do not see the social media has an effective tool for learning and has not made effort in adopting to the modern technology.

3.13 Conclusion

The study investigated the effect of social media and learning in an era of coronavirus among Chemistry students in tertiary institution in Rivers State Nigeria The results revealed that students are aware of social media for learning such as Zoom, WhatsApp, Facebook etc. The outcome of this investigation also showed that there is poor application of social network site for learning among Chemistry students in Rivers State owned universities. Finance, travel restriction, assessment and evaluation, poor internet reception, availability of electricity and others were identified as challenges while mental health of student, lack of before class preparation and associating with real friends were not considered to be a challenges to the use of social network sites for learning. Extent to which students apply social media does not depend on university types. Furthermore, the level of awareness and application of social media for learning do not significantly depend on school type.

3.14 Suggestions

The researchers made the following suggestions based on the findings;

1. University in Rivers State should endeavor to engage their students in training that will avail them the opportunity to apply or utilize effectively social media on their learning activities.
2. Chemistry undergraduates should cultivate and maximize the potential of the different social media for their academic benefits.
3. Chemistry lecturers should make sure that they use social media as an instrument for enhancing learning and encouraging the educational performance of undergraduates in the university through academic discussions, assignment can be

posted there, even teachers can upload their lesson notes, they can also upload useful videos on various topics
4. Students should create an equilibrium between educational and noneducational activities on social network site by directing on the educational relevance of most sites instead of engaging in nonprofit surfing.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.
Research funding: None declared.
Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Chachrour M, Assi S, Bejjani M, Nasrallah AA, Salhab H, Fare MY, et al. A bibilometric analysis of COVID-19 research activity a call for increased output. Cureus 2020;12:e7357.
2. Cennimo JJ. Coronavirus disease 2019 (COVID 19). Available from: https//emedicine.medscape.com> 2 [Accessed 16 June 2020].
3. World Health Organization (WHO). Question and answer/COVID-19) health top WHO EMBRO. Available from: www.emro.who.int>corona-virus [Accessed 15 June 2020].
4. Coronavirus COVID-19 global cases by Centre for system Science and Engineering (CSSE) at Johns Hopkins university (JHU). Available from: https://coronavirus.jhu.edu/map/html [Accessed March 2020].
5. Ikegbunam CI. Learning approaches. In Ivowi UMO, editor. Curriculum theory and practice, curriculum organization of Nigeria. CON: Curriculum Organisation of Nigerian; 2009.
6. Amichai-Hamburger T, Hayat T. Social networking. In Rossler P, editor. The international encyclopedia of media effects; 2017, https://doi.org/10.1002/978111883764.wbieme0170.
7. Adejoh MJ, Tse TRS. The impact of social networks on students academic achievement in biology in Benue state. In: Communication technology and STEM education 57th annual conference proceedings of STAN. Abuja Nigeria: Heinmenn Publishers; 2016:30–5.
8. Rouse M. Definition of social media. Available from: Whatis.com [Accessed 12 Dec 2017].
9. Akaninwor GIK. Educational technology: theory and practice. Owerri: Odessa Educational Books Publishers; 2017.
10. Available from: https://www.history.com/this-day-in-history/facebook-launches-mark-zuckerberg. Facebook Launch [Accessed 20 June 2020].
11. Cassidy E, Britsch J, Griffin G, Manlolovitz T, Shen I, Turney L. Higher education and emerging technologies: student usage preferences and lessons for library services. Ref User Service Q 2011; 50:380–91.
12. Barikpe B. Usage of blogs for educational purpose by undergraduate students [Unpublished M Ed Dissertation]. Port Harcourt: University of Port Harcourt; 2018.
13. Halic O, Lee D,Paulus T,Spence M. To blog or not blog: studies perceptions of Blog Effectiveness for learning in a college-level course. Internet High Educ 2010 13, 206–13.
14. Omekwu OC, Eke HN, Odoh NJ. The use of social networking site among the undergraduate students of University of Nigeria Nsukka. Available from: www unn.edu.ng [Accessed 20 Apr 2020].

15. UNESCO. Coronavirus impacts education. Available from: htps://en.unesco.org/themes/education emergence/coronavirus_ school_ closures.
16. Kakuchi S. COVID-19 hits student finance amidst call for wider reforms. University World News: The Global Window on High Education; 2020.
17. Smalley A. Higher education response to coronavirus (COVID-19). In: National Conference of State Legislatives. Washington; 2020.
18. Al-Rabiaahab A, Temsahabc MH, Al-Eyadhy A. Middle East respiratory syndrome-corona virus (MERS-CoV) associated among Medical students at a University Teaching Hospital in Saudi Arabia. J Infect Public Health 2020;5:10–8.
19. Zhai Y, Du X. Mental health care for international Chinese students affected by the COVID-19 outbreak. Lancet Psychiatry 2020;7. https//doi.org/10.1016/s2215-0366(20)30089-4.
20. Sahu P. Closure of Universities due to Coronavirus Disease 2017 (COVID- 19)Impact on education and mental health of students and Academic staff. Cureusiz 2020;4:7541–50.
21. Alruwais N, Wills G, Wald M. Advantages and challenges of using e- Assessment. Int J Inf Educ Technol 2018;8:34–7.
22. Willams C, Adesope RY. Undergraduates' attitude towards the use of social media for learning purposes. World J Educ 2017;6:90–5.
23. Oye ND, Aiahad N, Abrahim N. Awareness adoption and acceptance of ICT Innovation in higher education institutions. Int J Eng Res Afr 2017;4:1393–9.
24. Fatokun VK. Effect of social media on Undergraduate students Achievement and interest in Chemistry in the North Central geo-political zone of *Nigeria*. Int J Sci Technol Educ Res 2019;2:9–15.
25. Omachonu CG, Akanya J. Effect of social media on the Academic Achievement of student: A case of study of student of the Department of Arts education Kogi state University Anyigba Nigeria. Eur Am J 2018;14–23. https://doi.org/10.1183/13993003.00869-2018.
26. Asemah ES, Okpanachi RA, Edegoh LN. Influence of social media on the academic performance of the undergraduate student of Kogi State University Anyigba, Nigeria [unpublished B.Ed thesis]. 2013.
27. Priti-Bajpai M. Analyzing effect of social media and academic performance of University graduates. ICIEI Sociol 2018;10. https://doi.org/10.1145/3234825.3234830.
28. Nwankwo OC. A practical guide to research writing for student of research enterprise. Port Harcourt: University of Port Harcourt Press; 2016.

Adeleke Adeniyi* and Olayiwola Giwa

4 Accumulation and health effects of metals in selected urban groundwater

Abstract: The contamination of water sources as a result of man's activities is of concern because of its potential impact on the health of humans. Samples of groundwater were collected from four households within metropolitan Lagos between the months of April and August, 2019. The samples were analyzed for cadmium, calcium, iron, lead, manganese and zinc using atomic absorption spectrometry. Structured questionnaire was administered to the residents in households where the water samples were collected. Results obtained were compared with global background values and WHO guidelines for drinking water. The pH values ranged from 5.16 ± 0.26 to 5.29 ± 0.44, whereas, the control pH values were within the WHO guidelines of 6.5–8.5. The concentrations (mg/L) ranged from 2.04 ± 1.01–23.48 ± 8.81 (calcium); 3.35 ± 1.94–3.60 ± 2.25 (iron); 0.31 ± 0.42–0.47 ± 0.51 (manganese) and 0.27 ± 0.04–0.77 ± 0.69 (zinc), respectively. Cadmium and lead were not detected. The health risk indices (HRI) values were found to be in the order of Fe > Zn > Mn and were below the threshold value of 1. Statistical analysis of variance (ANOVA) was used to ascertain statistical significant differences of metal concentrations in the four locations. Metal pollution source control and periodic water quality monitoring is recommended.

Keywords: cadmium, groundwater, health risk, lead, metals

4.1 Introduction

Groundwater holds the largest reserve of available freshwater in the world, providing water for drinking and irrigation among others to an estimated 7.8 billion people. Urbanization and industrialization have led to increasing global levels *of environmental degradation* with unpleasant impact on groundwater quality [1–3]. The impact of urbanization and industrialization is more severe in developing countries, most of whom have relatively unplanned cities with poor waste management systems [1, 4–7]. Urbanization has been implicated in the modification of groundwater quality and flow pattern; however, these modifications evolve with time [2]. According to the United Nations (UN) over 1.1 billion humans lack access to improved water sources [8]. By year 2050, it is estimated that about four billion people representing 52 % of the global

---

***Corresponding author: Adeleke Adeniyi**, Department of Chemistry, Lagos State University, Ojo, Lagos, Nigeria, E-mail: lekeadeniyi@yahoo.com

Olayiwola Giwa, Centre for Environmental Studies and Sustainable Development (CESSED), Lagos State University, Ojo, Lagos, Nigeria

This article has previously been published in the journal Physical Sciences Reviews. Please cite as: A. Adeniyi and O. Giwa "Accumulation and health effects of metals in selected urban groundwater" *Physical Sciences Reviews* [Online] 2021, 7. DOI: 10.1515/psr-2020-0089 | https://doi.org/10.1515/9783110726145-004

population will live in areas that suffer scarcity of potable water for at least one month each year [9]. Ensuring availability of clean drinking water is adjudged to be one of the most cost-effective methods of improving public health [7, 10, 11]. The Goal 6 of the United Nations Sustainable Development Goals (SDGs) is to ensure universal access to water and sanitation [12]. Nigeria and many developing countries missed the 2005–2015, World Health Organization (WHO) target decade aimed at ensuring full access to water and sanitation for all people [12, 13]. Hopefully, developing countries will key into the "Water Action Decade" (2018–2028) by among others adopting a pragmatic approach in the management of their water resources with a view to reaching the millions of people that still lack access to safe drinking water. In most countries, there is the absence of an institution charged with the oversight and management of urban groundwater resources [1, 2]. The tamed response of some governments, to manage groundwater resources in some cities is always with the view to generate additional income [14]. The aim is always to tax residents, who out of necessity have to provide water for their households by digging shallow wells or boreholes [15, 16].

The main sources of pollution are, respectively, the open waste dumps that leach into groundwater and the often untreated wastewater from domestic and industrial processes [13, 14, 17]. Lagos with the highest population among Africa's cities is densely populated and produces large quantities of wastes. Lagos city's unwholesome waste management practices exacerbate the risk of groundwater contamination [15, 17]. The municipal water supply in Lagos is grossly inadequate leaving most residents to rely on water wells/boreholes for their water needs [4, 15, 16]. It is therefore imperative to continuously monitor groundwater quality, and the risk posed, carefully assessed and acted upon. Identifying the critical metal pollution sources is equally crucial for long term sustainable groundwater resource management program. The aim of the study is to determine the concentration of cadmium, calcium, iron, lead, manganese and zinc in the groundwater sources from selected locations in Aboru, Igando, Akesan and Obadore, Lagos, Nigeria. The risk associated with the water usage is also assessed.

The findings are expected to provide information to residents with respect to the wholesomeness of their water. It will equally serve as a wake-up call for government to work assiduously toward providing potable water for residents in line with the United Nation's sustainable development goals Agenda number 6.

4.2 Materials and methods

4.2.1 Materials and chemicals

Analytical grade nitric acid, standard metal solutions, deionized/distilled water, glass wares, hot plate, sample bottles and plastic containers were used. The chemicals were purchased from Fluka Chemie GmbH (Buchs, Switzerland).

Table 4.1: GPS coordinates of the sampling locations.

Location	GPS Coordinates (Latitude)	GPS Coordinates (Longitude)
Aboru	6° 37′18.68268″N	3° 16′23.8602″E
Igando	6° 33′47.2086″N	3° 14′8.0898″E
Akesan	6° 31′40.10664″N	3° 13′25.49568″E
Obadore	6° 31′32.25576″N	3° 12′46.67796″E

4.2.2 Sampling area

Samples were collected from selected households within the Alimosho axis of Lagos, Nigeria. The study area is densely populated. The residents are not covered by the government's municipal water supply, hence they provide for their water needs through shallow wells and boreholes. The waste management practices are largely unsustainable. Unwholesome practices like open burning of solid wastes, dumping of refuse on open spaces, usage of nonsanitary landfills and individual dug up pits for domestic liquid waste collection are still operational. Government's refined petroleum products pipelines from the port of import to the depots passes through parts of the study area. The study area comprises predominantly sedimentary and basement rocks complexes. The global positioning system (GPS) data of the sampling locations are indicated in Table 4.1.

4.2.3 Sampling and sample preparation

Water samples ($n = 25$) from groundwater sources were collected from households between the months of April and August, 2019 following standard sampling techniques [13, 18] in other to analyze their metal contents. After pH determination, each sample was acidified by adding 3–4 mL nitric acid. A structured questionnaire was administered to members of the participating households. 50 mL of the acidified water samples were taken from their respective containers and 5 mL of nitric acid was added. The acidified water samples were placed on a hot plate for digestion, allowed to cool and filtered into a 25 mL volumetric flask for analysis [13]. Blank samples were prepared using distilled de-ionized water to assure quality. Similarly, predigested water samples were spiked with metal standards in triplicate for metal recovery studies. The AAS setting and operational conditions were done in accordance with the manufacturer's specifications, and were calibrated with analytical grade standard metal solutions (1000 mg/L) after appropriate dilutions.

4.2.4 FAAS analysis and quantification

Six metals – cadmium, calcium, iron, lead, manganese and zinc were determined in an air-acetylene flame (Flame Atomic Absorption Spectrophotometer FAAS, Model: Buck

Table 4.2: Chronic daily intake (CDI; µg/kg per day) of groundwater.

Location	Cadmium	Iron	Lead	Manganese	Zinc
Aboru	ND	9.81×10^{-2} (10.80×10^{-2})	ND	1.31×10^{-2} (1.44×10^{-2})	0.75×10^{-2} (0.83×10^{-2})
Igando	ND	9.66×10^{-2} (10.34×10^{-2})	ND	1.0×10^{-2} (1.1×10^{-2})	1.5×10^{-2} (1.65×10^{-2})
Akesan	ND	9.31×10^{-2} (10.24×10^{-2})	ND	1.03×10^{-2} (1.13×10^{-2})	2.14×10^{-2} (2.35×10^{-2})
Obadore	ND	10×10^{-2} (11.1×10^{-2})	ND	0.86×10^{-2} (0.95×10^{-2})	1×10^{-2} (1.1×10^{-2})

Values in parentheses are for children; ND, not detected.

210 VGP). The results are presented in Table 4.2. These are metals that could be environmentally enriched by the anthropogenic activities around the sample locations. The water sample results were compared to the World Health Organization (WHO) guideline limits [19].

4.2.5 Statistical analysis

To estimate statistical significant difference, analysis of variance (ANOVA), and *t*-test statistical tool of SPSS version 22 was utilized.

4.2.6 Risk assessment

Analyzing potential health risk for adults and children, involves determination of the health risk indicators such as chronic daily intakes (CDI) and Health risk index (HRI). These were calculated for the samples [13, 20, 21] as follows: CDI (mg kg^{-1} day^{-1}) = $C_m \times I_w/W_b$, where C_m (mg/L) = metal concentration in water; I_w (L/day) = average daily intake of water (assumed to be 2 L per day for adult and 1 L per day is for children); W_b = the average body weight used (assumed to be 72 kg for adults and 32.7 kg for children). The Health risk Index is calculated from the CDI as follows: HRI = CDI/Rfd, where CDI is the chronic daily intake from ingestion of metal in drinking water (mg kg^{-1} day^{-1}); Rfd is the oral reference dose (mg/kg) of a particular metal. The Rfd values for Fe, Mn and Zn are 7×10^{-1}, 1.4×10^{-1} and 3×10^{-1}, respectively [22]. The CDI data is presented in Table 4.2.

4.3 Results and discussion

The pH values (Table 4.3), ranged from 5.16 in Obadore to 5.29 in Igando. The results are generally below the guideline limit (6.50–8.50) set by WHO. These values differ from

Table 4.3: Mean metal concentration (mg/L) in the groundwater samples and control.

Location	pH	Ca	Cd	Fe	Mn	Pb	Zn
Control	7.19 ± 0.22	64.08 ± 12.55	ND	3.31 ± 2.40	0.29 ± 0.39	ND	2.94 ± 0.62
Aboru	5.29 ± 0.37	23.48 ± 8.81	ND	3.53 ± 2.02	0.47 ± 0.51	ND	0.27 ± 0.04
Igando	5.29 ± 0.44	4.16 ± 4.85	ND	3.38 ± 1.90	0.36 ± 0.40	ND	0.54 ± 0.27
Akesan	5.23 ± 0.78	2.13 ± 0.78	ND	3.35 ± 1.94	0.37 ± 0.40	ND	0.77 ± 0.69
Obadore	5.16 ± 0.26	2.04 ± 1.01	ND	3.60 ± 2.25	0.31 ± 0.42	ND	0.36 ± 0.33
WHO limits	6.5–8.5	200	0.003	0.3	0.4	0.01	3.0

WHO, World Health Organization; BV, background values; ND, not detected.

values reported earlier for Chikhwawa, Malawi borehole water (6.90–7.70), Lao PDR and Swat, northern Pakistan (6.50–8.60), respectively [20, 21, 23], and in Akure metropolis, Nigeria [24], with mean values of 6.59 in the dry season and 6.85 in the rainy season. The values are however similar to that of Ibadan groundwater samples, with mean values of 5.7–5.8 [5]. The pH of drinking water has no extreme negative effects on human health but acidic water has been related to abdominal discomfort due to gastrointestinal irritation [25]. Acidic pH affects water quality parameters such as metal solubility. Water with a lower pH has the tendency to leach metal ions such as iron, manganese, copper, lead and zinc from aquifers and plumbing materials [26].

The metal mean concentrations are shown in Table 4.3. Cadmium and lead were not detected in the water samples across the four locations and control. Aboru groundwater however, recorded the highest levels of calcium and manganese with mean concentrations of 23.48 ± 8.81 and 0.47 ± 0.51 mg/L, respectively. Whereas, Obadore groundwater has the highest concentration of iron (3.60 ± 2.25). Nonetheless, the zinc mean concentration of 0.77 ± 0.69 for Akesan samples are the highest recorded across the four locations. Iron and manganese are higher than the control values while calcium and zinc are lower than the control values. Manganese, lead and cadmium are below WHO guideline limits (0.4 mg/L (Mn), 0.01 mg/L (Pb) and 0.003 mg/L (Cd)), except for manganese in Aboru (0.47 ± 0.51 mg/L). The concentration of iron in all the samples are above the WHO guideline limits (0.3 mg/L), with values ranging from 3.35 ± 1.94 mg/L to 3.60 ± 2.25 mg/L. The concentration of zinc are however below the WHO guideline limits (3.0 mg/L) with values ranging from 0.27 ± 0.04 mg/L to 0.77 ± 0.69 mg/L. The concentration of calcium in the locations is in the order Aboru > Igando > Akesan > Obadore. Their values are less than 60 mg/L, indicating that they are soft water [27]. Calcium plays a critical role in inhibiting the binding of Cd and Zn to binding sites. This is, as a result of the competition of Cd and Zn with Ca and Mg ion for binding sites [3, 28]. The higher the calcium concentration (hardness), the lesser the potential toxicity of Cd, Zn and also Pb^{2+}. The mean calcium concentrations in the study locations were generally lower than values reported earlier for central Benue trough, Nigeria (6.20 mg/L to 281 mg/L) and the 58.0–324.0 mg/L values for Uyyakondan channel, groundwater, south India [29, 30]. The values for iron and manganese in selected areas of Ibadan varied with the population density of the area. Wells

Table 4.4: Health risk index (HRI) off metals through water consumption.

Location	Cd	Fe	Pb	Mn	Zn
Aboru	ND	14.01×10^{-2} (15.43×10^{-2})	ND	9.36×10^{-2} (10.29×10^{-2})	2.50×10^{-2} (2.77×10^{-2})
Igando	ND	13.80×10^{-2} (14.77×10^{-2})	ND	7.14×10^{-2} (7.86×10^{-2})	5×10^{-2} (5.5×10^{-2})
Akesan	ND	13.3×10^{-2} (14.63×10^{-2})	ND	7.36×10^{-2} (8.09×10^{-2})	7.13×10^{-2} (7.83×10^{-2})
Obadore	ND	14.29×10^{-2} (15.86×10^{-2})	ND	6.14×10^{-2} (6.79×10^{-2})	3.33×10^{-2} (3.37×10^{-2})

Values in parentheses are for children; ND, not detected.

located in the medium density area had the highest average iron concentration (1.64 ± 0.2 mg/L) while boreholes in the low density area had the highest average iron concentration (1.89 ± 0.8 mg/L). The lowest average manganese concentration for well and borehole water sources (0.29 ± 0.1 mg/L and 0.26 ± 0.2 mg/L) were found for medium density area [31]. These values are below those reported for this study. The concentration of groundwater iron reported for Tamil Nadu, India, Alahsa Oasis farms, Saudi Arabia and Basal basin, southeastern Iran [32–34] were generally lower than the mean values recorded for Aboru, Igando, Akesan and Obadore water samples (Table 4.3). The values for zinc in the sample locations are consistent with the values of Zn reported for groundwater sourced from Basal basin, southeastern Iran and Tamil Nadu, India [32, 34]. The measured concentrations of heavy metals follows the order Fe > Mn > Zn in Aboru and Igando, while the trend, Fe > Zn > Mn was observed in Akesan and Obadore. A similar heavy metal order was observed for groundwater sourced from the Virudhunagar industrial township, India [13].

Health risk index (HRI) of the heavy metals is shown in Table 4.4. HRI values were scaled as follows: <1 = less risk; >1 = health risk. HRI values for iron, manganese and zinc in all locations were found to be <1 for adults and children. This is an indication of minimal risk [4, 35]. However, the bioaccumulation of metals over time is a cause for concern [22, 28].

The *t*-test results shown in Table 4.5 are comparison with the control parameters. It indicates for pH, that the difference in means is statistically significant at 0.05 level. Thus, the calculated t-values for all the sample locations are higher than the critical value

Table 4.5: *t*-statistical analysis of control vs sample location.

	Aboru	Igando	Akesan	Obadore
pH	10.16*	12.73*	17.37*	19.31*
Ca	6.37*	9.87*	11.22*	11.58*
Fe	0.36^{ns}	0.078^{ns}	1.57^{ns}	0.36^{ns}
Mn	0.82^{ns}	2.4*	0.43^{ns}	0.27^{ns}
Zn	9.81*	10.79*	18.72*	13.21*

*significant at $p < 0.05$; ns, nonsignificant at $p < 0.05$; $t_{tab} = 2.15$ at $p < 0.05$.

Table 4.6: ANOVA of metal levels in groundwater in the four locations and control.

. Parameter	pH	Cd	Ca	Fe	Pb	Mn	Zn
$F < 0.05$	34.48*	–	68.73*	0.30^{ns}	–	0.24^{ns}	30.10*

*Significant at 95% confidence level; ns, nonsignificant at $p < 0.05$; $F_{tab} = 2.87$ at $p < 0.05$.

(2.13). The t_{cal} values are (10.16), (12.73), (17.37) and (19.31) for Aboru, Igando, Akesan and Obadore, respectively. Similar significant values have been reported earlier with control samples [4, 36]. The *t*-test statistic for calcium ion indicates that the difference in means is statistically significant at $p < 0.05$ level. Thus the calculated t-values for all the sample locations are higher than the critical value (2.13). The values are (6.37), (9.87), (11.22) and (11.58) for Aboru, Igando, Ilado-Akesan and Obadore, respectively. Iron concentrations across the sample locations are nonsignificant compared with the control. However, only Igando recorded a statistically significant t_{cal} value for manganese. Statistical nonsignificant values are indications of wholesomeness as far as those parameters are concerned with respect to the control samples. The *t*-test on zinc indicates that the difference in means is statistically significant at 0.05 level.

The comparison of pH and metal ions from the sample locations and control using the analysis of variance (ANOVA) (Table 4.6) indicates significant variations of pH, calcium, and zinc at 95 % confidence level. This may be as a result of differences in the aquifer compositions in the respective locations. This inference is supported by the study of the groundwater concentration of some metal ions in Agbor and Owa communities, Nigeria [36]. However, there is no significant difference in iron and manganese. This infers a common origin of iron and manganese ions in the sample locations. This outcome is supported by results published earlier for Ibadan and north eastern United States of America groundwater samples as it relates to surface-soil-aquifer connection [5, 37].

4.4 Conclusion

This study is based on the determination of six metals in selected groundwater sources in urban Lagos and potential health effects. It is clear from this study, that the groundwater from the sampled locations is slightly acidic and characterized by low level of calcium, < 60 mg/L. The concentrations of iron, manganese and zinc were relatively high. Cadmium and lead were not detected which is heartwarming. The HRI values for groundwater in the sample locations are below the threshold value of 1. This indicates that no significant health risk from the metal is observed. There is need to restructure the Water Corporation to enable the provision of potable water to all residents in line with the United Nations sustainable development goal, Agenda 6 on water and sanitation. Adopting a sustainable waste management regime is imperative to control metal pollution sources.

Acknowledgments: The authors are grateful to the Department of Chemistry, Lagos State University for providing most of the facilities. We are equally grateful to Dr. Ojo Oluwole and Mr. Mutiu Sowemimo for valuable assistance.
Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.
Research funding: None declared.
Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Fienen MN, Arshad M. The international scale of groundwater issue. In: Jakeman AJ, Barreteau O, Hunt RJ, Rinaudo JD, Ross A, editors. Integrated groundwater management. Cham: Springer; 2016.
2. Foster S. Global policy overview of groundwater in urban development – a tale of 10 cities. Water 2020;12:456–63.
3. Chaturvedi A, Bhattacharjee S, Kumar V, Singh AK. A study on the interdependence of heavy metals while contributing to groundwater pollution index. Environ Sci Pollut Res 2021;66:1–10.
4. Adeniyi AA, Yusuf KA, Okedeyi O, Sowemimo M. Classification and health risk assessment for borehole water contaminated by metals in selected households in south west Nigeria. J Water Resour Protect 2016;8:459–71.
5. Adeniran A. Assessment of water quality in slum area Ibadan. Hydrol Curr Res 2018;9:8.
6. Belkhiri L, Tiri A, Mouni L. Assessment of heavy metals contamination in groundwater: a case study of the south of Setif area, East Algeria. In: Komatina D, editor. Achievements and challenges of integrated river basin management. London: IntechOpen; 2018.
7. Vetrimuruga E, Brindha K, Elango L, Ndwandiwe OM. Human exposure risk to heavy metals through groundwater used for drinking in an intensively irrigated river delta. Appl Water Sci 2017;7: 326–3280.
8. Cunningham WP, Cunningham MA. Environmental science: a global concern. New York: McGraw-Hill; 2014.
9. Boretti A, Rosa L. Reassessing the projections of the world water development report. Clean Water 2019;2. https://doi.org/10.1038/s41545-019-0039-9.
10. Vaishaly AG, Mathew BB, Krishnamurthy NB. Health effects caused by metal contaminated groundwater. Int J Adv Sci Res 2015;1:60–4.
11. Liu Y, Ma R. Human health risk assessment of heavy metals in groundwater in Luan river catchment within the North China plain. Geofluids 2020;2020:7.
12. United Nations. Sustainable development goal 6. New York: Synthesis report on water and sanitation; 2018.
13. Raja U, Lakshmi RV, Sekar CP, Chidamaran S, Neelakantan MA. Health risk assessment of heavy metals in groundwater of industrial township Virudhunager, Tamil Nadu, India. Arch Environ Contam Toxicol 2021;80:144–63.
14. Ighalo JO, Adeniyi AG. A comprehensive review of water quality monitoring and assessment in Nigeria. Chemosphere 2020;260:127569.

15. Balogun II, Sojobi AO, Galkaye E. Public water supply in Lagos State, Nigeria: review of importance and challenges, status and concerns and pragmatic solutions. Congent Engin 2017;4. https://doi.org/10.1080/23311916.2017.1329776.
16. Shiru MS, Shahid S, Shiru S, Chung ES, Alias N, Ahmed K, et al. Challenges in water resources of Lagos mega city of Nigeria in the context of climate change. J Water Clim Change 2019;11:1067–83.
17. Singha S, Pasupuleti S, Singha SS, Kumar S. Effectiveness of groundwater heavy metal pollution indices studies by deep-learning. J Contam Hydrol 2020;235:103718.
18. America Public Health Association. Standard methods for the examination of water and wastewater, APHA, AWWA and WPCE, 20th ed. Springfield, Byrd Progress: American Public Health Association; 1998.
19. WHO. Guidelines for drinking water quality, 4th ed. Geneva: World Health Organization; 2011.
20. Chanpiwat P, Lee B, Kim K, Sthiannopkao S. Human health risk assessment for ingestion exposure to groundwater contaminated by naturally occurring mixtures of toxic heavy metals in the Lao PDR. Environ Monit Assess 2014;186:4905–23.
21. Sheng D, Wu J, Wen X, Wu M, Zhang C. Contamination and ecological risk of heavy metals in groundwater of a typical agricultural area in NW China. Geochem Explor Environ Anal 2020;20:440–50.
22. Javed M, Usmani N. Accumulation of heavy metals and human risk assessment via the consumption of freshwater fish *Mastacembelus armatus* inhabiting, thermal power plant effluent loaded canal. SpringerPlus 2016;5:776.
23. Grimason AM, Morse TD, Beattie TK, Masangwi SJ, Jabu GC, Taulo SC, et al. Classification and quality of groundwater supplies in the lower Shire valley, Malawi—part 1: physico-chemical quality of borehole water supplies in Chikhwawa, Malawi. Water SA 2013;39:563–72.
24. Nwakor EK, Ogbu KN, Orakwe CC, Chukwuma EC, Nwachukwu CP. Assessment of seasonal groundwater quality for domestic use in Akure metropolis, Ondo State, Nigeria. Int J Agric Biosci 2013;3:16.
25. Kempster PL, Van Vliet HR, Kuhn A. The need for guidelines to bridge the gap between ideal drinking-water quality and that quality which is practically available and acceptable. Water SA 1997;23:163–7.
26. Ho KC, Chow YL, Yau JTS. Chemical and microbiological qualities of the east river (Dongjiang) water, with particular reference to drinking water supply in Hong Kong. Chemosphere 2003;52:1441–50.
27. McGowan W. Water processing: residential, commercial, light-industrial, 3rd ed. Lisle, Illinois: Water Quality Association; 2000.
28. Adeniyi AA, Yusuf KA, Okedeyi OO. Assessment of the exposure of two fish species to metals pollution in the Ogun river catchments, Ketu, Lagos, Nigeria. Environ Monit Assess 2008;137:451–8.
29. Okonkwo A. A re-appraisal of groundwater quality in parts of central Benue trough, Nigeria. Int J Advan Mat Res. 2015;1:102–12.
30. Brindha K, Kavitha R. Hydrochemical assessment of surface water and groundwater quality along Uyyakondan channel, south India. Environ Earth Sci 2015;73:5383–93.
31. Moyosore JO, Coker AO, Sridhar MKC, Adejumo M. Iron and manganese levels of groundwater in selected areas in Ibadan and feasible engineering solutions. Euro Sci J 2014;10:11.
32. Sridhar SGD, Sakthivel AM, Sangunathan U, Balasubramanian M, Jenefer S, Mohamed RM, et al. Heavy metal concentration in groundwater from Besant Nagar to Sathankuppam, south Chennai, Tamil Nadu, India. Appl Water Sci 2017;7:4651–62.
33. Fahad NA. Assessment of the levels of some heavy metals in water in Alahsa Oasis farms, Saudi Arabia, with analysis by atomic absorption spectrophotometry. Arabian J Chem 2015;8:240–5.
34. Rezaei A, Hassani H, Hassani S, Jabbari N, Mousavi SF, Rezaei S. Evaluation of groundwater quality and heavy metal pollution indices in Bazman basin, southeastern Ira. Groundwater Sustain Dev 2019;9:100245.

35. Majolagbe AO, Adeyi AA, Osibanjo O, Adams AO, Ojuri OO. Pollution vulnerability and health risk assessment of groundwater around an engineering landfill in Lagos, Nigeria. Chem Inter 2017;3: 58–68.
36. Oyem HH, Oyem IM, Usese AI. Iron, manganese, cadmium, chromium, zinc and arsenic groundwater contents of Agbor and Owa communities of Nigeria. SpringerPlus 2015;4:104.
37. McMahon PB, Belitz K, Reddy JE, Johnson TD. Elevated manganese concentrations in United States groundwater, role of land surface–soil–aquifer connections. Environ Sci Tech 2019;53:29–38.

Fawzia Narod* and Vickren Narrainsawmy

5 Evaluation of the Chemistry curriculum at the lower secondary level: feedback from educators

Abstract: Mauritius is presently witnessing a major educational reform, which has necessitated a review of the lower secondary curriculum in all subjects, including Science. Educators were called to evaluate the Science curriculum (which includes Biology, Chemistry and Physics components) by providing feedback on the curriculum content and content organisation. One hundred and thirty-three educators took part in this exercise. This paper focuses on a detailed analysis of the feedback obtained from educators regarding the lower secondary Chemistry curriculum (LSCC) to identify the challenges encountered in its implementation. The Process component of the Stufflebeam's (Stufflebeam DL. The CIPP model for evaluation. In: Evaluation models. Dordrecht: Springer; 2000:279–317 pp) Context, Input, Process and Product (CIPP) Evaluation model has been used as a framework for the study. Based on qualitative thematic analysis, four main challenges were identified in the implementation of the LSCC namely, ensuring curriculum continuity, avoiding curriculum overload, the need for more laboratory experiences and knowledge transfer.

Keywords: Chemistry curriculum; curriculum continuity; curriculum load; knowledge transfer; laboratory experiences; lower secondary

5.1 Introduction

Education is a human right and a catalyst for the development of human capital. The terms education and curriculum are two sides of the same coin, as a curriculum provides a structure and a plan of action for an effective pursuit of educational goals, thus ensuring that learners experience quality education. With unprecedented challenges and possibilities in a complex, uncertain and unpredictable world, curricula should continue to evolve through informed educational reforms. In 2015, the United Nations (UN) developed the 2030 Agenda. This document included the Sustainable Development Goal 4 (SDG 4) which is an attempt to prepare students for the demands of the future world [2]. In view of meaningfully aligning educational goals with the UN SDG 4 on education and its 10 targets, there was a universal and collective commitment across nations for educational reforms. The main aim of these educational reforms was to

---

***Corresponding author: Fawzia Narod,** Department of Science Education, Mauritius Institute of Education, Réduit, Mauritius, E-mail: f.narod@mie.ac.mu
Vickren Narrainsawmy, Department of Science Education, Mauritius Institute of Education, Réduit, Mauritius

This article has previously been published in the journal Physical Sciences Reviews. Please cite as: F. Narod and V. Narrainsawmy "Evaluation of the Chemistry curriculum at the lower secondary level: feedback from educators" *Physical Sciences Reviews* [Online] 2021, 6. DOI: 10.1515/psr-2020-0133 | https://doi.org/10.1515/9783110726145-005

endow all students with an inclusive and equitable chance by equipping them with the necessary knowledge, skills, and values through well-structured learning experiences [3]. These planned experiences were formulated to reshape and reform existing curricula so that they would respond to students' future needs and contexts.

Mauritius, a small island developing state with a population of about 1,265,577 [4], has witnessed several education reforms since its independence, to prepare learners as responsible citizens. In 2015, to strategically transform the education system in line with SDG 4, the Government of Mauritius introduced the Nine Year Continuous Basic Education (NYCBE) reform to address the excessive competition which favours a narrowly selected elite for further academic education [5]. To translate the desired educational goals into school programmes and to support processes of educational change, a new National Curriculum Framework (NCF) had to be developed. The development of the new NCF included a systematic approach of evaluating, reviewing and revising curricular areas and programmes from the preceding curriculum, NCF-2009 [6]. Legitimate changes to a curriculum can only be made after its evaluation, as it is a tool to inform and justify decisions that would help to enhance the quality of the curriculum and to improve its implementation.

5.2 The context

The NCF-2015 [5] that emanated from the NCYBE reform and review of curricular areas brought a change in the education structure. After compulsory pre-primary (children of 3–5 years), the first nine years of formal schooling consists of two levels— Level 1 and Level 2. Level 1 corresponds to the first six years of primary schooling (Grades 1–6) and Level 2 includes the three years corresponding to lower secondary schooling (Grades 7–9). The evaluation of the primary school curriculum (children of about 5–11 years) was followed by that of the lower secondary curriculum (children of about 12–14 years). Thus, all curricular areas and programmes, including Chemistry for lower secondary schooling had to be evaluated. Higher secondary curriculum (Grades 10–13) is endorsed by Cambridge Assessment International Education (CAIE).

Together with Biology and Physics, Chemistry as a formal disciplinary knowledge is one of the main Science components at lower secondary. The three Science components are integrated using specific unifying themes at Grades 7 and 8 and are implemented by Educators (who have majors in either Chemistry, Physics or Biology.) At Grade 9, the three components are taught separately, as it is deemed necessary to allow learners to recognise the different components in view of helping them for their subject choice at higher secondary schooling level [5]. At Grade 9 and onwards, the Chemistry curricula are implemented by Chemistry educators.

To align with the aims and objectives of the NYCBE reform, the Chemistry curriculum across the first three years of the lower secondary schooling was evaluated. Educators, the mediators between educational policy and practise, were invited to participate in the evaluation of the lower secondary Chemistry curriculum (LSCC). Besides being the quintessential decision-makers in the classroom, educators' role in curriculum development, due to their knowledge, experiences and competencies is vital [7–9]. In so doing, educators develop a sense of ownership and responsibility for the teaching process.

The present study was guided by an analysis of the educators' feedback regarding the evaluation of the LSCC, most specifically, the Chemistry curricular content and content organisation. The interest was to document the implementation of the LSCC and to identify the challenges encountered by educators in implementing the Chemistry curriculum at the lower secondary level, as curricular implementation is reported to be rarely "trouble-free" [10].

As implication, it is expected that this study could potentially contribute to an understanding of the LSCC and its implementation. An in-depth study of the challenges for the implementation of the LSCC could be conducted to identify potential measures to overcome these challenges, in view of improving students' learning experiences and motivation in Chemistry, as the number of students opting for Chemistry at higher secondary level is decreasing [11].

5.3 The rationale

Bharvad [12], and Kabilan and Khan [13] stated that curriculum evaluation is the critical analysis of a curriculum for determining its worth and value by informing about its strengths and weaknesses. Curriculum evaluation is also reported to provide detailed information about the structure and content of education programs [14]. Practising educators being conscious of the grassroots reality can provide information about any disconnection between theory and practise [5]. Hence, the analysis of educators' feedback was deemed important as it attempted to understand the challenges encountered by educators in the implementation of LSCC in view of enhancing students' learning experiences, motivation and conceptual understanding in Chemistry.

5.4 Aim of the study

The paper aimed at analysing educators' views regarding the content and content organisation of the LSCC, and at identifying the challenges in its implementation.

5.5 Research questions

This study was guided by the following research questions:

1) What are educators' views about the content and content organisation of the LSCC?
2) What are the challenges in the implementation of the LSCC?

5.6 Theoretical framework

Several curriculum evaluation models have been reported in literature [15–17] to assist curriculum designers to operate. Each of the curriculum evaluation models has its own characteristics, as well as its strengths and weaknesses [18]. For this study, the context, input, process and product (CIPP) evaluation model proposed by Stufflebeam [1] has been selected. The CIPP evaluation model provides relevant information for those who require valid and unbiased evaluative information [1]. Warju [19] informed that the CIPP model is the most used model to evaluate a curriculum as it serves to provide feedback to individuals and to account for the activities of the curriculum. The CIPP model is a powerful tool for making and implementing decisions and for post hoc accounting of those decisions and actions [20]. This model collects information about a program to identify strengths and limitations in content or delivery, and to improve program effectiveness or plan for the future of a program [1]. Hence, the most fundamental tenet of the model is “not to prove, but to improve” education systems [21]. The CIPP model has been refined over the years to enable curriculum evaluators to systematically analyse the four distinct parts of the curriculum, namely, context, input, process and product. As the main focus of this study is to analyse educators’ feedback on the implementation of the LSCC, the component III of the Stufflebeam CIPP evaluation model [1], namely, Process Evaluation has been used as a framework for the study.

Stufflebeam [1] reported that the Process Evaluation enables curriculum developers to identify the potential barriers during the implementation of the curriculum. Zhang et al. [22] and Aziz et al. [23] argued that the Process Evaluation includes adjustments or revisions to the curriculum for corrective programmatic changes and documenting the implementation process. According to Stufflebeam [1], the objective of the Process Evaluation is to record procedural events and activities for later analysis and judgement that would provide a basis for judging implementation and interpreting outcomes. Thus, the Process Evaluation would help to find out what is being done, is it being done well and what needs to be addressed for change in the LSCC through educators’ feedback.

The following are questions that guided this study as laid out by Halverson [24] for the Process Evaluation component of the CIPP model:

- What is the workload of students?
- How well actively do students participate?
- Are there any problems related to teaching?
- Are there any problems related to learning?
- Is knowledge only transferred to students, or do they use and apply it?

5.7 Methodology

5.7.1 The participants

A purposive sampling technique was used for the evaluation of the LSCC. Palinkas et al. [25] suggest that purposive sampling is widely used for the identification and selection of information-rich cases related to the phenomenon of interest. The participants included 133 Science educators who have been teaching Science (Chemistry, Physics and Biology) at Grades 7 and 8. These educators took part in the evaluation process of the Grades 7 and 8 Science curriculum (which includes the Chemistry content). Out of these 133 participants, 34 were Chemistry educators who have also been teaching Chemistry at Grade 9; they took part in the evaluation process of the Grade 9 Chemistry curriculum. The participants were educators from both state and private secondary schools. They were informed about the NCYBE reform, its aims, objectives and the rationale for the evaluation process.

5.7.2 Instrument

For the evaluation of the LSCC, questionnaires were used to gather feedback from the participants. Three sets of questionnaires, namely, Grade 7 Feedback Questionnaire, Grade 8 Feedback Questionnaire and Grade 9 Feedback Questionnaire were designed for gathering data regarding the content and organization of the LSCC. The participants were required to provide their views and suggestions regarding the content and content organisation of the LSCC, and its implementation. In addition, they were invited to provide justifications for proposed changes in the content and content organisation.

5.7.3 Data collection

The LSCC evaluation process was conducted in two phases – Phase I and Phase II. In Phase I, a total of 32 groups were constituted from the 133 Science (Biology, Chemistry and Physics) educators. Each group consisted of four or five educators, and included at least one educator from each Science component. The 32 groups of Science educators were administered the Grade 7 Feedback Questionnaire and Grade 8 Feedback Questionnaire to provide their views and suggestions regarding the Grade 7 and Grade 8 Chemistry curriculum respectively.

In Phase II, 34 Chemistry educators took part in the evaluation of the Grade 9 Chemistry curriculum. A total of nine groups of Chemistry educators were constituted. Each group consisted of three or four educators. The nine groups of Chemistry educators were administered the Grade 9 Feedback Questionnaire to provide their views and suggestions regarding the Grade 9 Chemistry curriculum.

For both phases, the educators self-assigned themselves into groups in an informal manner which was deemed appropriate for greater engagement, commitment and collective understanding. This improved the effectiveness of group decision-making during the evaluation process. To increase the level of focus, a minimum and a maximum number of individuals per group were required as given above. The educators were engaged in group discussions to reach a common consensus to fill the Questionnaires.

5.7.4 Data analysis

Qualitative thematic analysis was used to elicit meaning from participants' feedback in the study. Thematic analysis was chosen as it is a flexible method which allows researchers to extract meanings from and make sense of the data through "pinpointing, examining and recording patterns or themes" [26].

Participants' feedback regarding the LSCC content and its organisation were based on Chemistry concepts that they considered appropriate to teach at a specific Grade level (Grade 7, Grade 8 or Grade 9), and to prepare students for studying Chemistry at the higher secondary level. The Chemistry concepts as categorical data were analysed by using frequency count to determine participants' common suggestions that would function as foundations for further analysis. Sandelowski et al. [27] reported that quantitizing in qualitative research is done to "allow analysts to discern and to show regularities or peculiarities in qualitative data they might not otherwise see or be able simply to communicate.... ". Thus, the frequency count analysis allowed us to identify which Chemistry concepts the majority (above median value) of participants suggested appropriate to maintain, add (include) or remove (exclude) from the previous LSSC [5] at each grade level during evaluation exercise.

The data from the participants' justifications to their proposed changes regarding the content and content organisation were textual and narrative, and were based on their teaching experiences. To uncover the implied meanings of participants' justifications, qualitative thematic analysis was used. According to Maguire and Delahunt [28], "The goal of a thematic analysis is to identify themes, i.e. patterns in the data that are important or interesting, and use these themes to address the research or say something about an issue." The qualitative thematic analysis was used to analyse and make meaning from the participants' justifications to their proposed changes in the LSCC by identifying relevant themes. The analysis, through the lens of the Process component of the Stufflebeam's [1] CIPP evaluation model as an enabling framework, empirically identified the challenges in the implementation of the LSCC.

5.8 Results

This study aimed at analysing the participants' feedback regarding the content and content organisation of the LSCC. The analysis offers an understanding of the challenges in the implementation of the LSCC. In this section, the findings from the study are presented. Tables 5.1–5.3 present the participants' feedback regarding Grade 7, Grade 8 and Grade 9 Chemistry curriculum content and content organisation, respectively. The data presented below focuses on the most pertinent suggestions for changes in the LSCC content and content organisation made by the participants. In addition, the participants' justifications for these proposed changes are also provided in Tables 5.1–5.3. Through a thematic analysis of the participants' choices and suggestions during the decision-making process of the LSCC evaluation, four main challenges in the LSCC implementation have been identified. These will be elaborated in the next section.

5.9 Discussions of results

Based on the data analysis, four challenges were identified in the implementation of the LSCC namely, ensuring curriculum continuity, promoting knowledge transfer, fostering laboratory experiences and avoiding curriculum overload. These themes are elaborated below in line with the data collected.

5.9.1 Ensuring curriculum continuity

The analysis revealed that curriculum continuity was a major criterion that guided the evaluation process. This was evidenced by the participants' views on the Chemistry concepts to be maintained across Grades 7–9 Chemistry curriculum (Tables 5.1–5.3) to allow students sequentially build on what has been previously learned, thereby leaving no gaps.

Table 5.1: Analysis of participants' feedback regarding the Grade 7 Chemistry curriculum content and content organisation.

Participants' suggestions regarding the content and content organisation (Frequency count out of 32 groups of participants)	Participants' justifications to suggestions	Themes identified
Concepts to be maintained at Grade 7 'States of Matter' (30 groups) 'Composition of Air'. (30 groups) 'Physical Properties of Metals and non-Metals'. (22 groups) 'Uses of Metals and non-Metals'. (21 groups) 'Uses of Gases'. (20 groups)	To ease the transition from Grade 6 to Grade 7 as 'States of Water', 'Air is a mixture of Gases' and 'Properties of materials' have been introduced at Grade 6. To allow students to relate knowledge of 'Physical Properties and uses of Metals and non-Metals' and 'Uses of Gases' to everyday life situations.	Curriculum continuity Knowledge transfer
Concepts to be added to Grade 7 curriculum 'Importance of Metals Recycling' (20 groups) 'Test for Gases' (19 groups) 'Preparation of Compounds' (18 groups)	To relate knowledge of 'Metals Recycling' to real world problem. To engage students in laboratory practical work.	Knowledge transfer Laboratory experiences
Concepts to be excluded or removed from the Grade 7 curriculum 'Sources of Water' (23 groups) 'Uses of Water' (22 groups) 'Properties of Water' (22 groups)	To prevent duplication as these concepts are already addressed at Grade 6. To avoid curriculum overload.	Curriculum overload

Table 5.2: Analysis of participants' feedback regarding the Grade 8 Chemistry curriculum content and content organisation.

Participants' suggestions regarding the content and content organisation (Frequency count out of 32 groups of participants)	**Participants' justifications to suggestions**	**Themes identified**
Concepts to be maintained at Grade 8 'Symbol and valency of elements' (26 groups) 'Formulae of Compounds' (24 groups) 'Chemical Properties of Metals' (24 groups)	To build on knowledge of 'Elements' acquired in Grade 7 for further learning in Grade 8. To ensure coherence from learning of 'Symbol and valency of elements' to writing of 'Formulae of compounds'	Curriculum continuity Curriculum continuity
Concepts to be added to Grade 8 curriculum 'Uses of Alloys' (20 groups) 'Properties of Acids and Bases' (19 groups) 'Applications of Bases' (24 groups) 'Application of Neutralisation Reactions' (18 groups) 'Filtration' (20 groups) 'Magnetic Separation' (21 groups) 'Chemical Properties of Metals' (20 groups)	To enable students to relate concepts of Alloys, Acids, Bases and Neutralisation to everyday life experiences and needs. To create space for students to engage in laboratory practical activities. To de-load the Grade 9 curriculum (these concepts were addressed in Grade 9). To ensure uniform distribution of content in terms of complexity and difficulty level of Chemistry concepts across the three years of lower secondary schooling.	Knowledge transfer Laboratory experiences Curriculum overload
Concepts to be excluded or removed from the Grade 8 curriculum 'Elements and the Periodic Table' (25 groups) 'Metals and Non-Metals' (27 groups) 'Compounds and Mixtures' (27 groups) 'Physical and Chemical Changes' (26 groups)	The participants proposed that these concepts be addressed at Grade 7 level to de-load the Grade 8 curriculum and make space for addressing the concepts mentioned in the previous row.	Curriculum overload

Benyon [29] defined curriculum continuity as the transitions which students experience from one stage of schooling to another. The following quotes from the participants clearly indicate that ensuring curriculum continuity is essential for successful implementation of the LSCC: 'prior knowledge acquired in Grade 7 facilitated further learning in Grade 8', 'to have a hierarchical sequence of learning', 'continuity of learning experience', 'ease the transition to Grade 9', 'gradual increase in level of complexity from Grade 8 to Grade 9', 'good sequencing of concepts from one grade to another', 'continuity of conceptual understanding across the grades'.

From Tables 5.1–5.3, it is noted that to ensure curriculum continuity, the participants highlighted that concepts such as 'States of Matter' and 'Composition of Air' need to be maintained at Grade 7; concepts such as 'Symbol', 'Valency', 'Formulae of

Table 5.3: Analysis of participants’ feedback regarding the Grade 9 Chemistry curriculum content and content organisation.

Participants’ suggestions regarding the content and content organisation (Frequency count out of 9 groups of participants)	Participants’ justifications to suggestions	Themes identified
Concepts to be maintained at Grade 9 ‘Balancing Chemical Equations’ (All nine groups) ‘Reactivity Series of Metals’ (eight groups) ‘Displacement Reaction’ (seven groups) ‘Solubility of Salts’ (seven groups) ‘Chromatography’(five groups) ‘Simple Distillation’ must be maintained at Grade 9 (six groups) Applications of the separation techniques	To gradually increase the level of complexity from ‘Formulae of Compounds’ and ‘Word Equations’ at Grade 8 to ‘Balancing Chemical Equations’ in Grade 9. To sequentially build from ‘Chemical Properties of Metals’ at Grade 8 to ‘Reactivity Series of Metals’ in Grade 9. To engage students in laboratory practical activities. To apply knowledge gained to real-life experiences.	Curriculum continuity Curriculum continuity Laboratory experiences Knowledge transfer
Concepts to be excluded or removed from the Grade 9 curriculum ‘Rusting’ (seven groups) ‘Alloys’ (six groups) ‘Radicals’ (six groups) ‘pH Scale and Indicators’	To de-load the Grade 9 Chemistry curriculum. To ensure uniform distribution in complexity and difficulty level of Chemistry concepts over the first three years of secondary schooling.	Curriculum overload Curriculum continuity

Compounds’, ‘Chemical Properties of Metals’ need to be maintained at Grade 8; and concepts such as ‘Balancing Chemical Equations’, ‘Simple Distillation’, ‘Reactivity Series of Metals’ and ‘Solubility of Salts’ need to be maintained at Grade 9.

The importance of curriculum continuity for successful implementation of the curriculum at school level has recently been highlighted by Hopwood et al. [30] who reported that disconnection between primary and secondary schooling is a major barrier that impedes students’ progression. In addition, Coad and Jones [31] argued that there is evidence from studies that the problem of curriculum continuity exists due to differences in curriculum emphasis between primary and secondary schools and between the different stages of secondary schooling. In addition, the concept of progression which focuses on the advances in students’ learning within secondary schooling is central while planning the structure of secondary curriculum [32].

5.9.2 Promoting knowledge transfer

Our findings have revealed that relating Chemistry concepts to daily life experiences, was considered important by the participants for successful implementation of the

LSCC. This was evidenced by the participants' views regarding the concepts selected across Grade 7, Grade 8 and Grade 9 Chemistry curriculum that would enable students to connect and apply the knowledge gained in their everyday experiences and to understand societal issues pertaining to Chemistry. When providing feedback regarding the LSCC, the participants highlighted the following statements which emphasized the need for promoting knowledge transfer: 'for knowledge to be relevant, students should apply it effectively to everyday life situations', 'applying concepts learned to real world problems', 'use the knowledge gained in real-life experiences', 'for learning not to be divorced from students' lived experience'.

According to the participants, concepts such as 'Importance of Metals Recycling' at Grade 7; concepts such as 'Uses of Alloys', 'Applications of Bases' and 'Applications of Neutralisation Reactions' at Grade 8; and concepts such as 'Applications of Salts' and 'Applications of Separation Techniques' at Grade 9 are important ones that would ensure knowledge transfer. In fact, the participants highlighted that concepts such as 'Uses of Metals and non-Metals' and 'Uses of Gases' need to be maintained at Grade 7 (Table 5.1) to ensure knowledge transfer amongst the students. The participants focused on the selection of concepts across the grades that would enable the students to appreciate the applications of Chemistry in daily life.

Our findings thus reveal that promoting knowledge transfer is an important factor to be taken into consideration in the LSCC. These findings lend support to earlier reports by Tsurusaki [33] and Anilan, Atalay and Kiliç [34] who foregrounded the necessity for contextualising Science learning. According to earlier studies, when Chemistry education is disconnected from real-life context, students' understanding of concepts is hampered [35, 36].

5.9.3 Fostering laboratory learning experiences

Laboratory learning experiences are reported to be essential in Chemistry as they enhance conceptual understanding, interest and motivation in the learning of Chemistry [37]. In the present study, the participants highlighted the need for more practical experiments during the implementation of the LSCC.

According to the participants, fostering laboratory learning experiences would enable students to develop conceptual understanding and enquiry skills. Most participants were in favour of including the concepts 'Test for Gases' and 'Preparation of Compounds' at Grade 7 (Table 5.1) and 'Filtration', 'Magnetic Separation', 'Properties of Acids and Bases' and 'Chemical Properties of Metals' at Grade 8 (Table 5.2). In addition, they also proposed that concepts such as 'Chromatography', 'Simple Distillation', 'Displacement Reaction' and 'Neutralisation Reaction' are maintained at Grade 9 (Table 5.3). The participants were of the view that these concepts would provide opportunities for laboratory learning experiences at school level during the implementation of the LSCC.

The need for laboratory learning to enhance the implementation of the LSCC was clearly evidenced by participants' statements such as 'to conduct experiments', 'to develop enquiry skills through lab investigations', 'enable students interact with chemical substances to observe and understand concepts', 'for making laboratory experiences an essential part of teaching-learning of Chemistry', 'to provide laboratory experiences to students', 'to engage in practical investigations', 'integrate theory and practise through laboratory work'.

From the participants' statements, it can be inferred that fostering laboratory learning experiences is a major challenge in the implementation of the LSCC. To overcome this challenge, the participants have attempted to select some concepts across the grades that would encourage laboratory work. Various authors [38–40] have earlier reported that students' engagement in laboratory activities improves learning. Furthermore, Emendu and Okoye [41] reported that a major drawback of Chemistry curriculum in Nigeria was that it does not engage the students to do practical work.

5.9.4 Avoiding curriculum overload

Another important theme which emerged during this study pertains to curriculum overload across the LSCC. This was evidenced by participants' views on the distribution of the Chemistry content load in terms of complexity and difficulty level across the Grade 7, Grade 8 and Grade 9 curriculum. Curriculum overload refers to the excessive amount of content to be taught and learned in relation to the time available for instruction [42].

To adjust the Chemistry curriculum load, the participants proposed the exclusion of some Chemistry concepts as indicated in Tables 5.1–5.3 above. The participants' concern for the curriculum load with regards to the LSCC was clearly evident from statements such as 'avoid creating a crowded curriculum', 'minimising curriculum expansion and overload', 'de-loading curriculum content', 'keep the right balance between breadth and depth of Chemistry content', 'limiting time to cover the concept', 'decrease the size and volume of the Chemistry curriculum' and 'insufficient teaching time to teach' amongst others.

To reduce the LSCC load, the majority of the participants suggested excluding concepts such as 'Sources of Water', 'Uses of Water' and 'Properties of Water' at Grade 7 (Table 5.1), since these concepts are already addressed at the lower grade levels. In addition, they also proposed removing concepts such as 'Elements and the Periodic Table', 'Metals and Non-Metals', 'Compounds and Mixtures', 'Physical and Chemical Changes' at Grade 8 (Table 5.2) and the concepts 'Rusting', 'Alloys', 'Radicals', 'pH Scale and Indicators' at Grade 9 (Table 5.3). According to the participants, excluding these concepts would not only help to reduce the Chemistry curriculum load at the lower secondary level, but would also ensure a better distribution of the Chemistry content throughout the three levels.

Avoiding curriculum overload is a major challenge in Chemistry Education; Broman, Ekborg and Johnels [42] have earlier reported that curriculum overload in Chemistry can be an obstacle in the teaching and learning of Chemistry. Chambers [43] argues that 'reasonable work-load' is a precondition of good learning and an increasing amount of content to a curriculum does not improve educational standards.

5.10 Conclusions

As highlighted above, to align the LSCC with the philosophy of the NYCBE reform, the previous LSCC had to be evaluated. The present paper aimed at identifying the challenges in the implementation of the LSCC through educators' feedback using the Process Evaluation component of the CIPP model as an enabling framework. The study allowed an understanding of the challenges in the implementation of LSCC. The findings have revealed challenges related to curriculum continuity, knowledge transfer, laboratory learning experiences and curriculum overload.

Regarding curriculum continuity, the findings have revealed that there is a need to facilitate students' successful transition experiences from primary to secondary school, and within the distinct stages of secondary school. Ensuring curriculum continuity would enhance the teaching and learning of Chemistry at the lower secondary level. Curriculum overload was found to be another major challenge in the implementation of LSCC. A redistribution of Chemistry content across the three years of the LSCC was deemed appropriate keeping in mind the level of complexity of the content and scaffolding of the content. Another challenge brought to light in this study relates to knowledge transfer, the capacity to apply acquired knowledge and skills to real-life. There is a need to contextualize Chemistry learning; thus, the LSCC should lay more emphasis, as from Grade 7, on the applications of Chemistry in real-life situations. Lastly, lack of students' exposure to laboratory experiences was found to be another challenge in the implementation of the LSCC. Fostering more laboratory experiences would enable students to reinforce the theoretical Chemistry concepts taught in class by engaging them in meaningful practical work.

As a concluding remark, this study has shed light on factors that can support the implementation of the Chemistry curriculum at the lower secondary level. Based on the findings of the study, the main recommendations would be that curriculum developers and other stakeholders must ensure curriculum continuity and appropriate curriculum load when developing curriculum. In addition, it is important that there is a uniform distribution of content throughout the different grades in one level, taking into consideration the progression and complexity of the content and concepts across the different grades.

The need for engaging learners in laboratory practical investigations and relating Chemistry to everyday life situations were also found important for effective implementation of the LSCC. Based on findings from this study, it is recommended that laboratory experiences should be an integral part of the Chemistry curriculum at the lower secondary level. This is supported by recent findings which highlight that laboratory experiences are essential to improve the quality of education [44] and to promote the development of 21st century competencies amongst students [45]. Lastly, another important recommendation that emerges from this study is that curriculum developers must create space and opportunities for students to transfer or apply learned knowledge and skills to real-life situations during the implementation of the curriculum. This is in line with Zorluoglu et al. [46] who have reported that enabling students to practise knowledge transfer is becoming more widespread in school curriculum.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.
Research funding: None declared.
Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Stufflebeam DL. The CIPP model for evaluation. In: Evaluation models. Dordrecht: Springer; 2000: 279–317 pp.
2. IBE-UNESCO. Repositioning and reconceptualizing the curriculum for the effective realization of sustainable development goal four, for holistic development and sustainable ways of living. Discussion paper presented at the world education forum. Incheon, Republic of Korea: UNESCO International Bureau of Education (IBE-UNESCO); 2015.
3. UNESCO. Incheon declaration: education 2030: towards inclusive and equitable quality education and lifelong learning for all. Paris: UNESCO; 2015.
4. Mauritius S. Population and vital statistics Republic of Mauritius year 2018. Ministry of Finance and Economic Development; 2019.
5. Ministry of Education and Human Resources, Tertiary Education and Scientific Research and Mauritius Institute of Education. National Curriculum Framework. Nine Year Continuous Basic Education. Republic of Mauritius; 2015.
6. Ministry of Education, Culture and Human Resources. The National Curriculum Framework: Secondary. Mauritius; 2009.
7. Oloruntegbe KO. Teachers' involvement, commitment and innovativeness in curriculum development and implementation. J Emerg Trends Educ Res Pol Stud 2011;2:443–9.
8. Taole MJ. Teachers' conceptions of the curriculum review process. Int J Educ Sci 2013;5:39–46.
9. Alsubaie MA. Curriculum development: teacher involvement in curriculum development. J Educ Pract 2016;7:106–7.
10. Snyder J, Bolin F, Zumwalt K. Curriculum implementation. In: Jackson P, editor. Handbook of research on curriculum. New York: Macmillian; 1992:402–35 pp.
11. Maulloo AK, Naugah BJ. Upper secondary education in Mauritius: a case study; 2017.
12. Bharvad AJ. Curriculum evaluation. Int Res J 2010;1:72–4.

13. Kabilan MK, Khan MA. Assessing pre-service English language teachers' learning using e-portfolios: benefits, challenges and competencies gained. Comput Educ 2012;58:1007–20.
14. Mutinga ME, Krajenbrink VQE, Peerdeman SM, Croiset G, Verdonk P. Toward diversity-responsive medical education: taking an intersectionality-based approach to a curriculum evaluation. Adv Health Sci Educ 2016;21:541–59.
15. Hussain A, Dogar AH, Azeem M, Shakoor A. Evaluation of curriculum development process. Int J Humanit Soc Sci 2011;1:263–71.
16. Yazçayır N, Selvi K. Curriculum evaluation model-KÖNDEM. Elem Educ Online 2020;19:343–56.
17. Peyman N, Al-Badi A, Riasati MJ, Maata RL. Educational program and curriculum evaluation models: a mini systematic review of the recent trends. Univers J Educ Res 2020;8:4048–55.
18. Anh VTK. Evaluation models in educational program: strengths and weaknesses. VNU J Foreign Stud 2018;34:140–50.
19. Warju W. Educational program evaluation using CIPP model. Innovat Vocat Technol Educ 2016;12: 36–42.
20. Stufflebeam DL. The CIPP model for evaluation. In: Evaluation models. Dordrecht: Springer; 2003: 279–317 pp.
21. Stufflebeam DL. CIPP evaluation model checklist [Online]; 2007. Available from: https://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.401.1277&rep=rep1&type=pdf [Accessed 4 May 2021].
22. Zhang G, Zeller N, Griffith R, Metcalf D, Williams J, Shea C, et al. Using the context, input, process, and product evaluation model (CIPP) as a comprehensive framework to guide the planning, implementation, and assessment of service-learning programs. J High Educ Outreach Engagem 2011;15:57–84.
23. Aziz S, Mahmood M, Rehman Z. Implementation of CIPP model for quality evaluation at school level: a case study. J Educ Dev 2018;5:189–206.
24. Halverson LR. CIPP evaluation model [Online] Available from: https://lisahalverson.files.wordpress.com/2011/05/cipp-evaluation-model.pdf [Accessed 04 Apr 2020].
25. Palinkas LA, Horwitz SM, Green CA, Wisdom JP, Duan N, Hoagwood K. Purposeful sampling for qualitative data collection and analysis in mixed method implementation research. Adm Pol Ment Health 2015;42:533–44.
26. Javadi M, Zarea K. Understanding thematic analysis and its pitfall. J Client Care 2016;1:34–40.
27. Sandelowski M, Voils CI, Knafl G. On quantitizing. J Mix Methods Res 2009;3:208–22.
28. Maguire M, Delahunt B. Doing a thematic analysis: a practical, step-by-step guide for learning and teaching scholars. All Irel J Teach Learn High Educ 2017;9:3351–4.
29. Benyon L. Curriculum continuity. Education 3–13 2007;9:36–41.
30. Hopwood B, Hay I, Dyment J. The transition from primary to secondary school: teachers' perspectives. Aust Educ Res 2016;43:289–307.
31. Coad J, Jones K. Curriculum continuity in mathematics: a case study of the transition from primary to secondary school; University of Southampton Centre for Research in Mathematics Education Working Paper. Southampton: University of Southampton Centre for Research in Mathematics Education; 1999. https://www.researchgate.net/publication/242279644_Curriculum_continuity_in_mathematics_a_case_study_of_the_transition_from_primary_to_secondary_school [Accessed 12 May 2021].
32. Bennetts T. The links between understanding, progression and assessment in the secondary geography curriculum. Geography 2005;90:152–70.
33. Tsurusaki BK, Calabrese Barton A, Tan E, Koch P, Contento I. Using transformative boundary objects to create critical engagement in science: a case study. Sci Educ 2013;97:1–31.
34. Anilan B, Atalay N, Kiliç Z. Teacher candidates' levels of relating the scientific knowledge to their daily lives. Int J InStruct 2018;11:733–48.

35. Childs PE, Hayes SM, O'dwyer A. Chemistry and everyday life: relating secondary school chemistry to the current and future lives of students. In: Relevant chemistry education. Netherlands: Brill Sense; 2015:33–54 pp.
36. Sharon AJ, Baram-Tsabari A. Can science literacy help individuals identify misinformation in everyday life? Sci Educ 2020;104:873–94.
37. Lagowski JJ. The role of the laboratory in chemical education. Available from: https://www.researchgate.net/profile/Nizar_Matar/post/Any_paper_modeling_the_quality_dimensions_of_a_university_lab_course/attachment/59d62f10c49f478072e9f867/AS%3A273537049268229%401442227722911/download/jjl+Lab+Education.pdf [Accessed 02 Apr 2021].
38. Tobin K. Research on science laboratory activities: in pursuit of better questions and answers to improve learning. Sch Sci Math 1990;90:403–18.
39. Hofstein A, Lunetta VN. The laboratory in science education: foundations for the twenty-first century. Sci Educ 2004;88:28–54.
40. Hume A. Authentic scientific inquiry and school science. Teach Sci J Aust Sci Teachers Assoc: J Aust Sci Teach Assoc 2009;55:35–41.
41. Emendu NB, Okoye CM. Identifying problems associated with studying of chemistry in anambra state, Nigeria. Int J Sci Res Publ 2015;6:1–7.
42. Broman K, Ekborg M, Johnels D. Chemistry in crisis? Perspectives on teaching and learning chemistry in Swedish upper secondary schools. NorDiNa 2011;1:7.
43. Chambers E. Work-load and the quality of student learning. Stud High Educ 1992;17:141–53.
44. Rusmansyah R, Yuanita L, Ibrahim M, Isnawati I, Prahani BK. Innovative chemistry learning model: improving the critical thinking skill and self-efficacy of pre-service chemistry teachers. J Technol Sci Educ 2019;9:59–76.
45. Rahayu S. Promoting the 21st century scientific literacy skills through innovative chemistry instruction. AIP Conf Proc 2017;1911:1–8:020025.
46. Zorluoglu SL, Kizilaslan A, Yapucuoglu MD. The analysis of 9th grade chemistry curriculum and textbook according to revised bloom's taxonomy. Cypriot J Educ Sci 2020;15:9–20.

Jimmy Lowe* and John P. Canal

6 Polymers, plastics, & more – educating post-secondary students from different disciplines with polymer science

Abstract: Polymers are excellent materials that provide concrete examples of concepts and learning objectives covered in different post-secondary level courses. Modules focused on polymer science can be used for teaching general, organic, material and green chemistry. These modules can be tailored to build on the students' prerequisite knowledge. Science 300 is a course offered at Simon Fraser University (SFU) to non-science, post-secondary students focused on the impact of science in society. Prosthetics and Orthotics (PROR) is a diploma program offered at the British Columbia Institute of Technology (BCIT). Both programs have incorporated polymer science as part of the curriculum. Design of the modules illustrates polymers as an important class of materials that possess both beneficial and environmental unfriendly properties. A variety of learning strategies are incorporated within the courses to aid students with understanding polymer science.

Keywords: chemical education, curriculum design, polymer science, teaching

6.1 Introduction

Polymers are multi-application materials that people encounter daily. Food containers, electronics, personal protective equipment (PPE), vehicles and clothing are examples of macromolecules used everyday. Although polymers are essential materials for modern society, there is an environmental impact that polymers bring due to their properties. Polymer science modules can be presented at post-secondary programs tailored to match the different levels, course learning objectives and general interests of students. The content can be laddered to the students' backgrounds and their areas of study. Every student can benefit from increased knowledge about the types of polymers, properties, and applications as consumers and towards becoming a global citizen.

The literature has emphasized the importance of incorporating polymer science into the curriculum at all grade levels and for science outreach [1–3]. Many post-secondary institutes have adopted more polymer science into their general, organic,

---

***Corresponding author: Jimmy Lowe**, Department of Chemistry, British Columbia Institute of Technology, Burnaby, BC, Canada V5G 3H2, E-mail: Jimmy_Lowe@bcit.ca
John P. Canal, Department of Chemistry, Simon Fraser University, Burnaby, BC, Canada V5A 1S6, E-mail: jcanal@sfu.ca

This article has previously been published in the journal Physical Sciences Reviews. Please cite as: J. Lowe and J. P. Canal “Polymers, plastics, & more – educating post-secondary students from different disciplines with polymer science” *Physical Sciences Reviews* [Online] 2021, 7. DOI: 10.1515/psr-2020-0140 | https://doi.org/10.1515/9783110726145-006

physical chemistry and engineering courses [4–9]. The goals are to (i) increase student engagement and interest in chemistry at the first and second year levels, (ii) prepare students to apply polymer science in their careers, (iii) demonstrate chemistry concepts using polymers and their applications.

Polymer science modules were added to the curriculum at two neighboring post-secondary institutes in the same city. At Simon Fraser University (SFU), non-science students can take Science 300 as an elective [10]. The British Columbia Institute of Technology (BCIT) offers a two-year diploma in prosthetics and orthotics [11].

6.2 Course content for Science 300 (SCI 300) at SFU

SCI 300 introduces non-science students to all facets of science, its impact in society and the resulting technologies. This course was developed specifically for non-science students who are not majoring in the Faculty of Science, Schools of Computing Science or Engineering Science. SCI 300 covers the basics of science, including modules on numerical literacy, the properties of waves, states of matter and energy conversion. Students learn basic general chemistry related to bonding, properties of small molecules and intermolecular forces. Selected topics in environmental science are covered, as well as polymer science. The students' previous knowledge of polymers is laddered to the topics in the polymer science module (Figure 6.1). The learning objectives of the polymer science module are based on the major topics presented in the concept map. The concept map shows the organization of topics that are general enough to address students' interests, introduce new content and allow different instructors to introduce specialty topics. The current content, in-class activities, demonstrations and mini-discussions fits three lecture hours. Some specific topics covered in the polymer science module include the history of polymers, linking the environmental impact to the

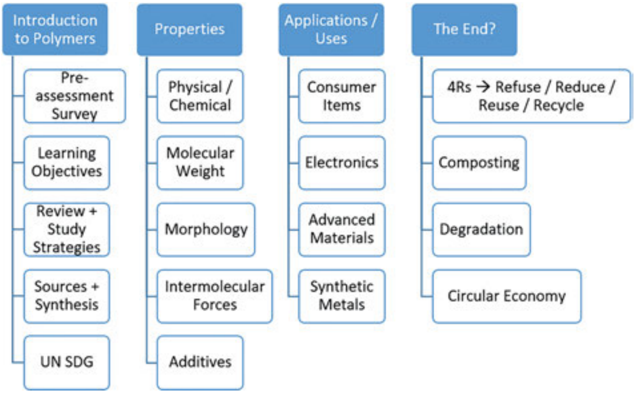


Figure 6.1: Concept map of polymer science topics for SCI 300.

United Nations Sustainability Development Goals and compostable polymers [12]. The polymer module is presented in class by faculty with many years of teaching and research experience in general and polymer chemistry [13].

6.2.1 Teaching practice for SCI 300

SCI 300 typically has 50–60 students registered per term from diverse areas such as business, arts, and languages, with most students completing an economics degree. The polymer module was added to the course over 7 years ago. Before the polymer module is presented, students are asked to complete an anonymous survey addressing what they (i) know, (ii) don't know and (iii) want to learn about polymers. They are informed that the polymer science module will cover the most popular themes chosen and the instructor will provide feedback and resources for less common topics [14–17]. The concept map used to organize the students' and instructors' topics is included as part of the skeleton notes presented to the students (Figure 6.1). The general topics starting from ‘Introduction to Polymers’ starts with feedstock molecules being made into polymers. This leads to the final topic of ‘The End?’ which discusses the disposal and possible end use of specific polymers. Instructors are able to add in the appropriate difficulty level with each of the subtopics. Students are given a problem set that helps them connect to the applications and properties of polymers in their lives. One question tasks them to find polymers that are in their homes. At the end of the polymer module they are tested on the content presented in lecture and the problem set.

Since some topics are more abstract, students are shown how to use different study strategies in order to learn the material and build on their previous chemistry knowledge. This can include graphic organizers such as mind maps, concept maps, and compare & contrast tables (Table 6.1). Concept maps can help students organize large amounts of material and link subtopics to the major topics [18]. Metacognitive

Table 6.1: Use of a Venn diagram (graphic organizer) to compare LDPE & HDPE with lecture annotations.

HDPE	Concept compared	LDPE
	Morphology *Study of structure*	
≅12,000	Molecular weight (g/mol)	≅20,000
105–120	Melting range (°C)	80–85
0.92–0.95	Density (g/cm^3)	0.89–0.91
15–40	Tensile strength (MPa)	5–25
Generally opaque	Optical clarity	Generally transparent

Table 6.2: Demonstrations of polymer properties.

Demonstration	Concepts/Applications
Density of polymer balls (nylon vs. polyethylene [PE])	*Density* – prediction of amorphous or crystalline structures./ Separation of plastics based on density (low tech recycling)
Light transparency of PE films	*Optical transparency*/Visual identification of films of HDPE vs. LDPE
Burning filter paper & filter paper saturated with NaHCO3	*Flammability of polymers*/Use of additives (e.g. flame retardants) in consumer plastics
Disappearing water in cup (sodium polyacrylate) [2]	*Hydrophilic super absorbent polymers*/Diapers and use as movie snow

strategies that are covered during the class include dual coding, concrete examples, and retrieval practice [19, 20]. An example of dual coding includes drawing the repeat unit of HDPE and LDPE as well as representing the morphology of the respective polymer chains with sketches.

To encourage student engagement, videos, polymer resin samples, and websites are shown to the class followed by short discussions. A set of classroom safe interactive demonstrations are performed to illustrate polymer properties (Table 6.2). When coupled with the course material, interactive demonstrations have been shown to enhance student learning [21].

Another topic presented is a life cycle analysis of polymers, including their effect on the environment [22–24]. The environmental connections were linked to the United Nations Sustainability Development Goals (UN SDGs) [12]. An exercise given to the students is the identification of plastics based on their recycling symbol. They need to research if the item could be recycled locally. Environmental solutions, such as compostable polymers were discussed to improve students' understanding of the process and issues. The differences between compostable and biodegradable polymers are compared. Specifically, poly(lactic acid) (PLA) was focused on since it is marketed as compostable and used by consumers for cups, take out food containers, and filament for 3D printing.

6.2.1.1 Online delivery of polymer module

Due to the Covid-19 pandemic, the most recent offering of the polymer module in SCI 300 (Summer 2020 semester) was moved to two synchronous 1.5-h long ZOOM webinars, which were presented a week apart. By using the share screen function, the instructor was able to add annotations on the PowerPoint slides during the webinar. Student participation was encouraged by using the ‘chat’ function for their comments/ questions and the ‘poll’ function for formative assessments. Videos of demonstrations and pictures of polymer resins and manufactured items were added to the webinar presentation. Multiple short breaks were taken to relieve eye strain and give the students a chance to stretch. The webinars were recorded in case students experienced issues with their hardware or Wi-Fi connections. These were also used by the students living in different zones as they had moved back home during the pandemic pause.

6.2.2 Feedback and findings

The feedback from the SCI 300 pre-assessment was presented to the class in the form of word clouds (Figure 6.2). From the question "What do you know about polymers? (Use one-word descriptors)" the most common response was *plastics* and *environment* followed by a number of descriptive words about polymers. When asked "What do you want to learn about polymers? (in this class)" the survey results showed many students were highly interested in learning about the environmental impact (e.g. recycling, disposal, lack of degradation, stability, health issues, harmful to animals, etc…), the synthesis, composition and applications of polymers.

Using student feedback and the time allotted, the content of the webinars was designed to give students a picture linking polymer synthesis to the polymer's potential end. In class, students were asked to identify polymers from their recycling symbol on an item and check for "compostable" labels on some products. Students were asked to link the UN Sustainability Development Goals (SDGs) that were impacted by polymers. During the discussion, they identified "clean water (#6)", "sustainable cities (#11)", "responsible consumption (#12) and "life below water (#14)" as SDGs that stood out.

Figure 6.2: SCI 300 class responses to "What do you know about polymers? (key words)" summarized in a word cloud.

Table 6.3: Poll Question to Assess Students' Knowledge about poly(lactic acid) (PLA).

Multiple Choice Question: ***Which statement is incorrect about poly(lactic acid) PLA?***	**% option chosen** **(*N* = 29)**
A) PLA is derived from renewable resources such as sugar cane.	37.9
B) PLA is composed for long chains for carbon, hydrogen, and oxygen atoms.	17.2
C) The material can function as a thermoplastics.	27.6
D) The polymer can be compostable in British Columbia.	17.2

Another mini-discussion focused on personal actions one could take to reduce single use plastics or minimizing microplastics (from trash, clothing fibers, etc…). The top responses include using reusable items (bags, cups, straws, utensils, etc…), shopping at bulk shops with personal containers, and repairing clothing or shopping at consignment stores.

The SDGs can be connected to the production of polymers that are compostable or biodegradable. Poly(lactic acid) (PLA) was used as the main example of commercially available polymers that is marketed as being compostable and biodegradable [25]. A final pre-webinar multiple choice question based on PLA's properties was answered by the students prior to the topics of compostable materials (Table 6.3). Students were assessed to gauge prior knowledge about PLA by choosing the *incorrect* statement option. The majority of the students chose the “true” statements about PLA and only 17% knew that PLA cannot be recycled in our region. This result was somewhat expected as many people are surprised once they become educated about the properties of PLA. Although PLA products are labeled as “compostable”, controlled conditions are required for the composting that are not available in our region. In addition, PLA has the recycling number 7 on clam shells but they cannot be added to the plastics recycling bin as PLA cannot be distinguished from other clear plastics (e.g. polyethylene terephthalate [PET], polystyrene [PS]) using the local current recycling processes [26].

6.2.2.1 Feedback and findings for webinars

A survey was used to evaluate student attendance and obtain their feedback regarding the module content. Approximately 74% of the 39 respondents reported attending one or both webinar sessions. The remaining 26% of the students stated they watched the recordings asynchronously. The student feedback on the material was ranked using a five-point Likert scale “Strongly Disagree” to “Strongly Agree” [5] (Table 6.4). Overall, the polymer science webinar was well received by the students based on the mean results and their specific comments (Table 6.5). The students felt the module was well organized, of interest, enjoyable and improved their understanding of polymers. The idea to have

Table 6.4: Polymer science webinar survey results.

Survey Statement for Response	Mean Score* ($N = 39$)
The topics covered in the polymer lecture stimulated my interest	3.61
The polymer lecture improved my knowledge and understanding of the subject	3.95
The polymer unit provided me with valuable resources	3.92
The polymer lecture was well organized	3.97
The polymer unit fulfilled my expectations	3.92
I Enjoyed the polymer unit	3.74

*Likert rating scale: strongly agree = 5; agree = 4; neutral = 3; disagree = 2; strongly disagree = 1.

Table 6.5: Student comments and feedback for the polymer science webinars.

Student comments
"I really enjoyed how the presentation was organized, and felt very engaged with the material. I definitely came out knowing a significant amount more about the topic then before"
"The slides are well organized and I enjoy to watch again and again the recorded lectures."
"The topic is boring. However, the presentation was informative and well explained about topic, I learned a lot."
"The presentations were interactive makes it more interesting than the pre-record lecture."
"I really liked the way that the presentation was organized and how the speaker encouraged students to participate and be involved. I also liked how real life examples were used that are not as complicated so it was not hard to follow along."
"this is my first time know about polymer. I can understand most of the presentation."

an expert in polymer chemistry present the module to improve student learning was also supported by the survey results.

It was important that changes to the module were introduced for the webinar to help create a positive learning experience for the students. This was evident throughout the survey results and feedback comments (Table 6.5). One take away from the feedback was the students expressed the desire to have more time allocated for discussions with their classmates or an open Q&A with the instructor. These aspects can be implemented for the next course offering.

6.3 Course content for prosthetics and orthotics (PROR) at BCIT

Admission into the PROR diploma program is limited to 12 students every two academic years. The students have either completed chemistry at the grade 12 level or at least one post-secondary chemistry course. A first term course in material sciences covers the

Table 6.6: Content and structure of PROR polymer science module.

Lecture	Student Assessment
Chemistry self-review & polymer science resources	Complete reading & practice problems
Introduction to polymer classes & naming	Practice problems
Morphology & structure–property relationships	Group presentation –journal article related to PROR and polymer testing
Thermal behavior (T_g, T_m)	
Criteria for selection of materials	Polymer profile assignment – research to compare and contrast polymers properties for applications

properties, structure and applications of engineering materials. The focus is on polymers, metals, ceramics and composites that are commonly used in prosthetic and orthotic devices. PROR students learn to work with a variety of polymers used in their profession and recognize the materials mostly by their trade names. In the clinic, students use a variety of thermoplastics and thermosets to make prosthetics [27]. In their final term, students complete a case studies course which uses the breadth of their knowledge and practical experience. The polymer module covers specific topics that will help the student understand (i) the property–structure relationships, and (ii) criteria to select an appropriate polymer for a prosthetic and minimize mechanical failure [14, 28–33]. The content and student evaluation components are shown in Table 6.6 for the course's polymer topics and covers six lecture hours.

6.3.1 Teaching practice

The case studies course is one of seven concurrent courses that are taken in the last academic term of the PROR program. The content is structured specifically to add knowledge to the current issues students deal with in constructing prosthetics. Much of the teaching in the case study is done in a discussion format where students present their clinical results. The content for the polymer module comes mainly from the perspective of a polymer chemist. One of the learning objectives is to increase students' knowledge so they can improve their communication with plastics suppliers, materials engineers and polymer scientists. The articles assigned for the group presentation are mostly from literature that the students are familiar with [34–38]. The content is strongly focused on the testing of polymers in PROR applications or design processes. The course is team taught with faculty that are certified prosthetists and orthotists.

6.3.2 Feedback and findings

Student feedback was obtained using anonymous surveys. Most students enjoyed the classes finding them informative, engaging and appreciative that the content was applicable to their projects. In addition, the knowledge was considered helpful for their careers. Most questions were directed towards trouble-shooting the failure of a prosthetic. Students were also curious about the methods that could be used to characterize the polymers for consistent performance. Additional resources were provided that detailed some of the instrumentation and testing available [39, 40].

6.4 Limitations and future studies

We are at the initial stages of obtaining data for the different aspects of both polymer modules – instructional effectiveness, relevance of content and increase in student achievement. Current feedback and data is limited because of (i) the short number of teaching hours available for the polymer module (SCI 300 is between 2 and 3 h, PROR is 6 h), (ii) the small number of students for each class offering and (iii) infrequency of course offering (SCI 300 is only offered once a year. PROR has their class every two years.) Future studies in SCI 300 will explore the effectiveness of the study strategies, and the different modes of presenting the material. An area that would be interesting to survey is the students' initial behavior on polymer use prior to the polymer modules followed by a post-module survey to see if there is any changes in their behavior. At SFU and BCIT, content will be added and updated as new research, applications and the end use of polymers changes. With the PROR students, we would like to add a section on 3D printed prosthetics and compare their properties to traditional industry methods [41, 42].

6.5 Conclusions

The versatility of polymers in applications make it possible to design course content and learning objectives that fits the students' level and background knowledge. The polymer module in the SCI 300 course at SFU builds on the basics of science and chemistry covered in the first few weeks of the course. Polymers are materials that the students recognize for their day-to-day applications but also their negative effects on the environment. Soliciting student feedback on their previous knowledge of polymers allows the instructor to address their interests, misconceptions and information to fill in knowledge gaps. With a wide range of applications, different instructors can incorporate different areas of industry. The electronic and optical applications of electrically conducting polymers would be an example of a specialty topic. Including additional topics such as the UN Sustainability Developments Goals, circular economy, and recycling allows students with a diversity of majors to understand the impact of polymers. Having a broader knowledge of polymers can help students assess their decisions for the use and disposal of plastics in their lives.

The BCIT PROR program focuses on the applied education and practical hands-on skills used in the profession. Students desire specific knowledge in areas such as material selection, prosthetic-orthotic design and construction. This means the polymer topics focus on comparing the structure–property relationships of commonly used polymers. Current research publications on the performance of prosthetics and orthotics are helpful for the students to analyze.

Student surveys provided feedback on the content and course activities. Overall the majority of students stated they acquired new knowledge and found the modules were taught in an engaging manner which resulted in a positive learning experience.

Acknowledgment: The authors would like to thank the Department of Chemistry at SFU and BCIT for financial support and the students of SCI 300 and the PROR program, who participated in the modules and provided feedback. We would also like to thank the PROR faculty Loren Schubert, Yvonne Jeffreys, Jason Goodnough and Desmond Cook for their collaborations.
Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.
Research funding: The study was financially supported by the Department of Chemistry at SFU and BCIT.
Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Ting JM, Ricarte RG, Schneiderman DK, Saba SA, Jiang Y, Hillmeyer MC, et al. Polymer day: outreach experiments for high school students. J Chem Educ 2017;94:1629–38.
2. Erdal NB, Hakkarainen M, Blomqvsit AG. Polymers, giant molecules with properties: an entertaining activity introducing polymers to young students. J Chem Educ 2019;94:1691–5.
3. Ford W. Introducing the journal of chemical education’s “Special Issue: Polymer Concepts across the Curriculum”. J Chem Educ 2017;94:1595–8.
4. Moore JW, Stanitski CL. Lengthening the chain: polymers in general chemistry. J Chem Educ 2017; 94:1603–6.
5. Avent CM, Boyce AS, LaBennett R, Taylor DK. Increasing chemistry content engagement by implementing polymer infusion into gatekeeper chemistry courses. J Chem Educ 2018;95:2164–71.
6. Howell BA. Incorporating polymer science lecture topics into the beginning organic chemistry course to engage students’ interest in current and future applications. J Chem Educ 2017;94: 1655–61.
7. Shulman JI. The distribution of macromolecular principles throughout introductory organic chemistry. J Chem Educ 2017;94:1662–7.

8. Schaller CP, Graham KJ, Jakubowski HV, Johnson BJ. Modules for introducing macromolecular chemistry in foundation courses. J Chem Educ 2017;94:1721–4.
9. Stenzel MH, Barner-Kowollik CB. Polymer science in undergraduate chemical engineering and industrial chemistry curricula. J Chem Educ 2006;83:1521–30.
10. Science 300: science and its impact on society. Available from: http://www.sfu.ca/outlines.html?2020/summer/sci/300/j100 [Accessed 27 Oct 2020].
11. BCIT Prosthetics and Orthotics Program. Available from: https://www.bcit.ca/study/programs/7100diplt [Accessed 27 Oct 2020].
12. Take Action for the Sustainable Development Goals. UN sustainable development goals. Available from: https://www.un.org/sustainabledevelopment/sustainable-development-goals/ [Accessed 27 Oct 2020].
13. Morris SR, Elsinghorst HM, Aronica SM. Making the most of science seminars. Am Biol Teach 2019;81:585–8.
14. Ebewele RO. Polymer science and technology. Boca Raton, FL, USA: CRC Press; 2000.
15. Aguilar MR, San Román J. Smart polymers and their applications. Cambridge, UK: Woodhead Pub; 2014.
16. Mather RR, Wardman RH. The chemistry of textile fibres, 2nd ed. Cambridge, UK: Royal Society of Chemistry; 2015.
17. Cotton S. Every molecule tells a story. London, UK: CRC Press LLC; 2011.
18. Schwendimann BA. Concept maps as versatile tools to integrate complex ideas: from kindergarten to higher and professional education. Knowledge Management E-Learning 2015;7:73–99.
19. Graham KJ, Bohn-Gettler CM, Raigoza AF. Metacognitive training in chemistry tutor sessions increases first year students' self-efficacy. J Chem Educ 2019;96:1539–47.
20. Rickey D, Stacy AM. The role of metacognition in learning chemistry. J Chem Educ 2000;77:915–20.
21. Crouch CH, Fagen AP, Callan JP, Mazur E. Classroom demonstrations: learning tools or entertainment? Am J Phys 2004;72:835–8.
22. Bode CJ, Chapman C, Pennybaker A, Subramaniam B. Developing students' understanding of industrially relevant economic and life cycle assessments. J Chem Educ 2017;94:1798–801.
23. Rhodes CJ. Solving the plastic problem: from cradle to grave, to reincarnation. Sci Prog 2019;102:218–48.
24. Azapagic A, Emsley A, Hamerton I. Polymers: the environment and sustainable development. New York, NY, USA: J. Wiley; 2003.
25. Corn Plastic to the Rescue. Royte E. Smithsonian magazine. Available from: https://www.smithsonianmag.com/science-nature/corn-plastic-to-the-rescue-126404720/ [Accessed 27 Oct 2020].
26. Francis R. Recycling of polymers: methods, characterization and applications. Weinheim, Germany: Wiley-VCH; 2016.
27. Shurr DG, Cook TM. Prosthetics and orthotics, 2nd ed. Upper Saddle River, N.J, USA: Prentice Hall; 2002.
28. Carraher CE. Introduction to polymer chemistry. Boca Raton: CRC/Taylor & Francis; 2007.
29. Wnek GE. Structure-property relationships of small organic molecules as a prelude to the teaching of polymer science. J Chem Educ 2017;94:1647–54.
30. Mateus ALML. Polymer processing demonstrations using PET bottles. J Chem Educ 2019;96:1696–700.
31. Fink JK. Reactive polymers fundamentals and applications: a concise guide to industrial polymers, 3rd ed. Amsterdam, Holland: William Andrew Publishing; 2018.
32. Peacock AJ. Handbook of polyethylene: structures, properties, and applications. New York, NY, USA: Marcel Dekker; 2000.

33. Mills NJ. Plastics: microstructure and applications, 3rd ed. Boston, MA, USA: Elsevier Butterworth Heinemann; 2005.
34. Terpenning JF. Orthotic cranioplasty: material and design considerations. Am Acad Orthot Prosthet 2004;16:S46–9.
35. Coombes AGA, Greenwood CD. Memory plastics for prosthetic and orthotic applications. Prosthet Orthot Int 1988;12:143–51.
36. Manero A, Smith P, Sparkman J, Dombrowski M, Courbin D, Kester A, et al. Int J Environ Res Public Health 2019;16:1641–56.
37. Sobhi H, Matthews ME, Grandy B, Maonovi J, Riga AT. Selecting polymers for medical devices based on thermal analytical methods. J Therm Anal Calorim 2008;93:535–9.
38. Sichina WJ. DSC as problem solving tool: measurement of percent crystallinity of thermoplastics; 2000. Available from: www.perkinelmer.com [Accessed 30 Sep 2020].
39. Holmes-walker WA. Life-enhancing plastics: plastics and other materials in medical applications. Singapore: World Scientific Publishing Company; 2004.
40. The macrogalleria. Available from: https://pslc.ws/macrog/ [Accessed 30 Sep 2020].
41. Noorani R. 3D printing: technology, applications, and selection. Boca Raton, FL: CRC Press, Taylor & Francis Group; 2017.
42. Herbert N, Simpson D, Spence WD, Ion W. A preliminary investigation into the development of 3-D printing of prosthetic sockets. J Rehabil Res Dev 2005;42:141–6.

Marie Constance Béavogui*, Irina Viktorovna Loginova,
Ahmed Amara Konaté and Sékou Amadou Condé

7 Influence of lime (CaO) on low temperature leaching of some types of bauxite from Guinea

Abstract: In Bayer process, low temperature treatment of bauxite generally applicable to gibbsite in the presence of a significant amount of boehmite (>3%), requires a temperature increase and the addition of an additive to improve the leaching conditions. This research is based on improvement of low temperature leaching conditions 108 °C and the addition of lime during the attack of some types of bauxite in Guinea. TRUhat is Low Mono Grade Bauxite (LMG), Standard Metal Grade (SMG) and Fria Bauxite (BF). The results of this study confirm an improvement in the extraction yields. Additionally, it shows an increase in yields of two points when the lime dosage is low, and between 0.5 and 3% of the bauxite weight. Based on the mineralogical and chemical composition findings, minerals contain of SMG bauxites are difficult to decompose while BF bauxites are easy to process. Sougueta limestone was used for testing. After calcination, we obtained CaO added at a rate of: 0.3; 0.5; 1; 3 and 6% of the bauxite weight to finally obtain the highest leaching efficiency compared to the leaching efficiency of bauxite without addition. The best leaching rate obtained for LMG, SMG and BF are respectively: 89.01, 87.15 and 89.74% for additions of 1, 0.5 and 3% CaO respectively.

Keywords: Bayer process, bauxite, Guinea, influence of lime (CaO), low temperature leaching

7.1 Introduction

The bauxite processing industry is now very active in several countries around the world [1]. The Bayer Process is an economic process and can allow up to 20% of alumina in the residues, which technically represents significant losses in attack yield [2, 3]. In recent years, some researchers [4–6] have been interested in the

---

***Corresponding author: Marie Constance Béavogui**, Laboratoire de Recherche Appliquée en Géoscience et Environnement, Institut Supérieur des Mines et Géologie de Boké, Boke, BP 84, Republic of Guinea, E-mail: beavoguimarie11@gmail.com
Irina Viktorovna Loginova, Department of Metallurgy of Non-Ferrous Metals, Institute of New Materials and Technologies, Ural Federal University, Prospekt Lenina, 51, Yekaterinburg, Sverdlovsk Oblast, 620075, Russia, E-mail: i.v.loginova@urfu.ru
Ahmed Amara Konaté, Laboratoire de Recherche Appliquée en Géoscience et Environnement, Institut Supérieur des Mines et Géologie de Boké, Boke, BP 84, Republic of Guinea, E-mail: konate77@yahoo.fr
Sékou Amadou Condé, Departement de Chimie, Usine Rusal Friguia, BP 197, Fria, Republic of Guinea, E-mail: sekou.conde@rusal.com

This article has previously been published in the journal Physical Sciences Reviews. Please cite as: M. C. Béavogui, I. V. Loginova, A. A. Konaté and S. A. Condé "Influence of lime (CaO) on low temperature leaching of some types of bauxite from Guinea" *Physical Sciences Reviews* [Online] 2021, 6. DOI: 10.1515/psr-2020-0141 | https://doi.org/10.1515/9783110726145-007

treatment of bauxite from Guinea; especially from the Boké province, by proposing the addition of various additives including CaO and $CaCO_3$ with a temperature increase of up to 250 °C in order to improve the leaching efficiency [7–9]. The samples used in this study, present different mineralogical characteristics. This difference in composition and the presence of impurities of iron, silicon, and titanium influence their further processing [10, 11].

Fria's bauxites are usually processed at 108 °C [12] and those of Low Mono Grade (LMG) and Standard Metal Grade (SMG) types are processed at temperatures between 143 °C and 235 °C because they usually contain mono; an isomorphic mixture of alumino-goethiteand boehmite, and are therefore difficult to process despite their high Al_2O_3 content [13–15]. The main concern remains the reduction of energy costs, the loss of chemical products [16], and the need to improve the yield, which vary according to the bauxite chemistry's data. Compared to other industrial ligatures, the addition of an additive such as CaO remains dominant in the attack in the Bayer process [17]. The addition of lime partly promotes the reaction with silica in the bauxite and prevents the formation of sodium silicate [18, 19].

One of the important factors for its use is that it is produced in the world in huge quantities and even currently in Guinea and its cost, apparently, is lower than others. Currently, the only processing plant in Guinea does not use CaO for attack and the temperature remains low 108 °C for an average yield of 88% and it only uses bauxite from the Fria's deposit [20].

Looking out the immense bauxite resources in Guinea, the intensification of on-site bauxite processing is crucial, which requires a lower-cost but profitable upgrading process.

The objective of this study is therefore to improve the leaching efficiency by the Bayer process by using a low temperature and additive (CaO), which would considerably reduce the production costs of alumina in Guinea in particular and in the large plants around the world where Guinean bauxite is used as raw material.

7.2 Data and methodology

Three samples were used for analysis and were identified as follows: LMG, SMG, and Fria Bauxite (BF) respectively. All three types of bauxite come from the Boke province in the Republic of Guinea. The LMG and SMG samples were taken at the Guinea Bauxite Company (CBG) plant in Kamsar precisely at corner tower number 10 (TA10) where the sample is automatically taken every 6 min and then sent to the Kamsar laboratory. The BF sample was taken from the entire surface of the strip every hour by a sampler at the Rusal Friguia plant.

In order to obtain the quicklime necessary for the attack, we took and treated calcium carbonate $CaCO_3$ from Souguéta, region of Kindia.

To prepare the lime, we proceeded as follows: The bauxite samples were crushed to grain sizes of 0.7 and 0.1 mm (indicate the characteristics of the mill) and dried for

35 min at a temperature of 300 °C in a kiln. They were then calcined for 2 h 30 min, 3 and 6 h at 1030 °C to eliminate the CO_2 while observing the evolution of the CaO content.

The method of attacking the bauxite's samples was as follows:

The bauxite samples were dried in a kiln at 100–150 °C for about 2 h in the laboratory of the Technology Department of Rusal Friguia after quarrying three consecutive times, then crushed to 2.5 mm grain size before determining: Al_2O_{3mae} (maximum extractable alumina), SiO_{2mae} (maximum extractable silica), Al_2O_3T (Total Alumina), SiO_2T (Total Silica) and Fe_2O_3T (Total Iron).

The different weights of bauxites to be attacked were determined by Formula (7.1)

$$\text{Pbxt} = \frac{\text{CLA} \times (\text{Rpv} - \text{Rpla}) \times 100}{\%Al_2O_{3mae} + (\text{Rpla} \times \text{Rpv}) \times \%SiO_{2mae}} \tag{7.1}$$

where:

- CLA is a concentration of leaching liquor (g/l);
- Rp-v is a target weight ratio;
- Rpla is a weight ratio leaching liquor.

Bauxite leaching is an endothermic reaction that takes place under atmospheric pressure. The aim is to dissolve the alumina from the bauxite in the caustic alkali liquor to form aluminate liquor in order to isolate the alumina (simple body) in liquid form from the heterogeneous bauxite mixture [13, 21].

The established leaching conditions are as follows: granulometry-2.5 mm for Fria's bauxites sand, and 1 mm for LMG and SMG respectively; temperature-107 °C; dwell time-1.5 h; concentration-190 g/l; Rp-v target weight ratio-1.055.

During the attack, we added for each type of bauxite a quantity of CaO according to the percentages (0, 0.3, 0.5, 1, 3, and 6% respectively) of the weight of the bauxite.

After the attack, we determined the following values: the weight ratio, the caustic, and the silica in the liquor.

The sand was washed and dried at 100 °C for 1 h 30 mn and then analyzed. The suspension was diluted with the water used to wash the sand. This suspension is sent for dessilication. During dessilication at about 3 h, 100 ml was taken to make the dry matter. At the end of the dessilication, a quantity of the suspension was taken and analyzed in order to determine the Rp (Al_2O_3/Na_2O), caustic and silica in the liquor.

To facilitate the settling, we have added a flocculent Hx400 which volume is calculated as follow:

$$V_{floc} = \frac{\text{Ms} \times \text{Vsup} \times \text{Dosing}}{\text{Cfloc} \times 1000} \tag{7.2}$$

- V_{floc} – Volume of the flocculent prepared (ml),
- Ms – Dry suspension materiel to be analyzed (g/l),
- Dosing – Determination of the suspension by the flocculent (g/t),

- Cfloc – Concentration of the prepared flocculent (g/l),
- Vsup – Suspension volume.

This volume obtained corresponds to the quantity of flocculent that must be used for the settling of fine mud particles. This flocculent will be injected twice at equal volumes, after the first one we stirred from bottom to top with a manual stirrer, this setting corresponds to the quantity of flocculent which arrives in the caisson. The final step was the determination of the attack yield from the chemical analysis of the bauxite before leaching, and the analysis of the mud and sand by means of the following formulas:

$$R, \mathrm{sand} = \left(1 - \frac{Al_2O_3\mathrm{sand} \times FeO_3T}{Al_2O_3T \times FeO_3\mathrm{sand}}\right) \times 100 \tag{7.3}$$

$$R, \mathrm{mud} = \left(1 - \frac{Al_2O_3\mathrm{mud} \times FeO_3T}{Al_2O_3T \times FeO_3\mathrm{mud}}\right) \times 100 \tag{7.4}$$

7.3 Results and discussions

7.3.1 Preparation of samples

The results of the calcination of calcium carbonate are shown in Tables 7.1 and 7.2. From these tables, with a grain size of 0.1 mm and a calcination time of 6 h, we obtain a content of 6.41% CaO compared to the grain size of 0.75 mm, which explains the choice of $CaCO_3$ dosage with the grain size of 0.1 mm. During calcination the crude dolomite releases CO_2 to form a refractory material which contains 52–61% CaO and 35–38% MgO.

Table 7.1: CaCO3 dosage with a grain size of 0.75 mm at a temperature of 1030 °C.

Samples	1	2	3	Initial
Time of calcination	2 h 35 min	3 h	6 h	–
Hydrochloric acid volume (ml)	21.3	21.1	21.6	0.5
%CaO	59.16	59.73	60.57	1.40

Table 7.2: CaCO3 dosage with a grain size of 0.1 mm at a temperature of 1030 °C.

Samples	1	2	3	Initial
Time of calcination	2 h 35 min	3 h	6 h	–
Hydrochloric acid volume (ml)	19.1	19.4	21.9	0.6
%CaO	53.56	54.39	61.41	2.52

7.3.2 Chemical analysis of samples before leaching

The chemical analysis was carried out by X-ray fluorescence (XRF) in order to determine the extractable maxima of alumina and silica as shown in Table 7.3. For this purpose, we took the average of three attempts for each type of bauxite. According to the results (Table 7.3), it can be seen in theory that the percentage of extractable alumina is much higher in Fria and LMG bauxite (94 and 97% respectively). SMG shows 89% compared to total alumina.

7.3.3 Analysis of the bauxite leaching

The reaction of the leaching is expressed by the chemical equation below

$$Al(OH)_3 + NaOH \rightleftharpoons Na[Al(OH)_4] + Q$$

In direction 1, the reaction is endothermic: it is the reaction of the leaching. In direction 2, it is exothermic: it is the opposite reaction used in decomposition.

In the first case, we obtain from the alumina contained in the bauxite and caustic alkali, an aluminate solution ($Na[Al(OH)_4]$) with water. In the second case, we dissociated the sodium aluminate into tri-hydrated alumina ($Al_2O_3\ 3H_2O$) and caustic alkali (NaOH). The operations that take place during the leaching have a great influence on the production circuit. It is from the etching operation that we look for the best leaching efficiency and productivity in the manufacturing process.

The weight ratio (Rp) is one of the parameters that influence the leaching operations. It is determined in relation to the weight of alumina and weight of caustic soda per liter of liquor. Figure 7.1 shows the evolution of weight ratio. If this ratio is lower, the less alumina there is in the liquor. On the other hand, the ratio is higher and approaches the Rp-v (see Figure 7.1). From Figure 7.1, if the alumina content is high, it is generally

Table 7.3: Results of bauxite analyses before the attack.

	Samples		
Chemical Composition (%)	**LMG**	**SMG**	**Bauxite Fria**
Al_2O_{3mae}	43.65	42.3	40.12
SiO_{2mae}	0.84	1.1	0.09
$Al_2O_{3\ T}$	44.7	47.1	42.6
$SiO_{2\ T}$	1.7	1.75	2.09
$TiO_{2\ T}$	2.27	2.94	2.11
$FeO_{3\ T}$	22.8	20.4	26.3
$V_2O_{5\ T}$	0.088	0.102	0.133
$P_2O_{5\ T}$	0.105	0.165	1.02

between 0.50 and 0.65 for the leaching liquor. Industrial and laboratory experience showed that one should not get too close to the Rp-v otherwise one will lose yield. Again from Figure 7.1, the graph showed us peak points close to the Rp-v which is 1.05 for the three samples.

The silica contained in the three types of bauxite exists in two forms: free silica and combined silica (about 2/3 of the total silica). The free silica or quartz is not attacked by the sodium liquors in the current temperature conditions (108 °C) at Fria and therefore remains with the residues. During the attack at 108°, a large part of the kaolinite dissolves, making its alumina and silica elements pass into solution. In order to prevent this silica from reappearing with the alumina on decomposition, it is made to reappear in solid form sodium silico aluminate ($NaOAl_2O_3$, $2SiO_2$, H_2O) on dessilication. Figure 7.2 shows the SMG-Silica content (%). From Figure 7.2’ we observe a gap between the silica leaving the attack and the dessilication. Additionally, a considerable decrease in the quantity of silica in the solution and each addition of CaO gives an increasing appearance to the curve in general. The free silica is unevenly distributed between the sands and the muds. We have about 3% in the muds and 0.2–0.3% in the sands.

7.3.3.1 Leaching efficiency

The analysis of the leaching efficiency is based on the sand and mud residues which allow us to determine the total leaching efficiency in %. According to our

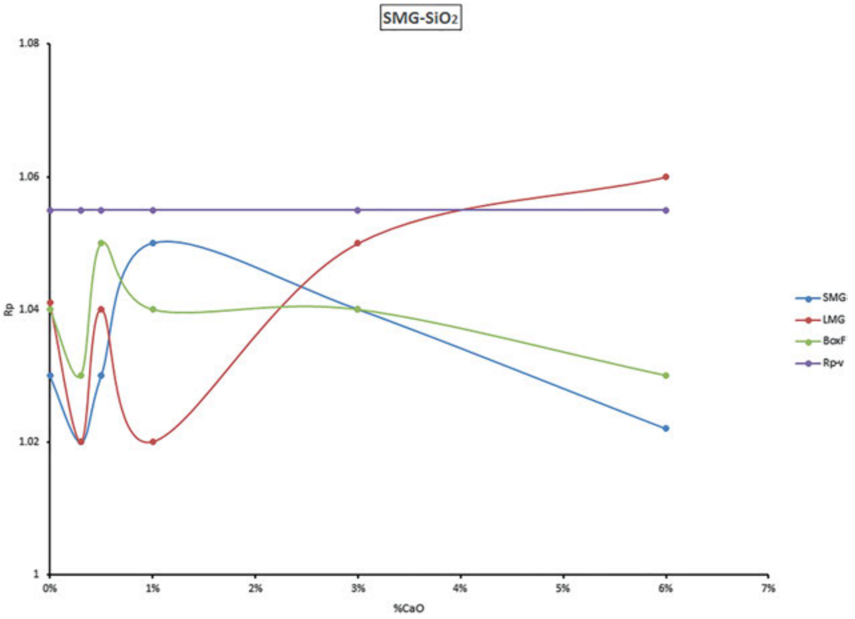


Figure 7.1: The evolution of weight ratio.

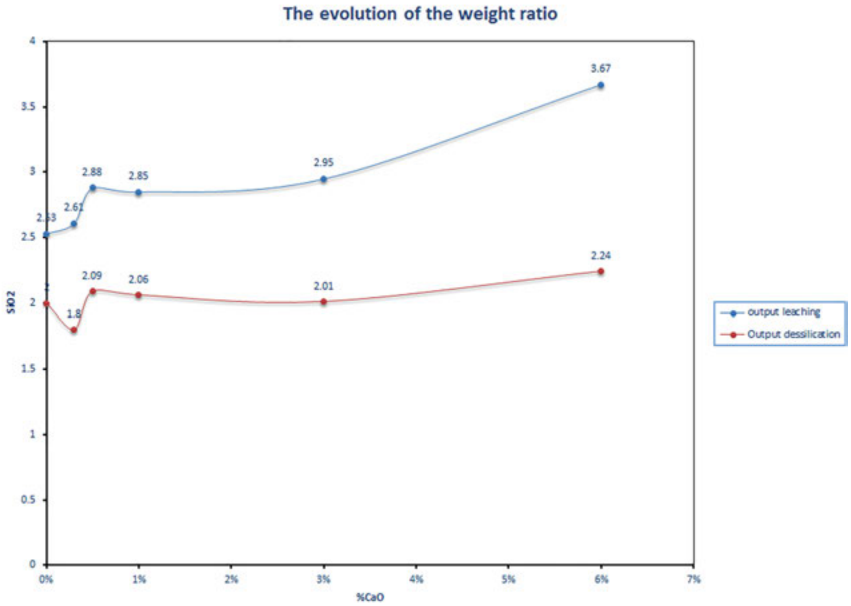


Figure 7.2: The SMG-Silica content (%).

experiments, the sand and mud residues which have been dried then crushed, and analyzed with a spectrometer (Tables 7.4 and 7.5) show a higher concentration of alumina and silica in the sand residues than in the mud. The leaching efficiency, sand and mud determined by Formulas (7.2) and (7.3) vary according to the addition of CaO (Tables 7.4 and 7.5). The total leaching efficiency shown in Table 7.6, shows that adding 1% CaO for LMG bauxite, and 0.5% CaO for Fria's bauxite gives a better leaching efficiency of 87.15, 89.01 and 89.0% respectively. Seventy four percent compared to the others, the leaching efficiency increases up to a certain level of CaO addition and we generally find that a further increase after this point decreases the leaching efficiency, and each type of bauxite is subject to a leaching efficiency variation depending on its characteristics (see Table 7.7).

For SMG bauxite, the leaching efficiency is not so considerable with the addition of 3% as we would have wished; which explains the particularity of processing these types of bauxites according to their mineralogical analyses contain boehmites at a percentage of more than 3%. In general, even with alkalis are very difficult to process. The loss of alumina is partly due to the presence of boehmite and alumino goethite [19, 22–24].

With our experimental parameters, we had a 2.4% gain in leaching efficiency (from 84.68 to 87.15%) at 108 °C. If we increase the temperature to 235 °C which is recommended by the Kamsar laboratory (CBG) for the treatment of these types of bauxite, we can have an average leaching efficiency of 93%, so an increase

Table 7.4: Result of the analysis of sands with and without the addition of lime (CaO).

Types of bauxite	%CaO	Chemical Elements (%)						Leaching efficiency (%)
		Al_2O_3	SiO_2	TiO_2	Fe_2O_3	V_2O_5	P_2O_5	
Standard metal grade	0%	16.9	1.87	3.06	60.5	0.315	0.188	87.9
	0.30%	15.7	1.97	2.63	59.8	0.306	0.196	88.63
	0.50%	15.3	1.54	3	60.1	0.314	0.188	88.97
	1%	14.4	1.53	3.07	59.1	0.317	0.185	89.45
	3%	14.2	1.82	2.68	60.4	0.307	0.197	89.82
	6%	16	2.05	2.56	59.5	0.304	0.193	88.35
Low-mono grade	0%	14.3	1.67	1.93	65.3	0.285	0.144	88.83
	0.30%	14.5	1.7	1.9	66.9	0.284	0.153	88.94
	0.50%	14	1.74	1.96	64.7	0.285	0.143	88.96
	1%	13.1	1.67	1.98	66.6	0.286	0.144	89.97
	3%	14.1	1.76	1.92	62.5	0.285	0.12	88.49
	6%	14.2	1.71	2.06	65	0.288	0.141	88.86
Bauxite fria	0%	12.8	1.43	1.95	68.9	0.286	0.153	88.09
	0.30%	11.8	1.46	1.94	66.2	0.287	0.156	88.58
	0.50%	11.3	1.43	1.9	69.9	0.285	0.158	89.64
	1%	11.3	1.35	2	69.9	0.288	0.152	89.64
	3%	11.9	1.29	2.02	68.6	0.288	0.093	88.88
	6%	12.8	1.54	1.94	69	0.286	0.154	88.11

Table 7.5: Result of the analysis of mud with and without lime addition (CaO).

Types of bauxite	%CaO	Chemical Elements (%)						Leaching efficiency (%)
		Al_2O_3	SiO_2	TiO_2	Fe_2O_3	V_2O_5	P_2O_5	
Standard metal grade	0%	20.7	3.23	7.88	53.7	0.407	0.158	83.3
	0.30%	21.6	4.53	7.38	49.9	0.395	0.164	81.25
	0.50%	20.4	4.37	7.28	49.5	0.393	0.181	82.15
	1%	20.4	3.86	6.35	48.4	0.375	0.212	81.74
	3%	18.05	4.97	5.43	55.9	0.352	0.24	86.01
	6%	19.5	5.2	6.8	52	0.228	0.129	83.76
Low mono grade	0%	14.8	3.13	6.96	47.8	0.38	0.14	86.59
	0.30%	14.7	3.4	6.5	49.9	0.372	0.175	87.24
	0.50%	14	7.38	3.54	51.6	0.31	0.364	88.25
	1%	13.5	3.76	6.21	51.3	0.364	0.194	88.6
	3%	14.7	5.41	5.08	49.2	0.338	0.194	87.06
	6%	18.2	6.97	4.14	45.2	0.316	0.227	82.56
Bauxite fria	0%	12.1	3.64	6.23	64.9	0.368	0.156	88.05
	0.30%	12.5	5.23	5.57	59.8	0.354	0.159	86.6
	0.50%	11.1	4.09	5.42	69.7	0.353	0.176	89.79
	1%	15.7	3.6	6.6	65.3	0.373	0.202	84.59
	3%	16.7	4.77	4.39	63.1	0.312	0.242	83.04
	6%	15.2	3.62	6.37	60.2	0.369	0.173	83.82

Table 7.6: Total leaching efficiency.

		Total leaching efficiency (%)		
Types of bauxite		Standard metal grade	Low-mono grade	Bauxite fria
%CaO	0%	84.68337	87.26171	88.06481
	0.3%	83.4648	87.75193	87.19621
	0.5%	84.19725	88.46296	89.74804
	1%	84.05518	89.0116	86.10661
	3%	87.15543	87.4893	84.7926
	6%	85.13649	84.44922	85.10699

Table 7.7: Technological parameter to be proposed.

	SMG	LMG	FRIA
Grain size (mm)	1	1	2.5
Concentration (g/l)	190	190	190
Temperature (°C)	235	143	105
Residence time (h)	1.30	1.30	1.30
Target weight ratio	1.055	1.055	1.055
%CaO by weight of bauxite	3	1	0.5
Expected leaching efficiency (%)	95	92	89.74

in energy cost allows to gain a leaching efficiency of 8.3%. However, with the addition of CaO obtained from Sougueta limestone for this temperature of 235 °C and an addition of 3% CaO, we can improve the leaching efficiency up to 95–96% which allows to save energy; because to wait for this level of leaching efficiency (according to Fedeev), we need a temperature of 260 °C and the addition of CaCO3 as an additive.

For LMG bauxite, the leaching efficiency is less significant with the addition of 1% for a yield of 89.01% compared without the addition of CaO (87.26%). So a gain of 1.8% for LMG bauxites. In general, the Kamsar laboratory offers mills an leaching temperature of 143 °C for an average yield of 90%. We find that from our study, we can reach 92% yield with 143 °C, LMG bauxite can be processed in the leaching conditions of the Fria plant because it contains little boehmite. So with a temperature between 105 and 143 °C, we can have an improved yield and save energy.

FB is in general gibbsite. According to our experimental parameters, we can improve the leaching efficiency with the addition of 0.5% CaO for a gain of 1.7% (88.06–89.74%).

7.4 Conclusion

Guinea has a rich and very varied bauxite potential and its treatment attracts Geoscientists attention. The objective of this study is therefore to improve the attack efficiency by the Bayer process by using a low temperature and additive (CaO).

The results of this study confirm an improvement in the extraction yields. Additionally, it shows an increase in yields of two points when the lime dosage is low, and between 0.5 and 3% of the bauxite weight. Based on the mineralogical and chemical composition findings, minerals contain of SMG bauxites are difficult to decompose while BF bauxites are easy to process. Sougueta limestone was used for testing. After calcination, we obtained CaO added at a rate of: 0.3; 0.5; 1; 3 and 6% of the bauxite weight to finally obtain the highest leaching efficiency compared to the leaching efficiency of bauxite without addition. The best leaching rate obtained for LMG, SMG and BF are respectively: 89.01, 87.15 and 89.74% for additions of 1, 3 and 0.5% CaO respectively.

From the overall results of this study, we can conclude that the addition of CaO influences the attack yield, and allows obtaining a yield of more than 2% on average. The other advantage of adding CaO is that, it is currently produced in large quantities around the world and is cheaper. In addition, production has already started in Guinea.

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.
Research funding: None declared.
Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Brault-Vattier T. L'aluminium au XX^e et XXI^e siècles/Etude d'économie industrielle. Université de Pau et des Pays de l'Adour; 2015:155–70 pp.
2. Loginova IV, Kyrchikov AV, Penyugalova NP. Alumina production technology: tutorial. Yekaterinburg: Ural Publishing House. University; 2015:81–111 pp.
3. Hind AR, Bhargava SK, Grocott SC. The surface chemistry of Bayer process solids: a review. Physicochem Eng Aspect 1999;146:359–74.
4. Fedyaev AN. Intensification of processes for processing of Guinean bauxites into alumina using the Bayer method. In: Abstract of thesis for Cand. Tech. Science. LNGTI (TU). St. Petersburg: disserCat - Electronic Library of Dissertations; 2011:19 p. https://www.dissercat.com/content/intensifikatsiya-protsessov-pererabotki-gvineiskikh-boksitov-na-glinozem-po-sposobu-baiera.
5. Mamedov VI, Makarova MA, Korrea Gomezh Z, Chausov AA, Okonov EA, Lopukhin MB. Particular qualities of bauxite-bearing laterite cover of the Sangaredi Region (Republic of Guinea). Int Sci Res J 2016;7:114–35.
6. Pan X, H Y, Tu G. Reduction of alkalinity in bauxite residue during Bayer digestion in high-ferrite diasporic bauxite. Hydrometallurgy 2015;151:98–106.

7. Kloprogge TJ, Duong LV, Wood BJ, Frost RL. XPS study of the major minerals in bauxite: gibbsite. bayerite and (pseudo-)boehmite. J Colloid Interface Sci 2006;296:572–6.
8. Solymar K, Ferenczi T, Papanastassiou D. Digestion alternatives of the Greek diasporic bauxite. In: Schneider W, editor. TMS. light metals-Warrendale-proceedings. Seattle. WA: TMS; 2002:75–81 pp.
9. Canale JS. FRIA un exemple d'industrialisation Africaine. Ann Geograph 1963;1:174–88.
10. Zubtsova EA, Zubtsova EA, Kirov CC, Vorobyov IB. Study of the influence of the mineral composition of Guinean bauxite on the main technological indicators of the leaching process. Nonferrous Met 2006:45–51.
11. Arikan H, Demir GK. Sema Vura Investigation of lime usage impacts on bauxite processability at ETI Aluminyum Plant. Int J Ind Chem 2019;10:57–66.
12. Okonov E, Frolikova M, Melkin A, Pekarskii and V, Mamedov V, Chausov A. The sangaredi unique bauxite deposit in Guinea. In: 6th International bauxite-alumina symposium "sustainable development of bauxite & alumina industry in Guinea". India: IBAAS; 2017:51–62 pp.
13. Maltz NS, Sizyakov VM, Shmorgunenko NS. Digestion kinetics of monohydrate bauxite. In: 112th AIME annual meeting Atlanta. GA. Light metals 1983. Warrendale, PA: Metallurgical Society of AIME; 1983:99–107 pp.
14. Whittington BI. The chemistry of CaO and Ca(OH)2 relating to the Bayer process. Hydrometallurgy 1996;43:13–35.
15. Volkov VV, Sobol MI, Eremin NI. The influence of lime additive on alumina extraction from alumina. Izvestia of higher educational institutions. Non-Ferrous Metall 1984;5:22–4.
16. Whittington BI. Quantification and characterisation of hydrogarnet and cancrinite present in desilication product (DSP) by powder X-ray diffraction. In: 4th international alumina quality workshop-AQW1996. Darwin-Australia: Hydrometallurgy; 1996:289–303 pp.
17. Suss A, Fedyaev A, Kuznetzova N, Damaskin A, Kuvyrkina A, Panov A, et al. Technology solutions to increase alumina recovery from alumina goethitic bauxites. In: Schneider W, editor. TMS 2010: TMS proceedings and publications. Seattle. WA; 2010:53–66 pp.
18. Mugnier N, Patrick LP. Method for attacking bauxite enhancing filterability of sludge in attack output. Patent no. WO/2004/039729 2004.
19. Whittington BI, Fallows T. Formation of lime-containing desilication product (DSP) in the Bayer process: factors influencing the laboratory modelling of DSP formation. Hydrometallurgy 1997;45: 289–303.
20. Guozhi L, Zhang T, Zheng C, Xiaofeng Z, Zhang W, Wang Y, et al. Research on the phase transformation in calcification - carbonation method for low-grade bauxite utilization. In: Sustainable industrial processing summit. Montreal, Canada: FLOGEN Star Outreach; 2016, 3: 137–44 pp.
21. Smith P. Reactions of lime under high temperature Bayer digestion conditions. In: 10th international alumina quality workshop. Australia: Hydrometallurgy; 2016:373–81 pp.
22. Xu B, Wingate C, Smith PG. The kinetics of quartz dissolution in caustic solutions and synthetic Bayer liquors. In: Schneider W, editor. TMS. Light metals 2008. New Orleans. LA: TMS; 2008: 157–61 pp.
23. Whittington BI, Fletcher BL, Talbot C. The effect of reaction condition on the composition of desilication produce (DSP) formed under simulated Bayer conditions. Hydrometallurgy 1998;49: 1–22.
24. Rousseaux JM. Milk of lime use in red side settling of Bayer alumina plants. In: 17th international symposium of ICSOBA-2006. Montreal-Canada; 2006:194–204 pp.

Johnson Oluwaseun Odukoya, Eugenie Kayitesi,
Mokgadi Precious Mphahlele, Charlotte Mungho Tata,
Jean Michel Njinkoue[†], Inocent Gouado, Monisola Itohan Ikhile and
Derek Tantoh Ndinteh*

8 Contribution of the volatile components from fresh egg, adult female and male of *Pestarella tyrrhena* to odour production

Abstract: Shrimps, including *Pestarella tyrrhena*, are highly susceptible to deterioration whereas odour production has been indicated as one of the factors determining the perishability and bait potential of shrimps. In this study, volatile components generated from fresh egg, adult female and male of *P. tyrrhena* were assessed using two-dimensional gas chromatography coupled to time-of-flight mass spectrometry to understand their contribution to odour production. Alkenes, alkynes, alcohols, aldehydes, a ketone, acids, esters, an amine, sulphur-containing and miscellaneous compounds were detected. Meanwhile, adult females and males of *P. tyrrhena* had a higher number of these volatile compounds. The detection of 2-methyl propan-1-ol with pungent odour only in the male sample of *P. tyrhenna* suggests that the male of this shrimp species may not completely attract fishes to hooks. Overall, the study established shrimp developmental stage and sex as additional factors influencing the production of volatile compounds, flavour/aroma/odour and fishing bait attributes of *P. tyrrhena*. Detection of *N*-nitrosodimethylamine (a carcinogen) in the shrimp samples, particularly the adult male, calls for caution in their direct human consumption and use as fishing bait.

Keywords: fishing bait; flavour; odour; *Pestarella tyrrhena*; shrimps; volatile compounds.

[†] This chapter is written in gentle memory of Dr. Jean Michel Njinkoue, who passed in before this work could be published.

***Corresponding author: Derek Tantoh Ndinteh**, Department of Chemical Sciences, University of Johannesburg - Doornfontein Campus, Doornfontein, Gauteng, South Africa, E-mail: dndinteh@uj.ac.za
Johnson Oluwaseun Odukoya, Department of Chemical Sciences, University of Johannesburg - Doornfontein Campus, Doornfontein, Gauteng, South Africa; and Department of Chemistry, The Federal University of Technology, Akure, Ondo State, Nigeria
Eugenie Kayitesi, Department of Food and Consumer Science, University of Pretoria, Pretoria, Gauteng, South Africa
Mokgadi Precious Mphahlele, Charlotte Mungho Tata and Monisola Itohan Ikhile, Department of Chemical Sciences, University of Johannesburg - Doornfontein Campus, Doornfontein, Gauteng, South Africa
Jean Michel Njinkoue and Inocent Gouado, Laboratory of Food Sciences and Nutrition, Faculty of Sciences, University of Douala, Douala, Cameroon

This article has previously been published in the journal Physical Sciences Reviews. Please cite as: J. O. Odukoya, E. Kayitesi, M. P. Mphahlele, C. M. Tata, J. M. Njinkoue, I. Gouado, M. I. Ikhile and D. T. Ndinteh “Contribution of the volatile components from fresh egg, adult female and male of *Pestarella tyrrhena* to odour production” *Physical Sciences Reviews* [Online] 2021, 6. DOI: 10.1515/psr-2020-0144 | https://doi.org/10.1515/9783110726145-008

8.1 Introduction

Crustaceans, one of the two broad classes of shellfish [1] and an extremely diverse group of aquatic animals with 40,000–60,000 species [2], include shrimps with over 300 species [1, 3, 4]. Generally, shrimps are one of the most vital classes of aquatic products in the global fishery trading communities [5] and are essential fisheries resources which can have strong ecological effects on benthic communities [6]. Shrimp aquaculture, with both nutritional and economic importance, is, however, more commonly practiced in tropical countries [7].

Among these and in the Mediterranean is *Pestarella* (=*Callianassa*) *tyrrhena* (Petagna, 1972) found in the east Atlantic [8]. It is the most encountered thalassinidean shrimps (Family: Callianassidae) in the sandy and muddy substrates of the lower intertidal and shallow subtidal zones [8–10]. Thalassinidean shrimps, which include *Pestarella tyrrhena*, have been indicated as one of the most effective bioturbating groups of macrofaunal organisms that has affected the benthic environment in no small measure [11].

As affirmed in the literature, *P. tyrrhena* is a sediment-processing deposit-feeding thalassinid shrimp [11–13] which feeds primarily on detritus encountered in the course of its burrowing activities [13]. The burrowing activity of this group of thalassinidean shrimps which greatly affects the chemical/geophysical properties of sediments has attracted special focus on them and are now regarded as important environmental engineers [8].

On the other hand, the growing global demand for seafood has led to the growth of commercial fishing as an industry [14] and recreational fishing has also contributed to fishing activities in several parts of the world [15]. For these two fishing activities, i.e., commercial and recreational fishing, Schram and Klien [16] recorded the use of *P. tyrrhena* as bait. Largely, the type of bait is considered a factor in assessing species diversity, population and fishing efficiency [17, 18]. Bait, according to Karunanithi et al. [19], also determines the quality and number of fish caught when traps are used.

As a good bait, among other attributes, must have a distinctive odour to attract fish to the hook [18, 20] and shrimps, on storage, are prone to deterioration/microbial spoilage [21], this research was aimed at evaluating the contribution of volatile components from fresh egg, adult female and male of *P. tyrrhena* to odour production which may influence their acceptability and effectiveness as fishing bait. This involved the use of two-dimensional gas chromatography (GC × GC) coupled to time-of-flight mass spectrometry (TOF MS). The investigation became needful as: (1) Kumar et al. [18] reported the need for alternative baits to edible fishes to reduce fishing pressures on these fish species, (2) some local fishermen use shrimp as bait to catch eels [22], (3) Dayal et al. [23] noted that shrimps have a neutral flavour and (4) flavour, which depends on the attributes of associated volatile compounds, determines food acceptability and quality [24–26].

8.2 Materials and methods

8.2.1 Preparation of samples

Fresh egg, adult female and male samples of *P. tyrrhena* were purchased at the Doula fishing seaport and transported immediately in an icebox containing ice to the laboratory. They were cleaned and subjected to soxhlet extraction to obtain the lipid.

8.2.2 Volatile components and fatty acid methyl esters analysis

Saponification of the obtained lipid was carried out by refluxing with KOH/EtOH, followed by conversion to methyl esters by reaction with methanolic HCl (hydrochloric acid in methanol). Analysis of the shrimp samples' volatile components was achieved using a modified Agilent 7890A GC system coupled to a LECO Pegasus 4D Time of Flight mass spectrometer (LECO Corporation, USA). A GC × GC modulator, secondary oven (LECO Corporation, USA) and a split/splitless inlet Rxi-5 SilMS (29.5 m × 0.25 mm × 0.25 um) was used as the primary column whereas the secondary column was Rxi 17 Sil MS (0.95 m × 0.25 mm × 0.25 um; Restek, USA). The used carrier gas was helium (flow rate: 1 mL/min). The oven was set to 40 °C for 30 s, ramped at 10 °C/min to 250 °C and then held for 30 s at 250 °C. Transfer line and source temperatures of the mass spectrometer were at 250 °C.

Estimation of percentage peak areas of eluted volatile compounds from the *P. tyrrhena* samples was carried out using ChromaTOF software (LECO, USA) whereas their identification involved the use of the mass spectral database in the NIST, Adams and EO libraries. A similarity match of ≥70% was adopted as the criterion for assigning a name to a compound [27].

8.2.3 Statistical analysis

A readily available bioinformatics web tool, Venn diagram (http://bioinformatics.psb.ugent.be/webtools/Venn/) [27], was used in evaluating the relationship between the volatile components detected in the shrimp samples. Thereafter, percentage peak areas of the eluted compounds were computed and presented statistically.

8.3 Results and discussion

Volatile compounds are key components of food flavour [26] and contribute to odour attributes [28]. Results of the Venn diagram constructed (Figure 8.1) showed a total number of 12 similar volatile components in the three samples, with zero (0), five (5) and eight (8) unique volatile compounds in the fresh egg, adult female and male of *P. tyrrhena*, respectively. With respect to the detected compounds in the egg sample, it also revealed that female and male *P. tyrrhena* samples have more volatile compounds in common. This indicates that the developmental stage of the shrimp influenced the production of volatile compounds and explains the higher number of volatile components recorded in the adult shrimp samples.

Generally, assessment of the distribution of volatile components in the three samples (fresh egg, adult female and male of *P. tyrrhena*) revealed the detection of alkenes, alkynes, alcohols, aldehydes, a ketone, acids, esters, an amine, sulphur-containing and miscellaneous compounds (Table 8.1).

Most of these detected compounds were found in the male shrimp species (82.86%) (Figure 8.2) and indicates the sex of shrimp as another determining factor in the production of volatile compounds by shrimps. According to Adebo et al. [26], only a portion of the numerous volatile compounds in food enhances its flavour/aroma. Distinctively, among the volatile compounds detected in the shrimp samples, Tylewicz et al. [35] identified only alcohols, carbonyl compounds (aldehydes and ketones), acids, esters, amines and sulphur compounds as part of the key aroma compound classes. Hence, male *P. tyrrhena* with the overall highest number of these specific volatile compounds and the highest percentage of detectable volatile components

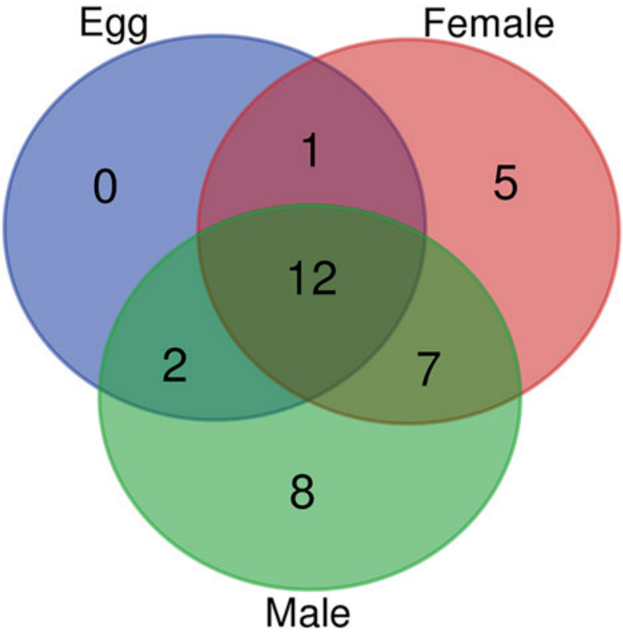


Figure 8.1: Venn diagram showing the relationship between the volatile components obtained from the GC × GC-TOF-MS analysis of fresh egg, adult female and male of *Pestarella tyrrhena*.

Table 8.1: Detected volatile components in the fresh egg, adult female and male samples of *Pestarella tyrrhena*.

Name	Chemical formula	Egg	Female	Male	Odour descriptor	References
Alkenes						
3-Bromocyclohexene	C_6H_9Br		√	√		
E,E–3-methyl-2,4-hexadiene	C_7H_{12}		√	√		
3-(Azidomethyl)cyclohexene	$C_7H_{11}N_3$	√	√			
7,8-Dioxatricyclo[4.2.2.02,5]dec-9-ene, 3-methyl-	$C_9H_{12}O_2$	√	√	√		
Alkynes						
3-Cyclopropyl-1-butyne	C_7H_{10}			√		
2-Methyl-3-hexyne	C_7H_{12}		√			
6-Chloro-6-methyl-1-octen-7-yne	$C_9H_{13}Cl$	√	√	√		
Alcohols						
1,3-Dichloro-2-propanol	$C_3H_6Cl_2O$	√	√	√		
1-Chloro-3-iodo-2-propanol	C_3H_6ClIO	√	√	√		
2-Methylpropan-1-ol	$C_4H_{10}O$			√	Solvent like, malty, pungent	[29, 30]
Aldehydes						
Methylene-cyclopropanal	C_5H_6O		√			
2,4-Hexadienal	C_6H_8O		√			
Ketone						
Oxacyclododec-10-en-2-one, (Z)-	$C_{11}H_{18}O_2$		√			
Acids						
2-Methylpentanoic acid	$C_6H_{12}O_2$	√	√	√		
11-Hydroxy-(3z,6z)-3,6-dodecadienoic acid	$C_{12}H_{20}O_3$			√		
Esters						
Acetic acid, methyl ester	$C_3H_6O_2$		√		Fragrant, fruity	[31]
Hexanoic acid, methyl ester	$C_7H_{14}O_2$		√	√	Fruity, sweet	[32]
Ethanol, 2,2′-oxybis-, diacetate	$C_8H_{14}O_5$	√		√		
Methyl-(3R)-(–)-5-oxo-3-propylpentanoate	$C_9H_{16}O_3$	√		√		
Nonanoic acid, methyl ester	$C_{10}H_{20}O_2$		√	√	Fruity, sweet, pear	[32]
Decanoic acid, methyl ester	$C_{11}H_{22}O_2$		√	√	Fresh, herbal, humidity	[33, 34]
(2,4-Hexadienylthio)-dimethylmalonate	$C_{11}H_{14}SO_4$			√		
Methyl 10-deuterio-10-(trideuteriomethyl) undecanoate	$C_{13}H_{22}D_4O_2$	√	√	√		
13-Tetradecynoic acid, 4-methyl-, methyl ester	$C_{15}H_{26}O_2$	√	√	√		
Amine						
N-nitrosodimethylamine	$C_2H_6N_2O$	√	√	√		

Table 8.1: (continued)

Name	Chemical formula	Egg	Female	Male	Odour descriptor	References
Sulphur-containing compounds						
Methanesulfonyl chloride	CH_3SO_2Cl	√	√	√		
Methane, sulfonylbis-	$C_2H_6O_2S$			√		
Bis(2-furfuryl)disulfide	$C_{10}H_{10}O_2S_2$		√	√		
Miscellaneous compounds						
1,3,5-Triazine	$C_3H_3N_3$		√	√		
2-Pyrrolidinone-5,5-d2	$C_4H_5D_2NO$			√		
Pyridine	C_5H_5N	√	√	√		
Pyridinium perchlorate	$C_5H_6ClNO_4$	√	√	√		
(2H) Benzene	C_6H_6	√	√	√		
5H-Tetrazol-5-one, 1-(2-cyclohexen-1-yl)-4-(1,1-dimethylethyl)-1,4-dihydro-	$C_{11}H_{18}N_4O$			√		
1,3-Dioxolane, 2-methyl-2-(4-methyl-3-methylenepentyl)-	$C_{11}H_{20}O_2$			√		

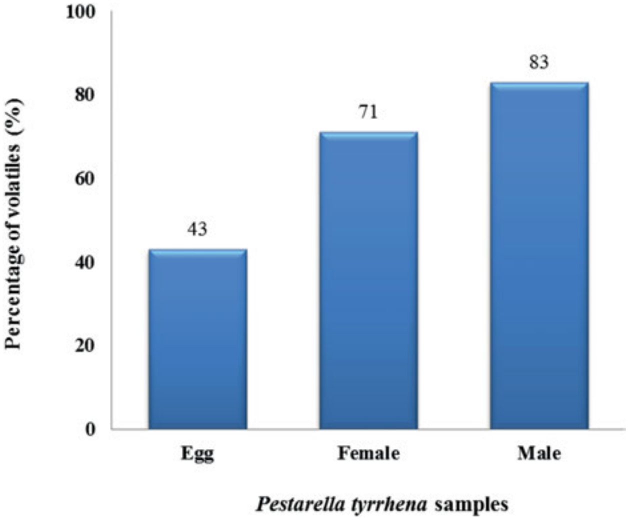


Figure 8.2: Percentage of all volatile components obtained from the fresh egg, adult female and male of *Pestarella tyrrhena*.

would have the most distinguished flavour/aroma as Adebo et al. [26] also linked the flavour of food to the number/quantity of volatile components.

As indicated in Spurvey et al. [36], hydrocarbons (which include alkenes and alkynes) may be generated from lipid autoxidation processes involving alkyl radicals or via carotenoids decomposition. Generally, they (i.e., hydrocarbons) present little contribution to overall flavour/aroma/odour [37–41]. Thus, the varied levels of alkenes and alkynes in the investigated fresh egg, adult female and male *P. tyrrhena* samples (Figure 8.3) would have a less significant impact on the flavour/aroma/odour of this shrimp.

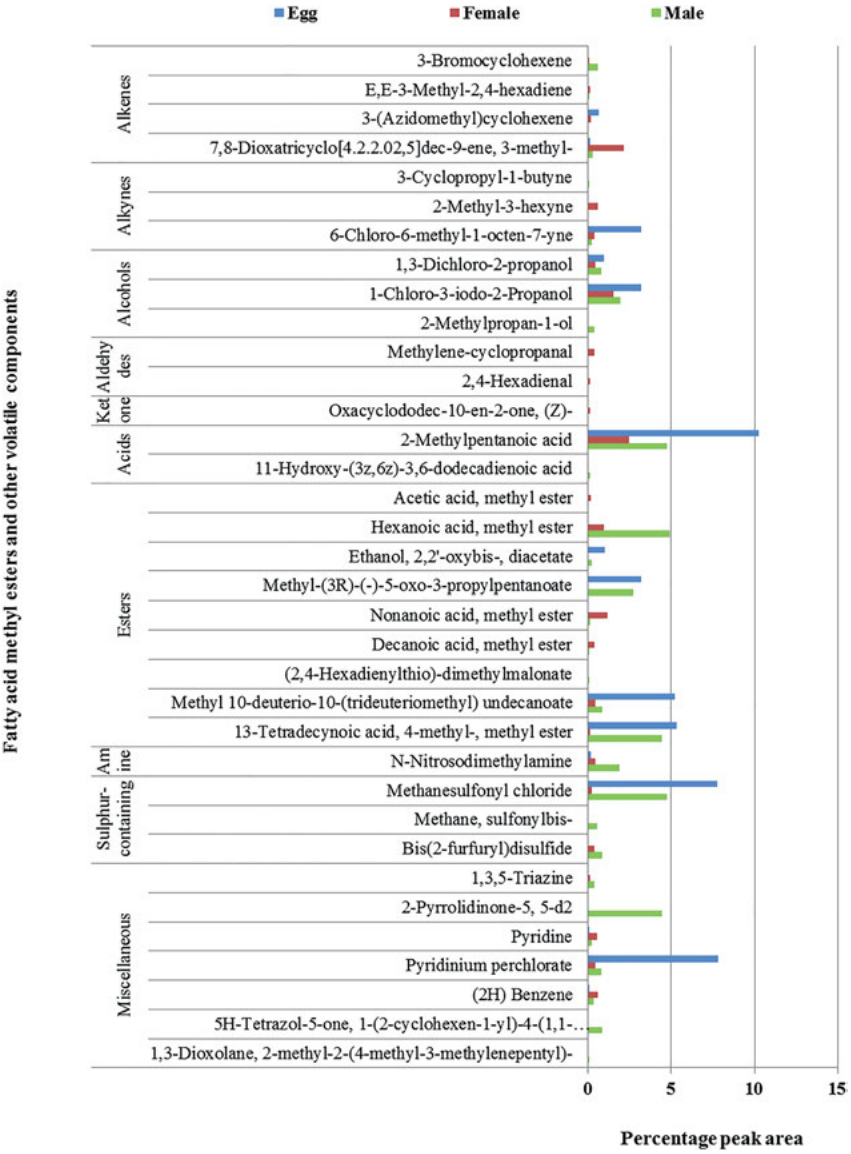


Figure 8.3: Relative abundance with respect to the peak area of volatile components (including fatty acid methyl esters) obtained from fresh egg, adult female and male of *Pestarella tyrrhena* samples.

Tylewicz et al. [35] noted that alcohols may be generated from metabolic pathways involving carbohydrates or amino acids, reduction of carbonyl group (aldehyde or ketone), and oxidation of long-chain polyunsaturated fatty acid (PUFA). Most times, they have fragrant, planty, rancid and earthy odours [36]. Zhang et al. [42] added that unsaturated alcohols generally have more influence than saturated alcohols and may affect food flavour greatly. In the current study, all the three (egg, female and male) samples of *P. tyrrhena* gave 1,3-dichloro-2-propanol and 1-chloro-3-iodo-2-propanol as part of their volatile constituents with the highest concentrations in the egg samples (Figure 8.3). Notwithstanding, only the male sample produced 2-methyl propan-1-ol with solvent-like/malty/pungent odour [29, 30] (Table 8.1). This implies that the use of male *P. tyrrhena* as a fishing bait might not completely attract fishes to hooks.

Meanwhile, carbonyl compounds which include aldehydes and ketones [35] are most times associated with a “fishy” odour [43]. In line with Zhuang et al. [24], aldehydes, important odour compounds of aquatic products, could result from the degradation of lipid oxidative and amino-acid Strecker reaction. In addition, Tylewicz et al. [35] noted that most of them have a fruity or floral aroma. The two aldehydes (methylene-cyclopropanal and 2,4-hexadienal) detected in the investigation were from the female shrimp species (Table 8.1). This detection of 2,4-hexadienal in female *P. tyrrhena* substantiates the release of a fatty and floral/fruity note from this shrimp typical of 2,4-alkadienals which are indicated to be from PUFA $n - 6$ [43].

Zhuang et al. [24] affirmed the report that ketones are mostly derived from thermal oxidation of PUFA, amino acid degradation, or Maillard reaction. Ketones containing 5–13 carbon atoms most times give fruity or musty notes whereas those with a lesser number of carbon atoms present a buttery flavor [35]. Oxacyclodocec-10-en-2-one was only detected in male *P. tyrrhena* which may contribute to the fruity note of this shrimp as Spurvey et al. [36] pointed out that ketones contribute to the sweet floral and fruity flavours of crustaceans.

Furthermore, organic acids, according to Tylewicz et al. [35], are one of the key groups of compounds that give rise to odour. They, i.e., Tylewicz et al. [35], explained that most fatty acids are generated via enzymatic or chemical lipid hydrolysis; whereas, short-chain linear or branched fatty acids are usually from amino acids or carbohydrates metabolism. Wu et al. [37] also indicated that microbial oxidation of aldehydes can give rise to branched-chain carboxylic acid. This suggests that 2-methyl pentanoic acid identified in all the samples (Table 8.1) with the highest concentration in the egg sample (Figure 8.3) is either from the microbial oxidation of an aldehyde or amino acids/carbohydrates metabolism. Nonetheless, 11-hydroxy-(3z, 6z)-3,6-dodecadienoic acid was only detected in male *P. tyrrhena* (Table 8.1).

Several authors like Tylewicz et al. [35], Odukoya et al. [41], Tao et al. [44], Pugliese et al. [45] and Xu et al. [46], among others, have established that esterification reaction between carboxylic acids and alcohols produces esters. These esters usually give rise to the aroma with fruity or floral notes [26, 35, 37, 46]. They, i.e., esters, including methyl esters, were the most abundant class of compounds detected in the assessed fresh egg, adult female and male *P. tyrrhena* samples (Figure 8.4).

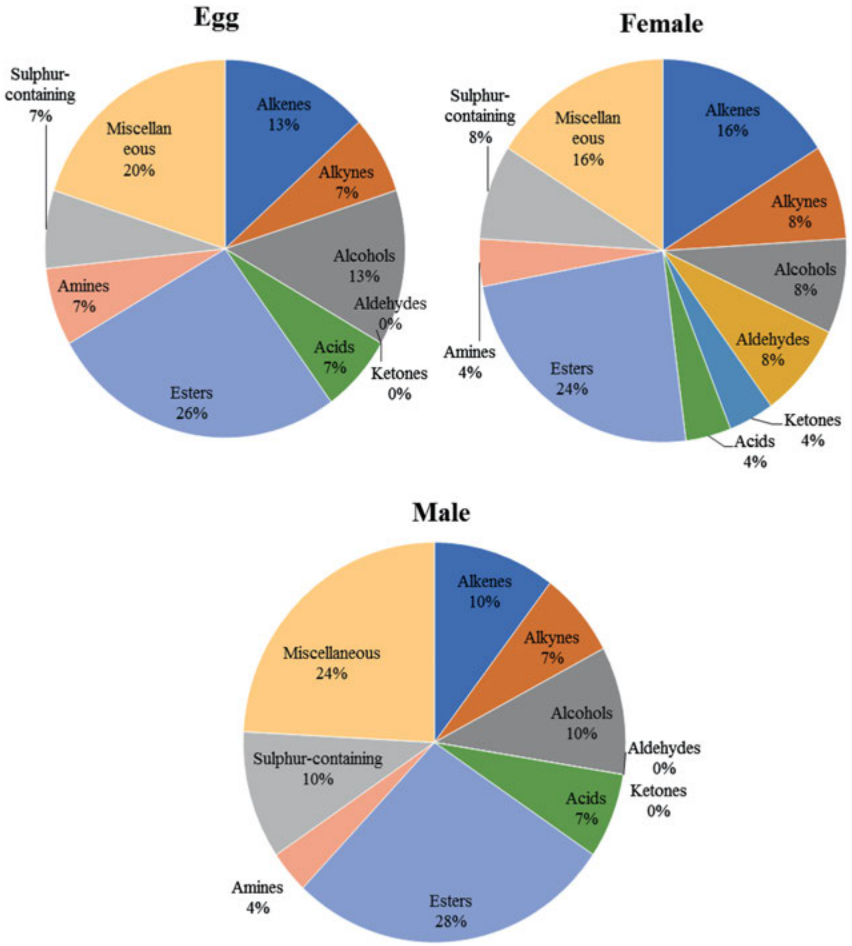


Figure 8.4: Percentage of the volatile components obtained from *Pestarella tyrrhena* samples.

From literature, the detection of acetic acid methyl ester in female *P. tyrrhena* would give a fragrant/fruity note [31] whereas hexanoic acid and nonanoic acid methyl esters in the adult shrimp samples produced a fruity/sweet note [32]. Interestingly, concentrations of some esters were also recorded in the egg samples (Figure 8.3).

As reported by Tylewicz et al. [35], volatile/non-volatile amines are usually generated via the decarboxylation of amino acids arising from proteolysis in which volatile amines mostly have alcoholic, fruity or vanishy odour. *N*-nitrosodimethylamine, a carcinogen [41], was the only amine detected in the three samples and *P. tyrrhena* male sample had the highest concentration (Figure 8.3). This revealed that direct consumption of the shrimp, particularly the male species, may affect human health.

On the other hand, sulphur-containing compounds, important odour-active components [24], are regarded as the most important contributors to the odour of shellfish alongside aldehydes, ketones and nitrogen-containing compounds [36]. They play a role in the generation of desirable/undesirable aromas [36] and are from the production and degradation routes of sulphur amino acids [35]. The number of these sulphur-containing compounds in *P. tyrrhena* samples was found in the order: male > female > egg. Nonetheless, female *P. tyrrhena* had the overall highest detection level of volatile compounds (aldehydes, ketone, nitrogen and sulphur-containing compounds) regarded as the most important contributors to the odour of shellfish followed by the male species. This revealed that male *P. tyrrhena*, though with a higher number of miscellaneous compounds (Table 8.1), is a better fishing bait than the female shrimp.

8.4 Conclusion

GC × GC-TOF-MS technique was used in providing a comprehensive understanding of the volatile components produced from *P. tyrrhena*. The investigation identified important odour active compounds in the fresh egg, adult female and male samples of this shrimp. It revealed that shrimps' (in this case *P. tyrrhena*) developmental stage and sex are two additional factors that will influence the production of volatile compounds and their flavour/aroma/odour. Based on odour production, the study also pinpointed adult males to be a better fishing bait than the female but its success rate/suitability still depends on the type of fish. To ensure food safety and protection of human lives, efforts should be made to apply appropriate processing methods to shrimps for direct human consumption or fish farming to avoid possible exposure to carcinogenic *N*-nitrosodimethylamine.

Acknowledgement: The service of Mr. Aliou Garga (Veterinary service, Doula Fishing Seaport) at the sample collection stage is gratefully acknowledged.
Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.
Research funding: The authors sincerely thank the National Research Foundation (NRF) of the Republic of South Africa, and the University of Johannesburg, for the support provided.
Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Venugopal V, Gopakumar K. Shellfish: nutritive value, health benefits, and consumer safety. Compr Rev Food Sci Food Saf 2017;16:1219–42.
2. Söderhäll I. Crustacean hematopoiesis. Dev Comp Immunol 2016;58:129–41.

3. Yang H, Gözaydln G, Nasaruddin RR, Har JRG, Chen X, Wang X, et al. Toward the shell biorefinery: processing crustacean shell waste using hot water and carbonic acid. ACS Sustain Chem Eng 2019; 7:5532–42.
4. Zhang X, Yuan J, Sun Y, Li S, Gao Y, Yu Y, et al. Penaeid shrimp genome provides insights into benthic adaptation and frequent molting. Nat Commun 2019;10:1–14.
5. Hou D, Huang Z, Zeng S, Liu J, Wei D, Deng X, et al. Intestinal bacterial signatures of white feces syndrome in shrimp. Appl Microbiol Biotechnol 2018;102:3701–9.
6. Osawa Y, Aoki MN, Bauer RT, Thiel M. Numbers and sizes of the shrimp *Rhynchocinetes uritai* Kubo, 1942 (Decapoda: Caridea) caught in bait and refuge traps. J Crustac Biol 2015;35:768–75.
7. Butcherine P, Benkendorff K, Kelaher B, Barkla BJ. The risk of neonicotinoid exposure to shrimp aquaculture. Chemosphere 2018;217:329–48.
8. Dworschak PC, Koller H, Abed-Navandi D. Burrow structure, burrowing and feeding behaviour of *Corallianassa longiventris* and *Pestarella tyrrhena* (Crustacea, Thalassinidea, Callianassidae). Mar Biol 2006;148:1369–82.
9. Papaspyrou S, Thessalou-Legaki M, Kristensen E. Impact of *Pestarella tyrrhena* on benthic metabolism in sediment microcosms enriched with seagrass and macroalgal detritus. Mar Ecol Prog Ser 2004;281:165–79.
10. Dworschak PC. The burrows of *Callianassa tyrrhena* (Petagna 1792) (Decapoda: Thalassinidae). Mar Ecol 2001;22:155–66.
11. Papaspyrou S, Gregersen T, Cox RP, Thessalou-Legaki M, Kristensen E. Sediment properties and bacterial community in burrows of the ghost shrimp *Pestarella tyrrhena* (Decapoda: Thalassinidea). Aquat Microb Ecol 2005;38:181–90.
12. Koller H, Dworschak PC, Abed-Navandi D. Burrows of *Pestarella tyrrhena* (Decapoda: Thalassinidea): hot spots for nematoda, foraminifera and bacterial densities. J Mar Biol Assoc UK 2006;86:1113–22.
13. Demiri A, Meziti A, Papaspyrou S, Thessalou-Legaki M, Kormas KA. Abdominal setae and midgut bacteria of the mudshrimp *Pestarella tyrrhena*. Cent Eur J Biol 2009;4:558–66.
14. Mileski JP, Galvao CB, Forester ZD. Human trafficking in the commercial fishing industry: a multiple case study analysis. Mar Policy 2020;116:103616.
15. Henriques MB, Fagundes L, Petesse ML, da Silva NJR, Rezende KFO, Barbieri E. Lambari fish *Deuterodon iguape* as an alternative to live bait for estuarine recreational fishing. Fish Manag Ecol 2018;25:400–7.
16. Schram FR, Vaupel Klein JC. The crustacea. Leiden: Koninklijke Brill NV; 2012.
17. Schmid K, Reis-Filho JA, Harvey E, Giarrizzo T. Baited remote underwater video as a promising nondestructive tool to assess fish assemblages in clearwater Amazonian rivers: testing the effect of bait and habitat type. Hydrobiologia 2016;784:93–109.
18. Kumar KVA, Pravin P, Meenakumari B. Bait, bait loss, and depredation in *Pelagic longline* fisheries – a review. Rev Fish Sci Aquac 2016;24:295–304.
19. Karunanithi M, Neethirajan N, Padmanaban V, Robinson JS. Development of dry artificial fish bait for trap fishing using tuna red meat and shrimp head wastes. J Aquat Food Prod Technol 2018;27: 1009–22.
20. Tangke U, Deni S, Aunaka A. The influence of using bait types to the number and composition of fishing traps catch in South Ternate waters. IOP Conf Ser Earth Environ Sci 2018;175:1–9.
21. Arancibia MY, López-Caballero ME, Gómez-Guillén MC, Montero P. Chitosan coatings enriched with active shrimp waste for shrimp preservation. Food Contr 2015;54:259–66.
22. Fachrurrazi T, Miswar E, Mustaqim M, Nur FM, Batubara AS, Muchlisin ZA. Effect of different bait on the catchment of eels *Anguilla marmorata* in the Brayeun River, *Aceh Besar dist*rict, Indonesia. IOP Conf Ser Earth Environ Sci 2019;348:5.

23. Dayal JS, Ponniah AG, Khan HI, Babu EPM, Ambasankar K, Vasagam KPK. Shrimps – a nutritional perspective. Curr Sci 2013:1487–91.
24. Zhuang K, Wu N, Wang X, Wu X, Wang S, Long X, et al. Effects of 3 feeding modes on the volatile and nonvolatile compounds in the edible tissues of female Chinese mitten crab (*Eriocheir sinensis*). J Food Sci 2016;81:S968-81.
25. Lv T, Wang Y, Pan D, Cao J, Zhang X, Sun Y, et al. Effect of trypsin treatments on the structure and binding capacity of volatile compounds of myosin. Food Chem 2017;214:710–6.
26. Adebo OA, Njobeh PB, Desobgo SCZ, Pieterse M, Kayitesi E, Ndinteh DT. Profiling of volatile flavor compounds in Nkui (a Cameroonian food) by solid phase extraction and 2D gas chromatography time of flight mass spectrometry (SPME-GC × GC-TOF-MS). Food Sci Nutr 2018;6:2028–35.
27. Kewuyemi YO, Njobeh PB, Kayitesi E, Adebiyi JA, Oyedeji AB, Adefisoye MA, et al. Metabolite profile of whole grain ting (a Southern African fermented product) obtained using two strains of *Lactobacillus fermentum*. J Cereal Sci 2020;95:103042.
28. Aprea E, Corollaro ML, Betta E, Endrizzi I, Dematte ML, Biasioli F, et al. Sensory and instrumental profiling of 18 apple cultivars to investigate the relation between perceived quality and odour and flavour. Food Res Int 2012;49:677–86.
29. Giri A, Osako K, Ohshima T. Identification and characterisation of headspace volatiles of fish miso, a Japanese fish meat based fermented paste, with special emphasis on effect of fish species and meat washing. Food Chem 2010;120:621–31.
30. Mohamed HN, Man YC, Mustafa S, Manap YA. Tentative identification of volatile flavor compounds in commercial Budu, a Malaysian fish sauce, using GC-MS. Molecules 2012;17:5062–80.
31. Ruth JH. Odor thresholds and irritation levels of several chemical substances: a review. Am Ind Hyg Assoc J 1986;47:A-142–51.
32. Queiroga RC, Neta MT, Sandes RD, Narain N, Galvao MS, Madruga MS, et al. An insight in key volatile compounds in goat milk based on their odor active values. J Food Sci Nutr Res 2019;2: 49–60.
33. Angerosa F, Servili M, Selvaggini R, Taticchi A, Esposto S, Montedoro G. Volatile compounds in virgin olive oil: occurrence and their relationship with the quality. J Chromatogr A 2004;1054: 17–31.
34. Zabaleta L, Gourrat K, Barron LJR, Albisu M, Guichard E. Identification of odour-active compounds in ewes' raw milk commercial cheeses with sensory defects. Int Dairy J 2016;58:23–30.
35. Tylewicz U, Inchingolo R, Rodriguez-Estrada MT. Food aroma compounds. In: Galanakis CM, editor Nutraceutical and functional food components. Amsterdam: Elsevier Inc.; 2017:297–334 pp.
36. Spurvey S, Pan BS, Shahidi F. Flavour of shellfish. In: Shahidi F, editor. Flavor of meat, meat products, and seafoods. London: Blackie Academic & Professional; 1998:159 p.
37. Wu H, Zhuang H, Zhang Y, Tang J, Yu X, Long M, et al. Influence of partial replacement of NaCl with KCl on profiles of volatile compounds in dry-cured bacon during processing. Food Chem 2015;172: 391–9.
38. Song G, Dai Z, Shen Q, Peng X, Zhang M. Analysis of the changes in volatile compound and fatty acid profiles of fish oil in chemical refining process. Eur J Lipid Sci Technol 2017;1700219:1–8.
39. Song G, Zhang M, Peng X, Yu X, Dai Z, Shen Q. Effect of deodorization method on the chemical and nutritional properties of fish oil during refining. LWT Food Sci Technol 2018;96:560–7.
40. Wang H, Zhang J, Zhu Y, Wang X, Shi W. Volatile components present in different parts of grass carp. J Food Biochem 2018;42:1–19.
41. Odukoya JO, Kayitesi E, Mphahlele MP, Tata CM, Njinkoue JM, Gouado I, et al. Effect of processing methods on the volatile components of *Ethmalosa fimbriata* using a two-dimensional gas chromatography-time-of-flight mass spectrometry (GC × GC-TOF-MS) technique. J Food Process Preserv 2021;45:1–11.

42. Zhang J, Cao J, Pei Z, Wei P, Xiang D, Cao X, et al. Volatile flavour components and the mechanisms underlying their production in golden pompano (*Trachinotus blochii*) fillets subjected to different drying methods: a comparative study using an electronic nose, an electronic tongue and SDE-GC-MS. Food Res Int 2019;123:217–25.
43. Varlet V, Knockaert C, Prost C, Serot T. Comparison of odor-active volatile compounds of fresh and smoked salmon. J Agric Food Chem 2006;54:3391–401.
44. Tao NP, Wu R, Zhou PG, Gu SQ, Wu W. Characterization of odor-active compounds in cooked meat of farmed obscure puffer (*Takifugu obscurus*) using gas chromatography-*mass spectrometr*y-olfactometry. J Food Drug Anal 2014;22:431–8.
45. Pugliese C, Sirtori F, Škrlep M, Piasentier E, Calamai L, Franci O, et al. The effect of ripening time on the chemical, textural, volatile and sensorial traits of *Bicep femoris* and *Semimembranosus* muscles of the Slovenian dry-cured ham *Kraški pršut*. Meat Sci 2015;100:58–68.
46. Xu Y, Li L, Regenstein JM, Gao P, Zang J, Xia W, et al. The contribution of autochthonous microflora on free fatty acids release and flavor development in low-salt fermented fish. Food Chem 2018;256: 259–7.

Héctor Hernández-Mendoza*, Nancy Lara-Almazán,
Abraham Kuri-Cruz, Elizabeth Teresita Romero-Guzmán and
María Judith Ríos-Lugo

9 Quadrupole inductively coupled plasma mass spectrometry and sector field ICP-MS: a comparison of analytical methods for the quantification of As, Pb, Cu, Cd, Zn, and U in drinking water

Abstract: A comparison was carried out between quadrupole inductively coupled plasma mass spectrometry (ICP-QMS) detection and sector field ICP-MS (ICP-SFMS) detection for quantification of elements such as arsenic (As), cadmium (Cd), copper (Cu), lead (Pb), zinc (Zn), and uranium (U) in drinking water. A drinking water sample obtained from the International Atomic Energy Agency was used for validation measurement methods. ICP-QMS and ICP-SFMS obtained recoveries of 95–107% and 95–105%, respectively. Moreover, the relative standard deviation for ICP-QMS was <5% in comparison with ICP-SFMS, which was <2%. The limits of detection obtained in ICP-MS and ICP-SFMS for each element were under ng L^{-1}, except for Zn. Both methods were applied to evaluate these elements in drinking water for consumption in Mexico. According to Mexican Regulation for Human Drinking Water NOM-201-SSA1-2015 and Environmental Protection Agency (EPA) from the United States, the values are within the allowable limits. In conclusion, ICP-QMS and ICP-SFMS are excellent choices for measurements of these toxic elements in water samples because of high precision and

---

***Corresponding author: Héctor Hernández-Mendoza,** Instituto de Investigación de Zonas Desérticas, Universidad Autónoma de San Luis Potosí, Altair 200, ZP 78377, San Luis, San Luis Potosí, México; and Universidad del Centro de México, Capitán Caldera 75, ZP 78250, San Luis, San Luis Potosí, México, E-mail: hector.mendoza@uaslp.mx

Nancy Lara-Almazán and Abraham Kuri-Cruz, Laboratorio Nacional de Investigación en Forense Nuclear, Instituto Nacional de Investigaciones Nucleares, Carretera México-Toluca S/N km 36.5, A.P. 18-1027, La Marquesa, ZP 52750, Ocoyoacác, México

Elizabeth Teresita Romero-Guzmán, Laboratorio Nacional de Investigación en Forense Nuclear, Instituto Nacional de Investigaciones Nucleares, Carretera México-Toluca S/N km 36.5, A.P. 18-1027, La Marquesa, ZP 52750, Ocoyoacác, México; and Departamento de Química, Instituto Nacional de Investigaciones Nucleares, Carretera México-Toluca S/N km 36.5, A.P. 18-1027, La Marquesa, ZP 52750, Ocoyoacác, México

María Judith Ríos-Lugo, Unidad de Posgrado, Facultad de Enfermería y Nutrición, Universidad Autónoma de San Luis Potosí, Avenida Niño Artillero 130, ZP 78210, San Luis Potosí, San Luis Potosí, Mexico

This article has previously been published in the journal Physical Sciences Reviews. Please cite as: H. Hernández-Mendoza, N. Lara-Almazán, A. Kuri-Cruz, E. T. Romero-Guzmán, and M. J. Ríos-Lugo “Quadrupole inductively coupled plasma mass spectrometry and sector field ICP-MS: a comparison of analytical methods for the quantification of As, Pb, Cu, Cd, Zn, and U in drinking water” *Physical Sciences Reviews* [Online] 2021, 7. DOI: 10.1515/psr-2020-0121 | https://doi.org/10.1515/9783110726145-009

accuracy in routine analysis minutes, while also exhibiting excellent precision and accuracy in routine analysis.

Keywords: drinking water, ICP-QMS, ICP-SFMS, toxic elements

9.1 Introduction

Water has been essential for the development of civilizations. However, today there is water crisis in the world; this is a reality due to lifestyle, population growth, industrialization, urbanization, and intensification of agriculture [1–3]. The water problem in several countries has focused on an irregular and unhealthy supply [4, 5]. On the other hand, it is estimated that 20% of the world's population face water shortage and in the world that than million people die each year from drinking contaminated water [6]. Moreover, the last report by the United Nations World Water Assessment Programme (WWAP) mentioned that 768 million people remain without access to water and 2.6 billion remain without access to adequate sanitation. These show that countries or regions have absolute water scarcity, and it could be considered that two-thirds of the world's population could be living under water-stressed conditions [7]. Moreover, today is considered one of the main problems of humanity and one of the greatest challenges for different regions of the world.

Humans need water in enough quantity and quality for consumption and in such a way to avoid diseases. The intake of drinking water should be safe and the content of toxic components must be frequently evaluated by each country. Water contamination by microorganisms is the main route of contamination, followed by chemical and radioactive contamination. Nevertheless, chemical contamination, especially with metalloids and heavy metals such as arsenic (As), lead (Pb), Mercury (Hg), cadmium (Cd), and uranium (U), has been highly toxic to human beings. These toxic elements are evaluated in underground water, surface water, rainwater, and drinking water to avoid diseases by its consumption [8–10].

The Environmental Protection Agency (EPA) from the United States has established levels of metallic ion concentration in drinking water and the World Health Organization (WHO) recommends these values [11, 12]. In the case of Mexico, Official Mexican Standard NOM-127-SSA1-1994 set the permissible limits for quality and purification treatments, use and consumption by humans, as well as for all public and private water supply systems [13], where the permissible limit values in the NOM-127-SSA1-1994 for Cd and Hg are similar to those of WHO and USEPA, and Pb and As have different values. Additionally, the NOM-127-SSA1-1994 shows the permissible limit of U in terms of total activity.

On the other hand, analytical methods for measuring metal ions in water samples are atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma atomic emission spectrometry (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS)

[14, 15]. ICP-MS is a technique more efficient in the analysis of metal ions at ultra-trace levels in comparison with AAS, ICP-OES, and ICP-AES [16, 17].

The main characteristics of ICP-MS are [16] high sensitivity (sub ng or fg per sample), good precision and accuracy (less than 5% in samples), multi-element detection, and faster preparation of the sample. However, ICP-MS has some limitations that can affect the measurement. These are isobaric and polyatomic interference, where isobaric interference cannot be eliminated and reaction/collision cell technology could be used to avoid polyatomic interference [18–20]. In addition, the sector magnetic ICP-MS (ICP-SFMS) has shown more capacity to avoid the interferences of atomic or molecular ions [21]. This is because of its three resolution modes [$m/\Delta m$ = ~300, ~4,000, and ~10,000]. For this reason, ICP-SFMS is a choice for analysis of heavy metals due to its high sensitivity, capability for interference-free analysis, and precision when compared with the ICP-MS [22, 23].

This work was to perform a comparison between quadrupole ICP-MS (ICP-QMS) and ICP-SFMS for the quantification of As, Cd, Cu, Pb, Zn, and U in drinking water.

9.2 Experimental

9.2.1 ICP-MS

Two different types of mass spectrometers were used for the analysis: ICP-QMS with reaction cell technology (7700, Agilent Technologies, USA) and ICP-SFMS (Element XR, Thermo Fisher Scientific, Germany). In ICP-SFMS, aqueous samples were introduced in a continuous flow rate through an autosampler (CETAC ASX-520 Technologies, Inc., USA) and a MicroMist U-series nebulizer (Elemental Scientific Inc., USA). For ICP-MS, samples were introduced using capillary tubing through a peripump introduction system and a MicroMist Nebulizer.

9.2.2 Materials and reagents

Standard solutions of As, Cd, Cu, Pb, Zn, and U (1000 µg mL^{-1}, SPEX CertiPrep) were used for the preparation of calibration curves. Aliquots of these solutions were taken and diluted with ultrapure nitric acid at 2% v/v, and high-purity water was used to afore, thus obtaining a standard solution of 1000 µg L^{-1} and 10 µg L^{-1}. The ICP-QMS instrument's condition was checked with a multi-element solution of 10 ± 0.05 µg L^{-1} of Ce, Co, Li, Tl, and Y (Agilent Technologies, USA). For ICP-SFMS, tuning of instrumental parameters was done using the multi-elemental XXIII standard (Ba, B, Co, Fe, Ga, In, K, Li, Lu, Na, Rh, Sc, Y, Tl, and U; Merck, Germany), which has 1.0 ± 0.2 µg L^{-1}.

Indium (In) was used as an internal standard (1.0 ± 0.2 µg L^{-1}, SPEX CertiPrep). High-purity water (>18 MΩ-cm) and ultrapure nitric acid were used in the sample preparation. Ar gas was used for the injection of samples (99.96%). All volumetric flasks that were used in the preparation were of borosilicate glass, class A, blue graduated, with PP stoppers, and these were decontaminated with 10% HNO_3 and high-purity water. A sample of drinking water obtained from International Atomic Energy Agency (IAEA, Interlaboratory comparisons: proficiency test IAEA-TEL-2015-01) was used as reference material; it was refrigerated at 4 °C until analysis. Moreover, 24 water samples from three companies in Mexico were collected between January and April 2015 (A=Bonafont, B=Ciel, and C=Epura), and these samples were stored at room temperature.

9.2.3 Sample preparation

The analysis was performed in November 2015; the analysis sequence is shown in Figure 9.1. The IAEA provided a plastic bottle with 500 mL of drinking water acidified at pH 2 with suprapure nitric acid. Sample analysis was carried out in aliquots with a final volume of 10 mL; these aliquots were measured in volumetric flasks, and 1 and 10 $\mu g \cdot L^{-1}$ of ^{115}In were added with an internal standard in the analysis by ICP-SFMS and ICP-QMS, respectively. The accuracy and precision criteria of the methods were determined with IAEA drinking water, which was measured 10 times in each instrument. In addition, external calibration curves were prepared in triplicate for the evaluation of the linearity of methods. The concentrations of the external calibration curve for both instruments were 0.01, 0.1, 0.5, 1, 5, 10, 25, and 50 $\mu g\ L^{-1}$. Two standard solutions were prepared. S1 was prepared with a dissolution 1:1000 from 1000 $\mu g\ mL^{-1}$ of As, Cd, Cu, Pb, Zn and U and standard S2 was prepared with a dissolution 1:100 from the standard S1. Standard S1 was used for the preparation calibration standards of 5, 10, 25, and 50 $\mu g\ L^{-1}$, and standard S2 was used for the

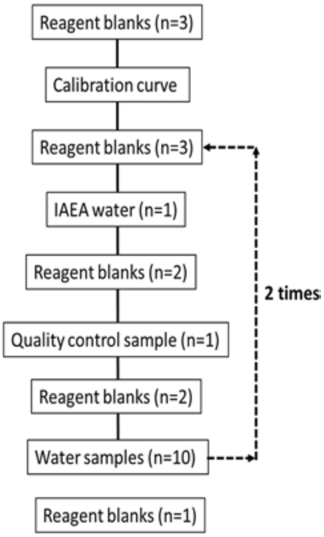


Figure 9.1: Analysis sequence for ICP-QMS and ICP-SFMS (in each analysis, the sample introduction system was washed for 2 min with 2% HNO_3).

preparation calibration standards of the curve of 0.01, 0.1, 0.5, and 1 µg L^{-1}. The final volume of standard solutions and calibration standards was 100 mL at 2% v/v HNO_3.

Drinking water samples A, B, and C were acidified with ultrapure nitric acid at 2% v/v. Analysis was carried out in triplicate in both instruments in this study. Moreover, reagent blanks (2% v/v HNO_3) in volumetric flasks of 10 mL were prepared in each set of measurements. Finally, a standard solution of 5 µg L^{-1} of As, Cd, Cu, Pb, Zn, and U was used as quality control.

9.3 Results and discussion

Nowadays, methods developed to measure heavy metals in water are varied and show good capabilities in the analysis at levels of under 10 µg L^{-1}. Many of them use AAS or ICP with versions (OES, AES, and MS). However, ICP-MS has high sensitivity, good accuracy and precision, and quick sample preparation for multi-elemental quantification [14–16]. On the other hand, when ICP-QMS is used to measure elements, it is necessary to eliminate polyatomic interference from sample preparation, acidic water impurities, and memory effect by introduction system and deposit of salts on the cones [23]. Moreover, there are also isobaric interferences (of isotopes with the same mass) and doubly charged ion interferences in ICP-QMS.

Polyatomic interferences are common in the analysis of element traces by ICP-QMS. Nevertheless, use of a collision reaction cell as the measurement mode in ICP-MS eliminates or reduces such interferences [18–20]. In the case of ICP-SFMS, polyatomic interference can be avoided through the selection of appropriate resolution (LR, MR, and HR). On the other hand, mathematical correction has been frequently used to reduce the interferences; these are automatic corrections in the software of ICP-QMS and ICP-SFMS. However, in the case of drinking water, it is not necessary to use additional mathematical correction because the concentration levels of heavy metals and metalloids are low.

The following parameters were evaluated in the methods developed with ICP-SFMS and ICP-QMS: (i) checking of the instrumental condition, (ii) linearity, LOD, and LOQ, (iii) accuracy and precision, and (iv) uncertainty. Moreover, it should be mentioned that these parameters were only evaluated in the development of the methods and not during the drinking water analysis.

9.3.1 Measurement parameter optimization

Table 9.1 shows the instrumental conditions to measure As, Cd, Cu, Pb, Zn, and U by ICP-SFMS and ICP-QMS. Tuning the ICP-SFMS parameters was performed in three phases:

1. Mass adjustment in the instrument was done at low (LR), medium (MR), and high (HR) resolution using the multi-elemental XXIII solution, and ICP-SFMS parameters at LR were also optimized, obtaining maximum intensities of ^{7}Li (1.7×10^5 cps), ^{115}In (1.2×10^6 cps), and ^{238}U (1.6×10^6 cps).

Table 9.1: ICP-SFMS and ICP-QMS optimized operational conditions for measurement of As, Cd, Cu, Pb, Zn, and U.

ICP-SFMS		**ICP-QMS**	
Solution uptake rate	0.1 mL min^{-1}	Solution uptake rate	0.5 mL min^{-1}
RF power	1325 W	RF power	1050 W
Cool gas flow rate	16.2 L min^{-1}	Plasma gas flow rate	15.02 L min^{-1}
Auxiliary gas flow rate	0.49 L min^{-1}	Auxiliary gas flow rate	0.68 L min^{-1}
Nebulizer gas flow rate	1.851 L min^{-1}	Nebulizer gas flow rate	0.79 L min^{-1}
Ion extraction lens potential	−2000 V	Reading per replicate	100
Isotopes	LR = ^{111}Cd, ^{208}Pb, ^{238}U, ^{115}In MR = ^{63}Cu, ^{66}Zn and ^{115} In HR = ^{75}As and ^{115}In	Isotope (Cell mode with He)	^{75}As, ^{63}Cu, ^{111}Cd, ^{115}In, ^{208}Pb, ^{66}Zn and ^{238}U
Samples per peak	40	Number of replicate	5
Settling time	0.3 ms	Total analysis time per sample	3 min
Sample time	0.0100 ms	Scan mode	Peak hop transient
Acqu points	10	Detection mode	Dual-pulse and analog
Peak shift	1.0	Resolution	10% peak integrated maximum
Mass window	100%	Integration type	Average
Integration window	30%	Sample cone	Pt-tipped with Cu base 1 mm
Scan type	E-Scan	Skimmer cone	Nickel 0.4 mm
Detection mode	Triple (ion counting, analog and Faraday)	Spray chamber	Quartz
Total analysis time per simple	2.18 min	Nebulizer	Micromist Microflow (PFA)
Sample/skimmer cone	Nickel		
Spray chamber	Twister with Helix, 50 mL cyclonic, borosilicate glass		
Nebulizer	MicroMist U-series nebulizer 0.1 mL min^{-1}		

2. A stability assay was performed for 15 min to monitor the ^{115}In and ^{238}U; results obtained were RSD < 2% for both elements.
3. 10 µg L^{-1} of all elements was used to optimize the signal intensities in LR (^{111}Cd, ^{208}Pb, ^{238}U, and ^{115}In), MR (^{63}Cu, ^{66}Zn, and ^{115}In), and HR (^{75}As and ^{115}In). Monitoring resolution of each analyte in the system turned out to be adequate to justify measurements in the sample analysis.

Optimization of ICP-MS with the collision/reaction cell was performed automatically with standard solution (^{7}Li, ^{59}Co, ^{89}Y, ^{140}Ce, and ^{205}Tl) introduced through capillary tubing, followed by adjusting hardware settings such as torch axis, pulse and analog factor (P/A factor), plasma correction, resolution/axis, and electron multiplier. Results obtained were 31.5×10^3 cps for ^{7}Li, 123.6×10^3 cps for ^{89}Y, and 158.9×10^3 cps for ^{205}Tl with RSD of less than 2%. Collision reaction with He was used for the analysis of ^{63}Cu, ^{66}Zn, ^{75}As, ^{115}In, ^{208}Pb, and ^{238}U in drinking water

9.3.2 Linearity, LOD, and LOQ

The linear correlation coefficient (R^2) for each analyte was over 0.999. The results obtained for the limit of detection (LOD), the limit of quantification (LOQ), and R^2 in both ICP-MS are shown in Table 9.2. LODs and LOQs were calculated from reagent blanks ($n = 10$) using Eqs. (9.1) and (9.2):

$$\mathrm{LOD} = \overline{X} + 3\sigma \tag{9.1}$$

$$\mathrm{LOQ} = \overline{X} + 10\sigma \tag{9.2}$$

where $\overline{X}$ = mean of blank signals and σ = standard deviation corresponding to the blank signals.

LODs were found in the order of ng·L^{-1}, and better values of LOQs were obtained with ICP-SFMS.

Table 9.2: R^2, LOD, and LOQ for each analyte by ICP-SFMS and ICP-QMS.

Analyte	R^2	ICP-SFMS		ICP-QMS	
		LOD (ng L^{-1}) ± $u_{(\mathrm{rep})}$	LOQ (ng L^{-1}) ± $u_{(\mathrm{rep})}$	LOD (ng L^{-1}) ± $u_{(\mathrm{rep})}$	LOQ (ng L^{-1}) ± $u_{(\mathrm{rep})}$
As	0.9999	0.73 ± 0.02	2.19 ± 0.21	12.5 ± 1.06	37.50 ± 1.89
Cd	0.9999	0.69 ± 0.05	2.07 ± 0.46	3.25 ± 0.15	9.75 ± 0.65
Cu	0.9999	0.70 ± 0.06	2.10 ± 0.58	4.98 ± 0.19	14.94 ± 1.02
Pb	0.9999	0.86 ± 0.03	2.58 ± 0.27	3.42 ± 0.16	10.44 ± 0.57
Zn	0.9995	2.91 ± 0.11	8.73 ± 0.52	18.03 ± 1.21	26.19 ± 1.48
^{238}U	0.9999	0.69 ±0.001	2.07 ± 0.08	1.79 ± 0.13	4.05 ± 0.20
$^{\mathrm{Total}}$U	0.9999	0.69 ±0.001	2.07 ± 0.08	1.79 ± 0.13	4.05 ± 0.20

9.3.3 Accuracy and precision

Accuracy for the proposed methods was evaluated using the drinking water obtained from IAEA as reference material. This reference material and quality control were re-analyzed during the analysis of water samples (Figure 9.1). Subsequently, a statistical analysis was performed on the results reported in the intercomparison to compare the accuracy in ICP-SFMS and ICP-MS. In this analysis, the general means of the reference values along with their respective uncertainty were considered. Individual results for each element with their respective uncertainty value were also taken into account, noting that accuracy in both methods has been similar. IAEA 2015 intercomparison results are summarized in Table 9.3, where accuracy is expressed as the recovery percentage of IAEA 2015 sample. Moreover, RSD was calculated during the analysis of reference material. The RSD values were less than 5% for both ICP-SFMS and ICP-MS

9.3.4 Uncertainty

Table 9.4 shows the summary contributions to the measurement uncertainty of each element. Uncertainty was measured according to the EURACHEM/CITAC guide [24]. The parameters that were considered in the calculation of measurement uncertainties were main calibration curve-related $(u_{(x_{\mathrm{smpl}},y)})$, stock solutions of standards $(u_{(\mathrm{std})})$, sample preparation $(u_{(\mathrm{smpl})})$, and repeatability $(u_{(\mathrm{rep})})$. The combined uncertainty can be calculated with Eq. (9.3):

$$u_{(c)} = \sqrt{\left(u_{(x_{\mathrm{smpl}},y)}\right)^2 + \left(u_{(\mathrm{std})}\right)^2 + \left(u_{(\mathrm{smpl})}\right)^2 + \left(u_{(\mathrm{rep})}\right)^2} \tag{9.3}$$

Table 9.3: Results resume for As, Cd, Cu, Pb, Zn ^{238}U, $^{\mathrm{total}}$U and in a drinking water sample during the international intercomparison test IAEA 2015.

		ICP-SFMS			ICP-QMS		
Analyte	**Assigned value: IAEA, 2015 (µg L^{-1}) ± U**	**Experimental average value (µg L^{-1}) *n* = 10 ± U**	**% Recovery**	**% RSD**	**Experimental average value (µg L^{-1}) *n* = 10 ± U**	**% Recovery**	**% RSD**
As	7.58 ± 0.61	7.91 ± 0.28	104.35	1.67	8.40 ± 0.42	110.82	3.2
Cd	1.99 ± 0.14	1.83 ± 0.10	91.96	1.29	2.03 ± 0.14	102.01	1.48
Cu	5.41 ± 0.88	3.45 ± 0.28	63.77	1.84	4.80 ± 0.42	88.72	3.6
Pb	9.70 ± 1.80	9.15 ± 0.32	94.33	1.54	9.90 ± 0.17	102.06	4.85
Zn	20.2 ± 3.4	24.32 ± 0.57	120.40	1.33	18.25 ± 1.43	90.35	3.41
^{238}U	3.06 ± 0.28	2.845 ± 0.13	92.97	1.60	2.99 ± 0.17	97.71	2.45
$^{\mathrm{Total}}$U	3.08 ± 0.28	2.905 ± 0.14	94.32	1.63	3.30 ± 0.18	107.14	2.18

Table 9.4: Summary contributions to the measurement uncertainty.

Parameter	**As**	**Cd**	**ICP-SFMS**					**As**	**Cd**	**ICP-QMS**				
			Cu	**Pb**	**Zn**	**^{238}U**	**^{Total}U**			**Cu**	**Pb**	**Zn**	**^{238}U**	**^{Total}U**
$u_{(x_{\text{smpl}},y)}$	0.01	0.01	0.09	0.04	0.09	0.01	0.01	0.01	0.05	0.11	0.01	0.09	0.01	0.01
$u_{(\text{rep})}$	0.13	0.02	0.10	0.15	0.27	0.05	0.05	0.26	0.03	0.17	0.47	0.71	0.07	0.07
$u_{(\text{smpl})}$	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
$u_{(\text{std})}$	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
$u_{(c)}$	0.14	0.05	0.14	0.16	0.29	0.06	0.06	0.21	0.07	0.21	0.08	0.71	0.08	0.08
U	0.28	0.10	0.28	0.32	0.57	0.13	0.13	0.42	0.14	0.42	0.17	1.43	0.17	0.17

The standard uncertainty was calculated using the regression according to Eq. (9.4):

$$u_{(x_{\text{smpl}},y)} = \frac{SD_{xy}}{b} \cdot \sqrt{\frac{1}{p} + \frac{1}{n} + \frac{\left(x_{smpl} - x_m\right)^2}{Q_{xx}}} \tag{9.4}$$

where

- $u_{(x_{\text{smpl}},y)}$ = Standard uncertainty for the determination of the x_{smpl} concentration due to the application of the determined calibration correlation.
- SD_{xy} = Residual standard deviation.
- b = Slope.
- p = Number of measurements (repetitions) carried out for a given sample.
- n = Total number of standard samples used for the determination of the calibration (number of points).
- x_m = Mean value x.
- Q_{xx} = Parameter calculated according to the relation described by Eq. (9.5):

$$Q_{xx} = \sum_{i=1}^{n} (x_i - x_m)^2 \tag{9.5}$$

The uncertainty of the standards S1 and S2 were calculated using the Eq. (9.6). This uncertainty is combined with the uncertainty of each elemental concentrations given in the certificates by the manufacturer ($u_{(\text{ele})}$) and uncertainty coming from the volumetric flasks ($u_{(vf)}$) and micropipettes ($u_{(mp)}$) used for dilution.

$$u_{std} = \sqrt{\left(u_{(\text{ele})}/C_{\text{ele}}\right)^2 + \left(u_{(vf)}/V\right)^2 + \left(u_{(mp)}/V\right)^2} x C_{\text{std}} \tag{9.6}$$

where

- C_{ele} = concentration of the element in the main stock solution (1000 mg L^{-1}).
- C_{std} = concentration of intermediate standard stock solution (1000 µg L^{-1} and 10 µg L^{-1}).

The Eq. (9.7) was used to calculate the uncertainty coming from the micropipettes as well as the volumetric flasks.

$$u_{(vf)}\ or\ u_{(mp)} = \sqrt{(u_{(\mathrm{vcal})})^2 + (u_{(\mathrm{vtem})})^2} \tag{9.7}$$

where

- $u_{(\mathrm{vcal})}$ = volumetric calibration standard uncertainty.
- $u_{(\mathrm{vtem})} = \frac{T - T_{20} * \alpha * V}{\sqrt{3}}$ = standard uncertainty of the temperature effect.
- T = water temperature (°C) at the time of measurement.
- T_{20} = calibration temperature of the volumetric material.
- $\alpha = 0.00021\,°\mathrm{C}^{-1}$ = coefficient of volume expansion of the water.

The uncertainty associated with sample preparation was calculated using Eq. (9.6), which involves the volumetric flasks ($u_{(vf)}$) (10 mL or 1 L) and micropipettes ($u_{(mp)}$) used for dilution to 2% with ultrapure nitric acid. Eq. (9.8) was used to calculate the uncertainty from the micropipettes as well as the volumetric flasks.

$$u_{\mathrm{smpl}} = \sqrt{(u_{(vf)}/V)^2 + (u_{(mp)}/V)^2} \tag{9.8}$$

The uncertainty for all possible sources is included in the uncertainty repeatability, for example contribution from parameters such as the placement of the measurement instrument, operator skill, consistency in measurement, and purity of acid. Moreover, the accuracy of calibration, stability, other temperature effects, and voltage drift should be considered in measurements by ICP-MS. The RSD (s) of the repeatability data represented the repeatability standard uncertainty, which was used to obtain the repeatability standard uncertainty of the mean (9.9):

$$u_{(\mathrm{rep})} = \frac{s}{\sqrt{n}} \tag{9.9}$$

The expanded uncertainty (U) was obtained with Eq. (9.10), where coverage factor $k = 2$, which was obtained from Student's t-test values at a confidence level of 95% (Eq. (9.10)):

$$U = ku_c \tag{9.10}$$

9.3.5 Analysis of samples

Today, groundwater contamination with heavy metals is a major environmental problem as they are toxic even at low concentrations. U is a radioactive element that emits alpha particles, and when consumed in water even at low concentrations, its toxicity can be similar to that of As, Pb, or Hg. Previous studies have shown that U as well as As, Hg, and Pb have severe teratogenic effects [25–29]. The permitted levels of these concentrations in drinking water are strict, with WHO recommending 30 µg L^{-1} of U as a maximum allowed concentration level [11]. Natural U is a mix of three isotopes:

^{234}U, ^{235}U, and ^{238}U. The chemical behavior of these isotopes is similar, where any combination of these produces the same effects. However, each of these isotopes has different radioactive properties, which is why the percentage of these isotopes must be determined [30, 31].

The presence of As in water has been a problem for many countries such as India, Arabia, Egypt, Greece, Italy, Turkey, Indonesia, Nepal, Myanmar, Mexico, Pakistan, Vietnam, Cambodia, and China, where high concentration of this element in groundwater has been shown [32]. Moreover, it is estimated that 230 million people worldwide are exposed to concentrations of As by drinking water, and these levels of As exceed the permissible limit recommended by the WHO, which is 10 μg L^{-1} for water intended for human consumption. In comparison with As, Pb is considered by WHO as a cumulative element toxicant, which can affect different organs of the human body, including the nervous, digestive, circulatory, renal, endocrine, and osseous systems [27, 28]. On the other hand, Pb has been long used in plumbing and soldering materials in closed domestic water and sewer systems, making water the first exposure pathway in humans [33].

Cd intake is usually less than 2 μg day^{-1} [34, 35]. WHO has considered extremely low levels of Cd (0.003 mg L^{-1}) in order to avoid possible health effects due to accumulation especially in the kidney, liver, and bones. Long-term exposure to Cd could cause cancer as well as cardiovascular and renal diseases [36].

Zn is considered relatively non-toxic to humans. The human body contains anywhere from 2 to 3 g of Zn, and nearly 90% of it is found in muscles and bones, where its main function is the transport of protein (albumin, α-microglobulin, and transferrin). However, human health effects due to intake of Zn have not been reported [37]. On the other hand, Cu exposure from consuming drinking water with a high concentration of Cu could cause renal, cardiovascular, and neurological damage. Moreover, WHO has recommended a limit of <2 μg mL^{-1} for Cu in drinking water [11].

Drinking water samples were compared with IAEA drinking water and quality control (Figure 9.1). Results obtained from drinking water samples were good by both methods (Table 9.5). In order to analyze the levels of Cu and Zn, the samples A, B, and C were diluted 1:5. Table 9.6 shows the average of results obtained in drinking water from both methods, which show that the bottled water from A has lower in comparison with B and C, whereas there were no differences in the levels of Cd in any of the samples. Pb concentration was higher in sample A. In the case of U, the concentration levels in drinking water were higher in C samples. Moreover, according to the Mexican regulation of drinking water or EPA, all samples were within the allowable limits.

On the other hand, results obtained in RSD in the analysis of IAEA drinking water and quality control during the analysis sequence for both detection methods were <5%. Finally, it should be mentioned that ICP-MS is a good technique for measuring elements at ultra-trace levels in a few minutes, with excellent precision and accuracy in routine analysis.

Table 9.5: Results obtained from drinking water samples using ICP-QMS and ICP-SFMS.

Equipment	Sample	Month	As, μgL^{-1}	Cd, μgL^{-1}	Cu, mg L^{-1}	Pb, μg L^{-1}	Zn, mg L^{-1}	^{238}U, μg L^{-1}	^{Total}U, μg L^{-1}
ICP-QMS	A	January	1.299 ± 0.044	0.065 ± 0.018	0.099 ± 0.011	1.400 ± 0.035	0.299 ± 0.011	2.554 ± 0.040	2.559 ± 0.037
		February	1.402 ± 0.040	0.072 ± 0.012	0.102 ± 0.013	1.459 ± 0.048	0.202 ± 0.013	2.774 ± 0.015	2.780 ± 0.027
		March	1.621 ± 0.066	0.078 ± 0.014	0.081 ± 0.011	1.519 ± 0.026	0.281 ± 0.011	2.495 ± 0.021	2.500 ± 0.026
		April	1.709 ± 0.037	0.069 ± 0.012	0.101 ± 0.013	1.612 ± 0.032	0.201 ± 0.013	2.715 ± 0.019	2.721 ± 0.038
	B	January	2.110 ± 0.033	0.065 ± 0.016	0.191 ± 0.013	1.501 ± 0.045	0.501 ± 0.022	2.210 ± 0.028	2.125 ± 0.032
		February	2.345 ± 0.039	0.052 ± 0.013	0.115 ± 0.019	1.001 ± 0.031	0.469 ± 0.043	2.205 ± 0.030	2.210 ± 0.045
		March	2.001 ± 0.051	0.062 ± 0.017	0.101 ± 0.010	1.450 ± 0.041	0.555 ± 0.035	2.109 ± 0.034	2.113 ± 0.030
		April	2.981 ± 0.065	0.071 ± 0.015	0.100 ± 0.012	1.025 ± 0.029	0.635 ± 0.050	2.129 ± 0.035	2.133 ± 0.037
	C	January	3.901 ± 0.072	0.075 ± 0.010	0.122 ± 0.011	1.201 ± 0.034	0.499 ± 0.030	2.515 ± 0.020	2.520 ± 0.029
		February	3.701 ± 0.070	0.081 ± 0.015	0.134 ± 0.010	1.504 ± 0.043	0.487 ± 0.024	2.789 ± 0.028	2.794 ± 0.022
		March	4.029 ± 0.095	0.074 ± 0.013	0.153 ± 0.013	1.145 ± 0.037	0.511 ± 0.021	2.660 ± 0.035	2.665 ± 0.041
		April	3.601 ± 0.065	0.070 ± 0.011	0.101 ± 0.015	1.323 ± 0.030	0.490 ± 0.025	2.740 ± 0.038	2.746 ± 0.032
ICP-SFMS	A	January	1.305 ± 0.025	0.067 ± 0.005	0.101 ± 0.004	1.450 ± 0.025	0.300 ± 0.010	2.540 ± 0.023	2.545 ± 0.020
		February	1.398 ± 0.029	0.072 ± 0.009	0.101 ± 0.003	1.420 ± 0.020	0.201 ± 0.009	2.814 ± 0.020	2.820 ± 0.017
		March	1.629 ± 0.031	0.071 ± 0.005	0.080 ± 0.004	1.553 ± 0.025	0.279 ± 0.010	2.532 ± 0.028	2.537 ± 0.016
		April	1.700 ± 0.030	0.070 ± 0.005	0.102 ± 0.007	1.603 ± 0.012	0.202 ± 0.007	2.694 ± 0.014	2.700 ± 0.014
	B	January	2.010 ± 0.020	0.066 ± 0.009	0.194 ± 0.016	1.465 ± 0.022	0.510 ± 0.025	2.106 ± 0.024	2.110 ± 0.012
		February	2.355 ± 0.028	0.055 ± 0.010	0.111 ± 0.013	1.018 ± 0.014	0.475 ± 0.032	2.219 ± 0.022	2.224 ± 0.017
		March	2.019 ± 0.025	0.059 ± 0.008	0.102 ± 0.008	1.417 ± 0.020	0.545 ± 0.029	2.091 ± 0.035	2.095 ± 0.015
		April	2.990 ± 0.026	0.070 ± 0.004	0.099 ± 0.011	1.033 ± 0.022	0.630 ± 0.040	2.146 ± 0.025	2.151 ± 0.010
	C	January	3.895 ± 0.016	0.076 ± 0.007	0.119 ± 0.003	1.189 ± 0.019	0.500 ± 0.010	2.552 ± 0.017	2.557 ± 0.020
		February	3.701 ± 0.031	0.079 ± 0.010	0.135 ± 0.005	1.545 ± 0.017	0.489 ± 0.012	2.774 ± 0.029	2.780 ± 0.019
		March	4.020 ± 0.024	0.074 ± 0.011	0.154 ± 0.009	1.124 ± 0.021	0.507 ± 0.015	2.698 ± 0.035	2.704 ± 0.023
		April	3.609 ± 0.033	0.073 ± 0.012	0.102 ± 0.007	1.313 ± 0.024	0.495 ± 0.017	2.715 ± 0.019	2.721 ± 0.027

Table 9.6: Average of the sum of all data obtained by ICP-QMS and ICP-SFMS.

Sample	**As (μg L^{-1})**	**Cd (μg L^{-1})**	**Cu (mg L^{-1})**	**Pb (μg L^{-1})**	**Zn (mg L^{-1})**	**^{238}U (μg L^{-1})**	**^{Total}U (μg L^{-1})**
A	1.638 ± 1.009	0.071 ± 0.004	0.187 ± 0.243	1.519 ± 0.085	0.246 ± 0.139	2.590 ± 0.127	2.595 ± 0.128
B	2.587 ± 0.658	0.064 ± 0.008	0.127 ± 0.041	1.204 ± 0.218	0.540 ± 0.064	2.208 ± 0.147	2.201 ± 0.151
C	3.241 ± 1.111	0.073 ± 0.005	0.128 ± 0.204	1.334 ± 0.154	0.497 ± 0.009	2.665 ± 0.104	2.670 ± 0.104

9.4 Conclusions

Method optimization in ICP-SFMS had the advantage of guaranteeing the equipment's stability and calibration throughout the analysis, as well as high capacity to solve interferences. Moreover, an easy, quick, and reliable method of analyzing water samples was used and the results were obtained in a few minutes, with good accuracy, precision, and low LODs and LOQs compared to those obtained by ICP-QMS. Additionally, the development of these detection methods has allowed evaluating the concentrations of As, Cd, Cu, Pb, Zn, and U in commercial bottled water from main brands in Mexico.

Acknowledgments: We are grateful to the CONACYT. Project No. 232762: National Laboratory of Nuclear Forensic) and Project No. 279860: National Laboratory of Science, Technology and Integration Management of Water.
Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.
Research funding: None declared.
Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Rashid H, Manzoor MM, Mukhtar S. Urbanization and its effects on water resources: an exploratory analysis. Asian J Water Environ Pollut 2018;15:67–74.
2. Chai Q, Gan Y, Zhao C, Xu HL, Waskom RM, Niu Y, et al. Regulated deficit irrigation for crop production under drought stress: a review. Agron Sustain Dev 2016;36:3.
3. Chowdhary P, Bharagava RN, Mishra S, Khan N. Role of industries in water scarcity and its adverse effects on environment and human health. Environ Concerns Sustain Dev 2020;12:235–56.
4. Li H, Smith CD, Cohen A, Wang L, Li Z, Zhang X, et al. Implementation of water safety plans in China: 2004–2018. Int J Hyg Environ Health 2020;223:106–15.
5. Howard G, Bartram J, Williams A, OverboGeere J-A. Domestic water quantity, service level and health, 2nd ed. Geneva: World Health Organization; 2020. Available from: https://apps.who.int/iris/bitstream/handle/10665/338044/9789240015241-eng.pdf [Accessed Jan 2021].
6. Prüss-Ustün A, Wolf J, Bartram J, Clasen T, Cumming O, Freeman MC, et al. Burden of disease from inadequate water, sanitation and hygiene for selected adverse health outcomes: an updated analysis with a focus on low-and middle-income countries. Int J Hyg Environ Health 2019;222:765–77.
7. WWAP (United Nations World Water Assessment Programme). The United Nations World Water Development Report 2014: water and energy. Paris: UNESCO. Available from: https://sustainabledevelopment.un.org/content/documents/1714Water%20Development%20Report%202014.pdf [Accessed Jan 2021].
8. Bajwa BS, Kumar S, Singh S, Sahoo SK, Tripathi RM. Uranium and other heavy toxic elements distribution in the drinking water samples of SW-Punjab, India. J Radiat Res Appl Sci 2017;10:13–19.

9. Romero-Guzmán ET, Hernández-Mendoza H, Reyes-Gutierrez LR, Ríos-Lugo MJ, Hernández-Santana J. Radionuclide determination in surface water samples by inductively coupled plasma with sector field mass spectrometry (ICP-SFMS). J Nucl Phy Mat Sci Rad A 2016;4:159–66.
10. Mendoza-Cano O, Sánchez-Piña RA, Barrón-Quintana J, Cuevas-Arellano HB, Escalante-Minakata P, Solano-Barajas R. Riesgos potenciales de salud por consumo de agua con arsénico en Colima, México. Salud Publica Mex 2017;59:34–40.
11. WHO (World Health Organization). A global overview of national regulations and standards for drinking-water quality; 2018. Available from: https://apps.who.int/iris/bitstream/handle/10665/272345/9789241513760-eng.pdf [Accessed Jan 2021].
12. USEPA (United States Environmental Protection Agency). National primary drinking water regulations; 2020. Available from: https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations [Accessed Oct 2020, Jan 2021].
13. Norma Oficial Mexicana NOM-127-SSA1-1994. Salud ambiental, agua para uso y consumo humano-límites permisibles de calidad y tratamientos a que debe someterse el agua para su potabilización. Norma Oficial Mexicana; 1994. México. Available from: http://www.salud.gob.mx/unidades/cdi/nom/127ssa14.html [Accessed Oct 2020, Jan 2021].
14. Mohammed H, Sadeek S, Mahmoud AR, Zaky D. Comparison of AAS, EDXRF, ICP-MS and INAA performance for determination of selected heavy metals in HFO ashes. Microchem J 2016;128:1–6.
15. Zhuravlev A, Zacharia A, Arabadzhi M, Turetta C, Cozzi G, Barbante C. Comparison of analytical methods: ICP-QMS, ICP-SFMS and FF-ET-AAS for the determination of V, Mn, Ni, Cu, As, Sr, Mo, Cd and Pb in ground natural waters. Int J Environ Anal Chem 2016;96:332–52.
16. Bäuchle M, Lüdecke T, Rabieh S, Calnek K, Bromage TG. Quantification of 71 detected elements from Li to U for aqueous samples by simultaneous-inductively coupled plasma-mass spectrometry. RSC Adv 2018;8:37008–20.
17. Xiong Q, Lin Y, Wu W, Hu J, Li Y, Xu K, et al. Chemometric intraregional discrimination of Chinese liquors based on multi-element determination by ICP-MS and ICP-OES. Appl Spectrosc Rev 2020; 2020:1–13.
18. Diez-Fernandez S, Isnard H, Nonell A, Bresson C, Chartier F. Radionuclide analysis using collision–reaction cell ICP-MS technology: a review. J Anal Atomic Spectrom 2020;35:2793–819.
19. Narukawa T, Shikino O, Chiba K. Application of neon to collision gas-Cell gas index for collision/reaction cell-ICP-MS determination. J Anal Atomic Spectrom 2020;35:2142–47.
20. Theiner S, Loehr K, Koellensperger G, Mueller L, Jakubowski N. Single-cell analysis by use of ICP-MS. J Anal Atomic Spectrom 2020;35:1784–813.
21. Zhuravlev A, Zacharia A, Arabadzhi M, Turetta C, Cozzi G, Barbante C. Comparison of analytical methods: ICP-QMS, ICP-SFMS and FF-ET-AAS for the determination of V, Mn, Ni, Cu, As, Sr, Mo, Cd and Pb in ground natural waters. Int J Environ Anal Chem 2016;96:332–52.
22. Croudace IW, Russell BC, Warwick PW. Plasma source mass spectrometry for radioactive waste characterisation in support of nuclear decommissioning: a review. J Anal Atomic Spectrom 2017; 32:494–526.
23. Evans EH, Pisonero J, Smith CM, Taylor RN. Atomic spectrometry update: review of advances in atomic spectrometry and related techniques. J Anal Atomic Spectrom 2020;35:830–51.
24. Ellison SLR, Williams A, editors. EURACHEM/CITAC Eurachem/CITAC guide: quantifying uncertainty in analytical measurement, 3rd ed. UK: National Measurement System; 2012. Available from: https://www.eurachem.org/images/stories/Guides/pdf/QUAM2012_P1.pdf [Accessed Oct 2020].
25. Yang L, Zhang Y, Wang F, Luo Z, Guo S, Strähle U. Toxicity of mercury: molecular evidence. Chemosphere 2020;245:125586.
26. Demir N, Başaranoğlu M, Huyut Z, Değer İ, Karaman K, Şekeroğlu MR, et al. The relationship between mother and infant plasma trace element and heavy metal levels and the risk of neural tube defect in infants. J Matern Fetal Neonatal Med 2019;32:1433–40.

27. Yıldırım E, Derici MK, Demir E, Apaydın H, Koçak Ö, Kan Ö, et al. Is the concentration of cadmium, lead, mercury, and selenium related to preterm birth? Biol Trace Elem Res 2019;191:306–12.
28. Flora SJ, Agrawal S. Arsenic, cadmium, and lead. Reproductive and developmental toxicology. U.S: Academic Press; 2017, 31:537–66 pp.
29. Wang S, Ran Y, Lu B, Li J, Kuang H, Gong L, et al. A review of uranium-induced reproductive toxicity. Biol Trace Elem Res 2020;196:204–13.
30. Ma M, Wang R, Xu L, Xu M, Liu S. Emerging health risks and underlying toxicological mechanisms of uranium contamination: lessons from the past two decades. Environ Int 2020;145:106107.
31. Shakia F, Zamanib E, Arjmandc A, Pourahmadc J. A review on toxicodynamics of depleted uranium. Iran J Pharm Sci 2019;18:90–100.
32. Shaji E, Santosh M, Sarath KV, Prakash P, Deepchand V, Divya BV. Arsenic contamination of groundwater: a global synopsis with focus on the Indian Peninsula. Geosci Front 2020;12:101079.
33. Ayuso RA, Foley NK. Surface topography, mineralogy, and Pb isotope survey of wheel weights and solder: source of metal contaminants of roadways and water systems. J Geochem Explor 2020;212: 106493.
34. Burke F, Hamza S, Naseem S, Nawaz-ul-Huda S, Azam M, Khan I. Impact of cadmium polluted groundwater on human health: winder, balochistan. Sage Open 2016;6:2158244016634409. https://doi.org/10.1177/2158244016634409.
35. Karaouzas I, Kapetanaki N, Mentzafou A, Kanellopoulos TD, Skoulikidis N. Heavy metal contamination status in Greek surface waters: a review with application and evaluation of pollution indices. Chemosphere 2021;263:128192.
36. Genchi G, Sinicropi MS, Lauria G, Carocci A, Catalano A. The effects of cadmium toxicity. Int J Environ Res Publ Health 2020;17:3782.
37. Plum LM, Rink L, Haase H. The essential toxin: impact of zinc on human health. Int J Environ Res Publ Health 2010;7:1342–65.

Lawrence Olusegun Ajala*, Ewa Ezeali Ali,
Emmanuel Okewe Nnachi and Valentine Ifenna Onwukeme

10 Design of locally sourced activated charcoal filter from maize cob for wastewater decontamination: an approach to fight waste with waste

Abstract: This research studied decontamination of laboratory wastewater with an activated carbon derived from maize cob, an agricultural waste to ascertaining its adsorption effectiveness for water treatment. The preparation conditions such as the concentration of the activating agent, impregnation ratio, impregnation temperature, impregnation time, activation temperature and activation time were optimized. The adsorbent's porous properties revealed its adsorption potency was correlated with the iodine value. The test adsorbent showed significant contaminants adsorption in the laboratory wastewater; the results obtained were within the standards for drinking water set by the regulatory agencies. This agricultural waste could be considered for the preparation of activated carbon which would ultimately serve as an alternative method of decontaminating laboratory wastewater.

Keywords: activated carbon, adsorbent, agricultural waste, laboratory wastewater, maize cob, water treatment

10.1 Introduction

Laboratory wastewaters are characterized with high concentrations of organic and inorganic pollutants that render them unfit for further uses. Large volumes of wastewaters from laboratories are discharged into the environment, which may cause pollution of surface and ground waters. The search for solutions to recycle laboratory wastewater is becoming urgent to avert wastewater pollution and to avoid water scarcity.

***Corresponding author: Lawrence Olusegun Ajala**, Department of Science Laboratory Technology, Akanu Ibiam Federal Polytechnic, Unwana, Nigeria, E-mail: loajala@akanuibiampoly.edu.ng. https://orcid.org/0000-0002-7969-6316

Ewa Ezeali Ali and Emmanuel Okewe Nnachi, Department of Science Laboratory Technology, Akanu Ibiam Federal Polytechnic, Unwana, Nigeria

Valentine Ifenna Onwukeme, Department of Chemistry, Nnamdi Azikiwe University Faculty of Natural Sciences, Awka, Nigeria

This article has previously been published in the journal Physical Sciences Reviews. Please cite as: L. O. Ajala, E. E. Ali, E. O. Nnachi and V. I. Onwukeme "Design of locally sourced activated charcoal filter from maize cob for wastewater decontamination: an approach to fight waste with waste" *Physical Sciences Reviews* [Online] 2021, 7. DOI: 10.1515/psr-2020-0096 | https://doi.org/10.1515/9783110726145-010

To overcome this challenge, various methods of water purifications such as electro-coagulation distillation, filtration, deionization and flocculation [1, 2] had been applied to decontaminate wastewaters for reuse. However, such treatment methods are faced with one or other drawbacks such as energy, time and labour intensive, expensive to maintain, not environmentally friendly, reintroduction of extracted contaminants as in the case of distillation, filters in filtration unable to remove dissolved material, microbial growth and release of particulates can be a haven from ion exchange beds used in deionization, inability of electro-deionization to remove organics, particles, pyrogens or bacteria and inability of ultraviolet oxidation to remove ions, colloids or particulates [3]. Lately, adsorption of pollutants in wastewater over activated carbons has proved to be efficient and adequate in the treatment of wastewaters [3–6]. This purification technique is becoming acceptable as a result of its versatility, environmental compatibility, relative abundance and low-cost starting materials (sometimes wastes), adsorption of a broad range of pollutants, fast adsorption kinetics and ease of production [7, 8]. This encompassing technique has been successfully used in effluent treatment [9, 10], water purification [11–14], pesticide adsorbent from wastewater [15] and heavy metal sorption from aqueous media [11, 16–19]. Activated carbons are also applicable for the removal of poisons [20] and prevention against novel Coronavirus (SARS-CoV-2) [8].

Commercial activated carbons are expensive due to the use of non-renewable and relatively high-cost starting materials such as coal, which is unjustifiable in pollution control measures [21]. In a country where economy plays a very big role, it is better to find relatively low-cost adsorbent for purification of laboratory water. Recently, researchers have tried to produce activated charcoals using renewable, readily available and cheaper precursors which are mainly industrial and agricultural waste products such as bagasse [22], groundnut shell [21], rice husk [14, 22, 23], sawdust [13, 24, 25], coconut shell [26], empty palm fruit bunch [27], physic nut waste [17], pruning mulberry shoot [2], bamboo [11], chickpea [18], acorn shell [28] and plant seeds [12, 16]. However, despite extensive scientific researches on the treatment of wastewaters with activated carbons, to date, no significant study has been conducted on the treatment of laboratory wastewater with maize cob activated carbon, hence, this study.

Maize cob is a waste that is largely generated after which the edible seeds had been removed. These waste products are usually burnt in an open air causing environmental pollution. Conversion of this cheap and abundant agricultural waste into activated charcoal will serve many purposes: firstly, unwanted agricultural waste is converted into a useful and value-added product; it will contribute to solving part of the laboratory water treatment problems; and helps in management of solid waste, thereby enhancing the aesthetic conditions of the environment.

10.2 Experimental details

10.2.1 Sample collection and treatment

Maize cob was collected from a processing plant at Abakaliki, Nigeria. This was transported to the research laboratory of Akanu Ibiam Federal Polytechnic, Unwana, Nigeria. Extraneous materials were removed and were repeatedly washed with deionised water to remove other impurities and then, sun-dried. The dried sample was pulverised and stored in an air-tight container for further analyses. The wastewater generated from the chemistry laboratory of the above institution was used for adsorption studies. Commercial activated carbon (calgon carbon, F-300) used as control and other chemicals were of analytical grades and were sourced from BDH Chemicals Limited, UK.

10.2.2 Carbonization, activation and optimisation

Preparation of the activated carbon was similar to as stated in our previous research [6]. Briefly, the raw material was fed into the reactor of a locally fabricated pyrolysis plant and carbonized at 400 °C for 1 h. After carbonization, it was removed, allowed to cool and pulverized. A portion of the char produced, maize cob carbon (MCC) was impregnated with zinc chloride of varying concentrations (0.5, 1.0, 1.5, 2.0, 2.5) mol dm^{-3} at 1:1, 1:2, 1:3, 2:1, 3:1 w/v precursor: $ZnCl_2$ ratios overnight at impregnation temperatures of 20, 40, 60, 80, 100 °C. The slurries formed were carbonised in a murfle furnace (Fisher-Thermo Scientific, USA) at varying temperatures (250, 350, 450, 550, 650) °C for 1.0, 1.5, 2.0, 2.5, 3.0 h after which they were removed and cooled in ice water bath. Excess water was drained out and allowed to stand at room temperature. The residual activating reagent ($ZnCl_2$) and surface ash were removed from the carbonized products with 0.10 mol dm^{-3} hydrochloric acid. They were further washed and rinsed with double-distilled deionized water to remove residual acid until pH ~7 was achieved. They were oven-dried (Gallenkamp, US) at 110 °C until constant weights were attained. The individual weight of maize cob activated charcoal (MAC) produced was taken and the yield calculated. Adsorption on iodine of the various activated carbons with respect to activation concentration, impregnation ratio, impregnation temperature, impregnation time, carbonization temperature and carbonization time was investigated to determine the optimum conditions for the preparation of MAC.

10.2.3 Physical and chemical characterization

The MCC and MAC were subjected to the appropriate physicochemical analyses. Carbon yields of MCC and MAC were calculated from the sample weights before and after activation to their initial weights. Bulk density, fixed carbon, volatile matter, ash and moisture contents were determined according to established methods [22]. Iodine value was determined according to the ASTM method [29]. Porous properties (surface area, porosity, pore size and pore volume) were estimated as outlined [22]. Surface morphologies and elemental compositions were examined with the aid of scanning electron microscope (Phenom ProX, Thermo Scientific) coupled with energy dispersive X-ray spectrometer (ED-XRS). The variations in the absorption bands of functional groups before and after the activation were studied with Fourier transform infra-red spectrometer (Carg 630, Agilent) in the range of 4000–400 cm^{-1}.

10.2.4 Fixed bed adsorption studies

The maize cob-based activated charcoal (MAC) prepared and the commercial activated carbon (CAC) were parked separately into different columns with two open ends. One end of the columns was closed with glass wool to prevent the adsorbents from flowing out. The columns were mounted vertically with the open ends upward. Through the open ends of the columns, the laboratory wastewater collected was poured through the columns already packed with the adsorbents. The filtrates were collected separately for physicochemical assay.

10.2.5 Physicochemical properties of untreated and treated wastewater

Physicochemical properties (pH, temperature, colour, odour, total suspended solids and total dissolved solids, alkalinity, hardness, chemical oxygen demand, biochemical oxygen demand, turbidity, conductivity, chloride, nitrate, phosphate, sulphate and heavy metal ions) that are essential to determine the quality of water in the untreated water, filtrate from the commercial activated carbon (FCAC) and filtrate from the maize cob-based activated carbon (FMAC) were determined following standard method [30].

10.2.6 Analytical method control

Appropriate parallel quality control and assurance measures were carried out. All chemicals used were checked for possible trace metal contamination. Double-distilled deionized water was employed for the preparation of all requisite solutions. Samples were carefully handled to avoid cross contamination. All glassware used for analyses were previously soaked in 10% nitric acid (v/v) for 24 h, washed with detergent, rinsed with double-distilled deionised water and dried in a clean laboratory oven. Standard solutions of all the heavy metals in the filtrates were prepared in five different concentrations to obtain respective calibration curves. Blanks were prepared and similarly treated as samples to give room for blank correction. Blanks and standard solutions were co-analysed with the analytical samples. Linear ranges were obtained for the target ions with good correlation coefficients ($R^2 \geq 0.9995$). The limits of detection of the elements analysed were determined and were found to be Cd^{2+} (0.003), Ni^{2+} (0.008), Pb^{2+} (0.005), Mn^{2+} (0.020), Fe^{2+} (0.015), Zn^{2+} (0.025), Cu^{2+} (0.010), Cr^{3+} (0.030) and As^{3+} (0.001) mg dm^{-3}. Recovery tests were also performed by spiking a known concentration of the analyte to the samples and results were in the range of 95–101%. The precision (relative standard deviation) of 10 replicate determinations of the target ions were calculated; this ranged from 1.20 to 3.20%.

10.2.7 Statistical and chemometric analyses

Three independent determinations were performed on each filtrate and the untreated water. Data were recorded as mean ± standard deviation of the replicate values. A one-way analysis of variance (ANOVA) was used to analyse the difference between experimental groups. Means were compared by the Duncan' multiple range test and significance was established at $p = 0.05$ using SPSS for Windows 2008 (version 15.0). Principal component analysis (PCA) was employed to express differences among the treated and untreated water samples. Inter-correlation of physicochemical properties of the water samples was studied with agglomerative hierarchical clustering tools.

10.3 Results and discussion

10.3.1 Optimization studies

10.3.1.1 Effect of concentration of activating agent

The iodine adsorption capacity of HAC was carried with various concentrations of $ZnCl_2$ solution prior to activation. The optimum value (930 mg g^{-1}) of iodine adsorption of the test adsorbent was reached at a corresponding concentration of 1.00 mol dm^{-3} (Figure 10.1a). At this concentration, a higher reaction could have occurred leading to the release of more volatiles with the resultant affinity for more iodine molecules [18, 28]. Before the optimum value, the iodine number was lowered. This could be due to insufficient activating agent to create more internal pore structures in the precursor. Further increase in the concentration of $ZnCl_2$ led to a progressive decrease in iodine adsorption capacity. This could be attributed to the collapse of micro-porous structures of the carbon as a result of excessive activation [16].

10.3.1.2 Effect of impregnation ratio

The variation in iodine value of the activated charcoal under test versus the impregnation ratio is shown in Figure 10.1b. At a constant precursor weight, there was an increase

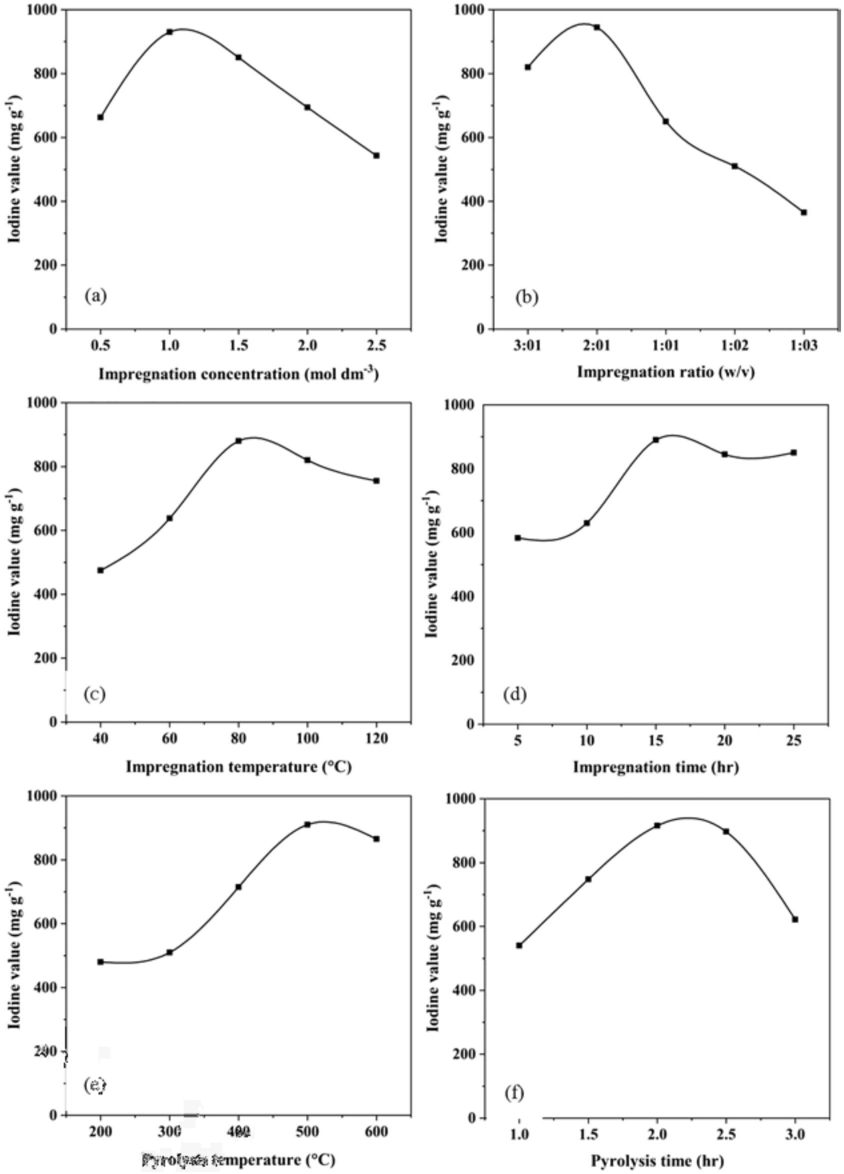


Figure 10.1: Effect of (a) impregnation concentration (b) impregnation ratio (c) impregnation temperature (d) impregnation time (e) activation temperature (f) activation time on the iodine adsorption capacity of maize cob activated carbon.

in the iodine values with concomitant increase in the volume of the activator until an optimum value was reach at the ratio of 2:1 (activator:precursor). The increase in iodine number could be linked to the reaction facilitating the release of volatiles in the carbon while creating porous structures [16, 28] in the adsorbent. Thereafter, the iodine value sharply dropped as the weight of the precursor increased. This could be credited to an insufficient activator to react with the precursor.

10.3.1.3 Effect of impregnation temperature

The impregnation temperature is known to influence the pore structure of activated charcoal with respect to adsorption capacity [2]. The iodine values increased gradually with the temperature of impregnation. Equilibrium was attained when the temperature was extended to 80 °C (Figure 10.1c). As the temperature was increased beyond the critical value, iodine number was observed to decrease gradually. This could be as a result of expansion of micro-pores and collapse of pore walls leading to the release of more volatile components [16].

10.3.1.4 Effect of impregnation time

Iodine adsorption efficiency of MAC increased with a corresponding increase in the impregnation time until equilibrium was attained at 15 h (Figure 10.1d). At this time, the porous pores might have been saturated with the activating agent [24]. When the impregnation time was extended beyond the critical time, there was no significant change in the iodine adsorption capacity of the test adsorbent, indicating that there were no more porous networks for diffusion of the activating agent to occupy.

10.3.1.5 Effect of activation temperature

The iodine value increased progressively with an increase in the activation temperature, and then decreased as the temperature exceeded 550 °C (Figure 10.1e). Increase in temperature promoted chemical changes that might have occurred in the precursor, resulting to the formation of more pores ready for adsorption at lower temperature. As the critical value was exceeded, there was a decrease in iodine value, which could be attributed to the excessive carbon burnt-off to form ash at higher temperature resulting to the widening of pore diameters and collapse of pore walls [16, 25, 28].

10.3.1.6 Effect of activation time

Adsorption efficiency increased with a corresponding increase in the activation time before equilibrium was attained (Figure 10.1f). As the pyrolysis time increases, there seemed to be opening of pore walls for adsorption. The rate of iodine adsorption increased until optimum time of 2 h was reached, and then started decreasing when the activation time was extended to 2.5 h. This could be connected with collapse of surface areas available for adsorption at longer time [28].

Table 10.1: Results of characterization of maize cob charcoal (MCC) and maize cob-based activated carbon (MAC).

Property	MCC	MAC
Yield (%)	82.26 ± 2.15	71.13 ± 1.38
Volatile matter	13.21 ± 0.23	14.08 ± 0.28
Fixed carbon	67.40 ± 0,75	56.74 ± 0.17
Ash content (%)	10.42 ± 0.16	3.27 ± 0.09
Moisture content (%)	4.66 ± 0.43	2.89 ± 0.33
Bulk density (g cm^{-3})	0.70 ± 0.05	0.46 ± 0.03
Iodine number (mg g^{-1})	451 ± 4.07	989 ± 2.17
Surface area (m^2 g^{-1})	432 ± 1.06	759 ± 1.38
Pore volume (cm^3 g^{-1})	0.23 ± 0.05	0.68 ± 0.07
Pore size (nm)	1.63 ± 0.01	0.81 ± 0.00
Porosity (cm^3 g^{-1})	0.20 ± 0.02	0.22 ± 0.01
Carbon (wt %)	20.90 ± 0.47	9.51 ± 0.25
Potassium (wt %)	6.52 ± 0.91	2.05 ± 0.02
Nitrogen (wt %)	0.35 ± 0.14	0.14 ± 0.04
Oxygen (wt %)	1.88 ± 0.21	1.07 ± 0.06
Sulphur (wt %)	2.96 ± 0.03	1.43 ± 0.05
Zinc (wt %)	0.00 ± 0.00	14.42 ± 0.48
Chlorine (wt %)	2.53 ± 0.09	3.34 ± 0.03
Calcium (wt %)	3.78 ± 0.07	1.92 ± 0.01
Silicon (wt %)	4.08 ± 0.16	4.98 ± 0.33
Phosphorus (wt %)	10.43 ± 0.50	5.83 ± 0.02
Magnesium (wt %)	2.69 ± 0.01	1.66 ± 0.02
Iron (wt %)	1.62 ± 0.04	0.00 ± 0.00
Aluminium (wt %)	2.17 ± 0.08	1.89 ± 0.03
Sodium (wt %)	0.86 ± 0.00	4.58 ± 0.05
Silver (wt %)	1.58 ± 0.10	0.95 ± 0.02
Titanium (wt %)	0.91 ± 0.06	1.38 ± 0.01

10.3.2 Characterization of adsorbent

10.3.2.1 Physicochemical properties of MCC and MAC

The physical and chemical properties of MCC and MAC were compared in Table 10.1. The lower yield of MAC compared to MCC could be as a result of carbonization and activation at higher temperature, hence more volatiles were released and more carbon was burnt-off which was converted into ash. This could have led to a corresponding increase in porosity and surface area [31]. High density carbons had been adjudged to be highly effective for water treatment [12] as it helps to improve the filtration rate by forming an even cake on the filter surface [17]. The bulk density of MAC was lower than 0.59 g cm^{-3} reported for groundnut shell activated carbon [26].

Researchers had reported that the lower the moisture of an adsorbent, the more the adsorption efficacy [17, 32]. The moisture content was reduced after the char was activated, suggesting that the carbon networks had become more porous [27]. Moisture content was better than 8.96% reported for *Borassus aethiopum* shells [5] but less superior to 0.5% reported for coconut shell activated carbon [26]. Ash is an indication of inorganic constituent; therefore carbon with low ash (higher proportion of carbon) could be used effectively to remove inorganic contaminants in wastewater [5, 12, 27]. Ash content of MAC in this study was less effective than 1.9 and 1.88% found in bagasse activated carbon [22] and coconut shell activated carbon [26], respectively but was better than 4.01% reported for *B. aethiopum* shells activated carbon [5].

The volatile matter of MCC was lower than that of MAC while fixed carbon was greater. This is expected because carbonization temperature promoted the release of volatiles from breaking of bonds in organic matrices [27]. MAC had high fixed carbon and low ash content which are the factors that substantiated its utilisation in production of high performance activated charcoal [17].

Activated carbon functions by the adhesion of substances to the walls of the pores. The greater the available surface area, the better the adsorption efficiency [23]. The surface area of MAC was far greater than that of MCC and fell within the range of 500–1500 $m^2\ g^{-1}$ specification of activated carbon approved for water purification [8, 33]. The activating agent could have caused swelling of the molecular structure of the precursor cellulose resulting in the breaking of bonds during activation and carbonization [28], with an improved surface area. The value reported in this study was within the range of 718–1018 $m^2\ g^{-1}$ for water treatment carbons determined in some local materials [9] and in consonant with 923 and 927 $m^2\ g^{-1}$ determined in activated carbons produced from bagasse and rice husk, respectively [22]. The value was higher than 791.56 $m^2\ g^{-1}$ determined in granulated activated carbons [34] and 435.10 $m^2\ g^{-1}$ in coconut shell activated carbon [26].

Furthermore, the pore volume and pore size showed that MAC exhibited type I adsorption isotherm according to IUPAC classification [8, 27, 35], indicating the formation of micro-porous carbon with higher porosity. The pore volume as observed in the MAC was higher compared to 0.53 and 0.56 $cm^3\ g^{-1}$ determined respectively, in bagasse and rice husk activated carbons [22] while the pore size was consistent with 0.80 nm found in both the bagasse and rice husk activated carbons [22]. MAC porosity agreed well with 0.21 $cm^3\ g^{-1}$ obtained for bamboo activated carbon [36].

The iodine number is an indication of the available surfaces for adsorption in an adsorbent [28]. A carbon with higher iodine number has a better adsorption capacity [26]. The iodine number in this study was in agreement with 942 $mg\ g^{-1}$ in coconut shell activated carbon [26] and within the range of 828.39–995.38 $mg\ g^{-1}$ determined in activated carbons produced from some local raw materials [9]. Iodine value of MAC denotes that it had excellent adsorptive properties, which can be used for adsorption of organic and heavy metal pollutants [17].

Elemental compositions of the MAC revealed that the carbon content was smaller compared to the MCC. The decrease in the content is expected since carbon was decomposed by $ZnCl_2$ [16] to form ash. Other principal elements present at the surface were silicon, phosphorus, sodium, chlorine and potassium with their atomic concentrations decreasing after activation (Table 10.1). The consequence of the presence of these elements in high proportion is that the MAC may not be employed in the adsorption of their metal ions [17]. However, there was an increase in the atomic concentration of zinc and chlorine after the activation. This is expected since zinc chloride was used as activating agent which was difficult to wash out completely after the activation and carbonization.

10.3.2.2 Infra-red spectroscopy

The adsorption capacity of an activated carbon depends largely on several factors in which the chemical reactivity of the functional groups at the surface is the main [31]. Therefore, the knowledge of surface functional groups helps to elucidate the adsorption efficacy of an activated carbon [28, 31]. The FT-IR spectra of un-activated and activated carbons were recorded and their respective IR absorption frequencies and shown in Figure 2. There were noticeable differences in the absorption bands before and after the activation. The activated product showed an increase in the percentage transmittance of all the peaks compared to the un-activated product. This is an indication of a decrease in absorbance which may be due to the formation of more volatile compounds. The absorption peaks at 3272.6, 1438.8 and 1364.2 cm^{-1} assigned to the O–H stretching vibration [31], methylene group (C–H) symmetric stretch [31] and aromatic groups stretching vibration [37], respectively in the MCC were completely absent in MAC.

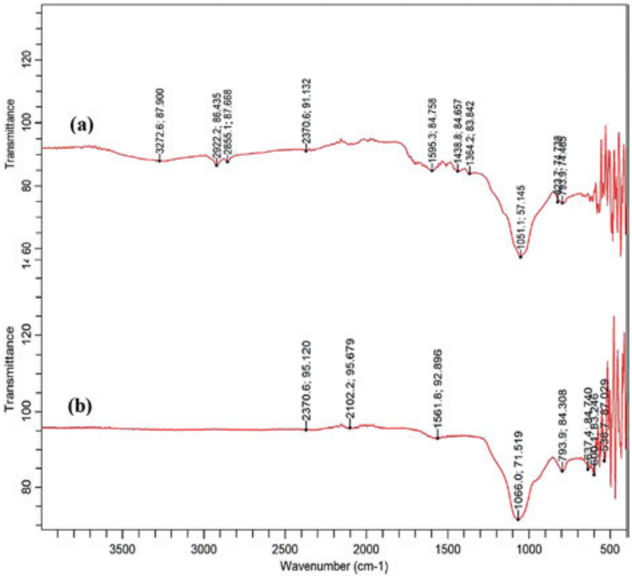


Figure 10.2: IR spectra of (a) un-activated maize cob carbon (b) activated maize cob carbon.

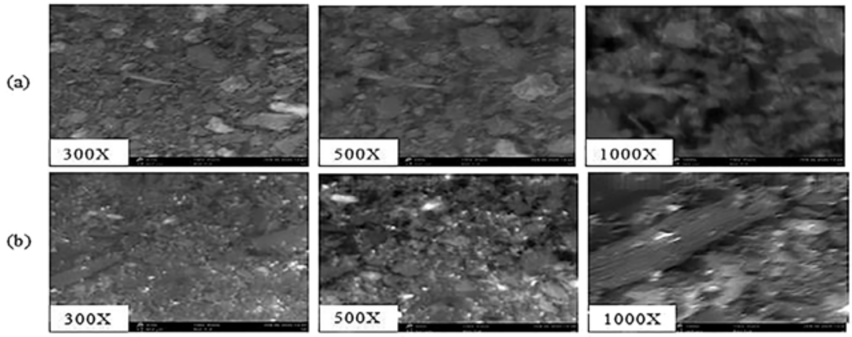


Figure 10.3: Micrographs of (a) un-activated maize cob carbon and (b) activated maize cob carbon at 300×, 500× and 1000× magnifications.

In addition, peaks at 2922.2 and 2855.1 cm^{-1} attributed to the C–H symmetric and asymmetric vibration of the aliphatic CH_2, respectively were absent in the MAC. The absence of these bands could be due to activation at higher temperature. The bands at 2370.6 cm^{-1} corresponding to stretching vibration of the C–O group for CO/CO_2 and 793.9 cm^{-1} were visible in both products, indicating that activation had negligible effect on these functional groups. It was observed that the original peak at 1595.3 cm^{-1} attributed to the ring vibration common with aromatic skeletons found in carbonaceous materials [28] slight shifted to 1561.8 cm^{-1} in the MAC. After the chemical modification, the strong and broad peak at 1051.1 cm^{-1} attributed to the asymmetric stretching of the Si–O bond [38] substantially shifted by 15 units. The shift in some absorption frequency bands and disappearances of many peaks in the MAC compared to the MCC proved that chemical modification occurred during the activation process.

10.3.2.3 Scanning electron microscopy

Surface morphologies of un-activated and activated carbons are presented in the SEM micrographs (Figure 10.3). The external surface of the MAC (Figure 10.3b) was filled with cavities of irregular sizes compared to the MCC (Figure 10.3a). The surface of the MCC was observed to be relatively organized without pores. Activation and carbonization at higher temperature produced activated carbon with uneven surface (Figure 10.3b). There existed many clear visible advanced networks within the microstructure, due to this, MAC possessed higher surface area [31]. Also, there were numerous pits distributed over the surface of the MAC signifying that activation had occurred. Activation is known to produce pores within the structure due to the release of volatiles [31]. The white spheres observed in the micrograph of the MAC could be due to the presence of Zn^{2+} which was difficult to wash out completely. The presence of rough and micro-porous structure which may offer more adsorption sites proved that MAC was chemically modified.

10.3.3 Properties of wastewater treated with CAC and MAC

10.3.3.1 Physicochemical properties

The results as presented in Table 10.2 showed the physicochemical properties of untreated wastewater, wastewaters treated with the CAC and MAC. The initial pale yellow and offensive odour of the untreated water was removed similar to a study elsewhere [36]. MAC balanced the pH of the wastewater to reasonable degree after the treatment; and the value was within the approved standards [39–41], thus indicating improvement in the water quality. Similar reports of pH adjustment in contaminated water with activated carbons had been documented [36, 34]. There were no significant differences ($p=0.05$) in the temperature before and after the adsorption process. The entire results (Table 10.2) fell within the minimum and maximum permissible limit [39].

Total dissolved solids (TDS) measure the amount of dissolved materials in a water sample. TDS in the wastewater was reduced to 65.0% after treatment with MAC but the efficiency was lower than 70.5% achieved by the CAC. However, it was more effective than activated carbon from bamboo [36], where only 24.3% dissolved solids were removed. High total suspended solids (TSS) in a water sample signify the presence of impurities, high BOD and NO_3^- due to the microbial oxidation of the suspended organics [42]. MAC adsorbed more suspended solids from the wastewater compared to the CAC but less effective compared to the adsorbent prepared elsewhere [34].

The values reported in this research for alkalinity in the untreated and treated water were higher than the recommended value of 100 mg dm^{-3} [39, 40]. However, alkalinity is not considered detrimental to humans but is generally associated with high pH values and hardness [42]. There were no significant differences ($p=0.05$) in the hardness values obtained in FCAC and FMAC but statistically differ with the value obtained in untreated wastewater (Table 10.2). Hard water considered as innocuous but may form scale in water heaters, pipes, boilers and cooking utensils [42].

Turbidity is a measure of water quality with respect to colloidal and residual suspended matter [34]. Low level of turbidity signifies appreciable purity [42]. MAC was very effective in reducing the turbidity reading by 70.0% as compared to 64.0% by the CAC. Turbidity was reduced to approximately 32.0% in untreated water using MAC which was at consonant to 31.1% turbidity left in well water treated with granulated activated carbon [34]. Yet, the test adsorbent was less effective compared to activated carbon prepared from waste bamboo [36], where 100.0% removal of turbidity was achieved. Conductivity is directly related to mineral contents of a water sample [42]. The MAC-treated water had lower conductivity measurement compared to untreated water (Table 10.2). This suggests that MAC had significant adsorption efficacies on the dissolved ions in the wastewater. Results obtained from FMAC and FCAC were within the acceptable limits [39–41]. The observed reduction was also reflected in the lower values of metallic and non-metallic ions determined in FCAC and FMAC (Table 10.2).

Table 10.2: Results of the analyses of untreated wastewater, filtrate from wastewater treated with the commercial activated carbon (FCAC) and filtrate from wastewater treated with the maize cob activated carbon (FMAC).

Parameter	Untreated water	FCAC	FMAC	WHO [39] limit	SON [40] limit	USEPA [41] limit
Odour	Offensive	Unobjectionable	Unobjectionable	Unobjectionable	Unobjectionable	3.00 TON
pH	5.52 ± 0.10^{c}	7.32 ± 0.20 a	7.29 ± 0.07^{b}	6.50–9.50	6.50–8.50	6.50–8.50
Temperature (°C)	25.40 ± 0.3^{a}	25.20 ± 0.20^{a}	25.30 ± 1.30^{a}	20–32	Ambient	NVA
Colour	12.20	2.10	2.00	15	15	15
TDS (mg dm^{-3})	441 ± 6.00^{a}	130 ± 5.00^{c}	175 ± 2.91^{b}	500	500	500
TSS (mg dm^{-3})	320 ± 2.00^{a}	85.0 ± 4.00^{b}	32.0 ± 0.25^{c}	500	NVA	NVA
Turbidity (NTU)	0.87 ± 0.05^{a}	0.21 ± 0.10^{b}	0.16 ± 0.09^{c}	NVA	5	0.5
Conductivity (µs cm^{-1})	882 ± 8.00^{a}	224 ± 4.00^{b}	236 ± 1.00^{c}	1200	1000	NVA
Alkalinity (mg dm^{-3})	154 ± 1.01^{a}	132 ± 2.30^{b}	110 ± 2.31^{c}	100	100	NVA
Hardness (mg dm^{-3})	36.00 ± 2.70^{a}	19.00 ± 2.00^{b}	16.00 ± 0.28^{c}	100	150	NVA
BOD (mg dm^{-3})	544 ± 10.0^{a}	198 ± 4.00^{b}	14.50 ± 0.43^{c}	NVA	NVA	NVA
COD (mg dm^{-3})	684 ± 9.23^{a}	200 ± 4.45^{b}	90 ± 0.72^{c}	NVA	NVA	NVA
NO_3^{-} (mg dm^{-3})	3.50 ± 0.50^{b}	3.20 ± 0.10^{b}	2.30 ± 0.11^{c}	50	50	10
SO_4^{2-} (mg dm^{-3})	$70.10 \pm 5.10\ ^{a}$	31.30 ± 2.28^{b}	22.00 ± 0.03^{c}	500	100	250
PO_4^{3-} (mg dm^{-3})	7.3 ± 2.51^{a}	3.22 ± 1.78^{b}	2.14 ± 0.08^{c}	NVA	NVA	NVA
Cl^{-} (mg dm^{-3})	53.1 ± 14.00^{a}	4.40 ± 4.00^{b}	5.80 ± 0.20^{c}	500	250	250
Cd^{2+} (mg dm^{-3})	<0.003	<0.003	<0.003	NVA	0.003	0.005
Ni^{2+} (mg dm^{-3})	0.03 ± 0.00^{a}	<0.008	0.01 ± 0.00^{a}	NVA	0.02	0.1
Pb^{2+} (mg dm^{-3})	0.01 ± 0.00	<0.005	<0.005	0.05	0.01	0.05
Mn^{2+} (mg dm^{-3})	0.40 ± 0.01^{a}	<0.02	0.30 ± 0.01^{b}	0.4	0.2	0.05
Fe^{2+} (mg dm^{-3})	0.92 ± 0.23^{a}	0.77 ± 0.11^{b}	0.52 ± 0.09	3.0	0.3	0.3
Zn^{2+} (mg dm^{-3})	1.88 ± 0.12^{b}	0.23 ± 0.01^{c}	2.35 ± 0.01^{b}	NVA	3	5
Cu^{2+} (mg dm^{-3})	0.30 ± 0.00^{a}	0.19 ± 0.00^{c}	0.17 ± 0.09^{b}	NVA	1	1
Cr^{3+} (mg dm^{-3})	0.25 ± 0.020^{a}	0.09 ± 0.005^{c}	0.15 ± 0.02^{b}	5.0	0.05	0.1
AS^{3+} (mg dm^{-3})	<0.001	<0.001	<0.001	NVA	0.01	0.01

$^{a-c}$Means ± SD with the same superscript letters within a row are not significantly different at $p=0.05$; <DL, less than detection limit; NVA, no value available.

Biochemical oxygen demand (BOD) signifies organic pollution and measures the productivity of water. The higher the value, the more polluted the water sample [42]. MAC removed 73.4% pollutants from the wastewater compared to 63.6% removed by the CAC. Similar degree of purification was observed in the results of Siong et al. [34] and Ademiluyi et al. [36] with 77.3 and 74.8% BOD reduction, respectively. Chemical oxygen demand (COD) is a measure of the amount of a specified oxidant that reacts with the water sample under controlled condition [34]. Approximately 78.3% reduction was achieved with MAC as adsorbing agent. This result was in agreement with 77.8% reduction of COD in well water with granulated activated carbon [34] but had a better reduction (62.2%) in the wastewater treated with bamboo activated carbon [36].

There were significant differences in the mean concentrations of the non-metal ions determined in the water samples. The results of these ions in treated filtrates (FCAC and FMAC) showed a significant reduction in their concentrations. Water sample high in chloride ions may result in an objectionable salty taste and produce a laxative effect [42]. The chloride content in the untreated water (531 mg dm^{-3}) was higher than maximum permissible level of 500 mg dm^{-3} [39]. MAC reduced the sulphate content from 70.10 (untreated water) to 4.60 mg dm^{-3}. The higher the concentrations of nitrate and phosphate of a water sample, the higher the level of pollution [42]. The low values of nitrate and phosphate in FMAC may not pose health hazard. There is a great tendency for bacteriological pollution if the nitrate concentration is above permissible recommended level [42]. Some of the heavy metal ions investigated in the water samples are carcinogenic, teratogenic, mutagenic and toxic [42]. Some were found below the limits of detection after the wastewater passed through the test adsorbent while there was a sharp decrease in the concentrations of others with exception of zinc, which had a higher value in FMAC. This is expected since $ZnCl_2$ was used as an activating agent, which might have added up to the Zn^{2+} concentration in the FMAC. Similar report of metal sorption from aqueous media with activated carbon had been documented [5].

10.3.3.2 Principal component analysis

The principal component analysis (PCA) was used to express an overview and variations among the untreated and treated water samples. The experimental value for each water sample (Table 10.1) was standardized to ascertain that each parameter contributed equally to the data set variance and carries the same weight in the principal component estimation. The cations showed that PC1 described 73.57% of the sum variance in the data set whereas PC2 described 26.43%. The anions showed that PC1 described 91.08% of the sum variance in the data set and PC2 described 8.92%. The other physicochemical characteristics showed PC1 to be 93.91% and PC2, 6.09%. The factor score plots and biplots for PC1 against PC2 for the cations, anions and other physicochemical attributes are presented in Figure 10.4(a–f).

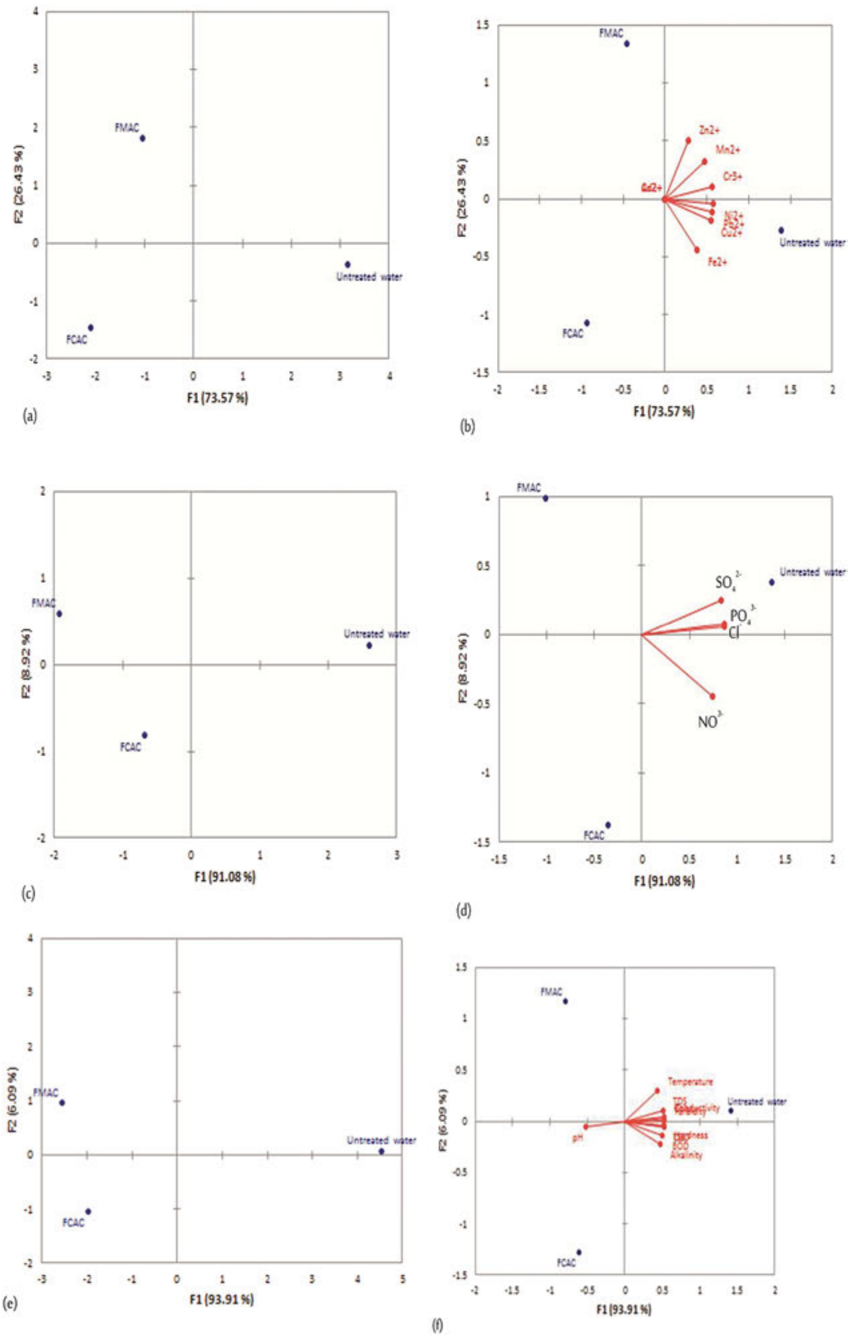


Figure 10.4: (a) Cations factor plot (b) cations biplot (c) anions factor plot (d) anion biplot (e) other physicochemical factor plot (f) other physicochemical biplot.

Figure 10.4(a) shows that the wastewaters treated with the maize cob activated carbon (FMAC) and the commercial activated carbon (FCAC) were better than the untreated wastewater. Wastewater treated with the MAC and CAC were on the left of the PC1 zero-point, whereas, untreated water was located on the right. Figure 10.4(b) shows that both MAC and CAC had a significant ($p<0.05$) effect on the cations in the wastewater. The CAC had stronger effects on Zn^{2+}, Mn^{2+} and Cr^{3+} than the MAC whereas, the MAC had a stronger effect on Fe^{2+}, Ni^{2+}, Pb^{2+} and Cu^{2+} than the CAC. The results showed that MAC could be used to reduce both the cations and the anions in wasterwater. Furthermore, the MAC had stronger potential in reducing NO_3^- than the CAC (Figure 10.4d). Figure 10.4(e–f) illustrates the effects of the MAC and CAC on the wastewater. The Figures showed that the test activated carbon had a significant ($p<0.05$) effect on the contaminant in the

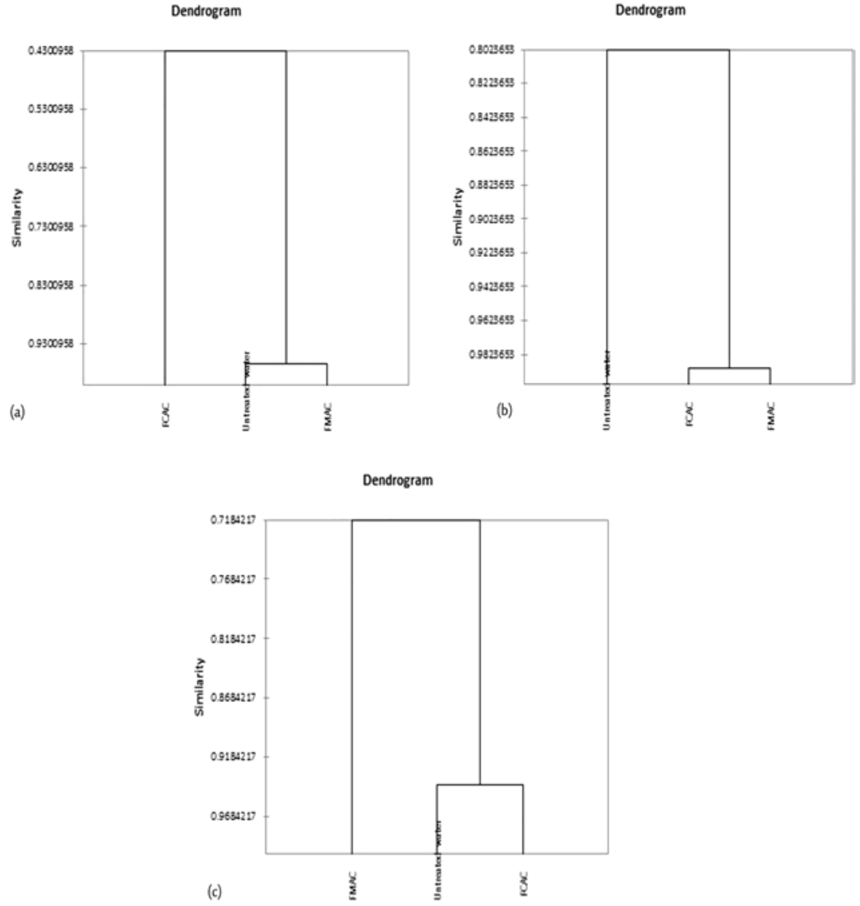


Figure 10.5: Dendrogram (a) cations (b) anions (c) other physicochemical properties.

wastewater. The MAC-treated water was similar to that of CAC-treated and these two samples were distinct from the untreated water. The distinction in the distance of the FMAC from other two water samples indicated that the test adsorbent could be used to decontaminate wastewater. Conclusively, the test product had similar characteristics to that of the commercial product when used in wastewater treatment. This study showed that MAC could be employed in water treatment.

10.3.3.3 Agglomerative hierarchical clustering (AHC)

The dendrograms for the water samples are shown in Figure 10.5. The results showed that the MAC and CAC were similar in activity when used in the treatment of water containing cations, anions and other physicochemical properties. However, the MAC compares favourably with the CAC and performed better in treating the wastewater for anions and other physicochemical parameters than the CAC. The untreated water was significantly different ($p<0.05$) from the MAC- and CAC-treated water. Thus, the MAC could be employed in the treatment of laboratory water.

10.4 Conclusions

The properties such as large surface area, iodine value, low ash content (highly carbonaceous) and high degree of porosity of maize cob activated carbon was investigated. A SEM image of the activated carbon showed external surface was filled with cavities of irregular sizes created by activation. The IR spectra revealed the presence of significant different peak frequencies in the two products by different functional groups. When the adsorption efficiencies of the product were tested with wastewater, the significant reduction of contaminants below the regulatory limits bares credence to the MAC adsorption prowess in the treatment of wastewater. In addition, the fact that these biomass is a good adsorbent as revealed in this study suggests that utilization of this agricultural waste-product in the production of activated carbon can serve as a better solid waste management option, this will greatly enhance the aesthetic value of the environment.

Acknowledgments: The authors express their profound gratitude to the Department of Science Laboratory Technology of Akanu Ibiam Federal Polytechnic, Unwana, Nigeria, for providing the facilities for this study. Also, the technical assistance of Gabriel Ocheja and Olusola Akinola of National Steel Raw Materials Exploration Agency, Kaduna, Nigeria and Central Laboratory of Obafemi Awolowo University, Ile-Ife, Nigeria respectively, are appreciated.
Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: This research was proudly supported and sponsored by Tertiary Education Trust Fund (TETFund) of the Federal Republic of Nigeria.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Tak B, Tak B, Kim Y, Park Y, Yoon Y, Min G. Optimization of colour and COD removal from livestock wastewater by electrocoagulation process: application of Box-Behnken design (BBD). J Ind Eng Chem 2015;28:307–15.
2. Wang J, Wu F, Wang M, Qui N, Liang Y, Fang S, et al. Preparation of activated carbon from a renewable agricultural residue of pruning mulberry shoot. Afr J Biotechnol 2010;9:2762–7.
3. Ajala LO, Ali EE. Potential of groundnut shell-based activated charcoal for laboratory water treatment. J Environ Sci Toxicol Food Technol 2020;14:54–9.
4. Abraham FA, Thenmozhi R, Sivakumar M, Sivakumar K, Sasikumar G, Thamaraimuthuayyanraj S. Waste water treatment unit using activated charcoal. Int Res J Eng Technol 2018;5:312–5.
5. Jacob AG, Okunola OJ, Uduma AU, TijjaniA HS. Treatment of waste water by activated carbon developed from *Borassus aethiopum*. Nig J Mat Sci Eng 2017;6:103–7.
6. Olagunju EO, Ajala LO, Farombi AG. Sustainable utilization of rice husk activated charcoal through phytoremediation. Phy Sci Int J 2015;5:81–7.
7. Amirza MAR, Adib MMR, Hamdan R. Application of agricultural wastes activated carbon for dye removal – an overview. MATEC Web Conf 2017;103:6–13.
8. Reza MS, Hasan ABM, Afroze K, Abu-Bakar MS, Taweekun J, Azad AK. Analysis on preparation, application, and recycling of activated carbon to aid in Covid-19 protection. Int J Integ Eng 2020;12: 233–44.
9. Yusufu MI, Ariahu CC, Igbabul BD. Production and characterization of activated carbon from selected local raw materials. Afr J Pure Appl Chem 2012;6:123–31.
10. Marichelvan MK, Azhagurajan A. Removal of mercury from effluent solution by using banana corm and neem leaves activated charcoal. Environ Nanotechnol Monit Manag 2018;10:360–5.
11. Ijaola OO, Ogedengbe K, Sangodoyin AY. On the efficacy of activated carbon derived from bamboo in the adsorption of water contaminants. Int J Eng Inv 2013;2:29–34.
12. Sivakumar V, Asaithambi M, Sivakumar P. Physic-chemical and adsorption studies of activated carbon from agricultural wastes. Adv Appl Sci Res 2012;3:219–26.
13. Ukpaka CP, Edwin I. Adsorbent in bioremediation of crude oil polluted environment: influence of physicochemical characteristics of various saw dusts. Int Res J Biotechnol 2013;4:124–41.
14. Hegazi HA. Removal of heavy metals from wastewater using agricultural and industrial wastes as adsorbents. HBRC J 2013;9:276–82.
15. Gokhale NA, Trivedi NS, Mandavgane SA, Kulkarni BD. Biomass ashes as potent adsorbent for pesticide: prediction of adsorption capacity by artificial neural network. Int J Environ Sci Tech 2020;17:3209–16.
16. Mopoung S, Moonsri P, Palas W, Khumpai S. Characterization and properties of activated carbon prepared from tamarind seeds by KOH activation for Fe (III) adsorption from aqueous solution. Sci World J 2015;2015:9.
17. Elelu S, Adebayo GB, Abduls-Salam N, Iriowen EM. Preparation and characterization of adsorbents from physic nut plant (*Jatropha curcas* L.). The Chemist 2019;91:42–9.

18. Özsin G, Kılıç M, Apaydın-Varol E, Pütün AE. Chemically activated carbon production from agricultural waste of chickpea and its application for heavy metal adsorption: equilibrium, kinetic, and thermodynamic studies. Appl Water Sci 2019;9. https://doi.org/10.1007/s13201-019-0942-8.
19. Ani JU, Akpomie KG, Okoro UC, AnekeLE, Onukwuli OD, Ujam OT. Potentials of activated carbon produced from biomass materials for sequestration of dyes, heavy metals, and crude oil components from aqueous environment. Appl Water Sci 2020;10. https://doi.org/10.1007/s13201-020-1149-8.
20. Jun W, Fu-An W, Meng W, Ning Q, Yao L, Shui-Qin F, et al. Preparation of activated carbon from renewable agricultural residue of pruning mulberry shoot. Afr J Biotechnol 2010;9:2762–7.
21. Ajala LO, Ali EE. Preparation and characterization of groundnut shell-based activated charcoal. J Appl Sci Environ Manage 2020;24:2139–46.
22. Boonpoke A, Chiarakorn S, Laosiripojana N, Towprayoon S, Chidthaisong A. Synthesis of activated carbon and MCM-41 from bagasse and rice husk and their carbon dioxide adsorption capacity. J Sust Energy Environ 2011;2:77–81.
23. Ajala LO, Onwukeme VI, Oji CO, Ejiagha MC. Sustainable utilization of rice husk activated charcoal as wastewater decontaminant. In: Tüzemen S, editor. New insights into physical science. India: Book Publisher International; 2020, vol. 2:111–25 pp.
24. Subramani T, Revathi PK. Production of activated carbon from agricultural raw waste. J Eng 2015;5: 54–63.
25. Alzaydien AS. Physical chemical and adsorptive characteristics of local oak sawdust based activated carbons. Asian J Sci Res 2016;9:45–56.
26. Gawande PR, Kaware JP. Characterization and activation of coconut shell activated carbon. Int J Eng Sci Inv 2017;6:43–9.
27. Hidayat A, Sutrisno B. Comparison on pore development of activated carbon produced by chemical and physical activation from palm empty fruit bunch. IOP Conf Ser Mater Sci Eng 2017;162.
28. Saka C. BET, TG-DTG, FT-IR, SEM, iodine number analysis and preparation of activated carbon from acorn shell by chemical activation with $ZnCl_2$. J Anal Appl Pyrol 2012;95:21–4.
29. ASTM. Standard test method for determination of iodine number of activated carbon. Philadelphia: American Standard of Testing and Measurement committee on standards; 2006.
30. APHA. Standard methods for the examination of water and waste water, 21th ed. Washington DC: American Public Health Association standard methods; 2005.
31. Abdul-Khalil HPS, Jawaid M, Firoozian P, Rashid U, Islam A, Akil HM. Activated carbon from various agricultural wastes by chemical activation with KOH: preparation and characterization. J Biobased Mater Bioenergy 2013;7. https://doi.org/10.1166/jbmb.2013.1379.
32. Rangaraj S, Moon SH, Sivabalan R, Arabidoo B, Murugesan V. Agricultural waste for the removal of organics: adsorption of phenol from water and wastewater by palm seed coat activated carbon. Waste Manag 2002;22:543–8.
33. Morlay C, Gasperi J, Guillossou R, Mailler R, Le Roux J, Rocher V, et al. Organic micropollutants in a large wastewater treatment plant: what are the benefits of an advanced treatment by activated carbon adsorption in comparison to conventional treatment? Chemosphere 2019;218:1050–60.
34. Siong YK, Idris AJ, Atabaki AMM. Performance of activated carbon in water filters; 2013. https://www.researchgate.net/publication/234060484mm [Assessed Nov 2019].
35. Zdravkov BD, Čermák JJ, Šefara M, Janků J. Pore classification in the characterization of porous materials: a perspective. Cent Eur J Chem 2007;5:385–95.
36. Ademiluyi FT, Amadi SA, Amakama NJ. Adsorption and treatment of organic contaminants using activated carbon from waste Nigerian bamboo. J Appl Sci Environ Manage 2009;13:39–47.
37. Williams D, Fleming I. Spectroscopic methods in organic chemistry, 6th ed. Berkshire, UK: McGrew Hill; 2008.

38. Pavia DL, Lampman GM, Kriz GS, Vyvyan JR. Introduction to spectroscopy, 5th ed. USA: Cengage Learning; 2015.
39. WHO. Guidelines for drinking water quality. Geneva: World Health Organization; 2003.
40. SON. Nigerian standard for drinking water quality. Lagos: Nigerian Industrial Standard (NIS) of Standard Organization of Nigeria; 2007.
41. USEPA. Drinking water standards and health advisories. Washington DC: United State Environmental Protection Agency; 2012.
42. Okonkwo EM, Eboatu AN. Environmental pollution and degradation, 2nd ed. Awka, Nigeria: Abimac Publishers; 2006.

Onome Ejeromedoghene*, Olayinka Oderinde and
Sheriff Adewuyi*

11 Advances in polymeric ionic liquids-based smart polymeric materials: emerging fabrication strategies

Abstract: Polymeric ionic liquids (PILs) are a class of materials characterized by fascinating physicochemical properties as well as tunable functionality that are quite interesting for the fabrication of materials. They have attracted tremendous attention because they are easy to prepare and can be manipulated into a polymeric matrix via covalent and noncovalent linkage/interactions to form new intelligent/smart polymeric materials with improved properties and multiple functionalities for application in many fields. These new materials are specially designed to change their performance properties when subjected to external environmental stimuli including pH, temperature, light, chemicals and electromagnetic fields. Therefore, this chapter presents the progress in the preparation of PILs via different polymerization reactions and highlights the emerging advances in the fabrication of PILs-based smart polymeric materials.

Keywords: polymeric ionic liquids; polymerization reactions; smart polymers; stimuli-responsive.

11.1 Introduction

In the past decade, polymeric ionic liquids (PILs) *See* have triggered a lot of attention as an interesting class of ion-conducting polymers due to their interrelated chemistry compared to those of ionic liquids [1, 2]. Although ionic liquids (ILs) were described as an ideal solvent for many chemical reactions, their toxicity, high cost of preparation and stability have greatly hindered their industrial applications [3, 4]. However, advancements in materials science have proffer alternatives based on PILs which are characterized with many advantages such as high conductivity, robust thermal and

---

***Corresponding authors: Onome Ejeromedoghene**, School of Chemistry and Chemical Engineering, Southeast University, Jiangning District, Nanjing, Jiangsu Province, 211189, P. R. China; and Department of Chemistry, College of Physical Sciences, Federal University of Agriculture, PMB 2240, Abeokuta, Ogun State, Nigeria, E-mail: oejeromedoghene@seu.edu.cn. https://orcid.org/0000-0002-5487-3267; and **Sheriff Adewuyi**, Department of Chemistry, College of Physical Sciences, Federal University of Agriculture, PMB 2240, Abeokuta, Ogun State, Nigeria, E-mail: adewuyis@funaab.edu.ng
Olayinka Oderinde, School of Chemistry and Chemical Engineering, Southeast University, Jiangning District, Nanjing, Jiangsu Province, 211189, P. R. China. https://orcid.org/0000-0002-2050-0948

This article has previously been published in the journal Physical Sciences Reviews. Please cite as: O. Ejeromedoghene, O. Oderinde and S. Adewuyi “Advances in polymeric ionic liquids-based smart polymeric materials: emerging fabrication strategies” *Physical Sciences Reviews* [Online] 2021, 6. DOI: 10.1515/psr-2020-0081 | https://doi.org/10.1515/9783110726145-011

enhanced chemical stability, improved processability, flexibility yet durable, tunable functionalities, and improved control over its meso- to nano-structures [5]. In addition, cation or anion monomers can be tethered to the polymer backbone in a PIL to form new intelligent/smart polymeric materials with multiple functionalities [6, 7].

Thus, the fabrication of smart polymeric material has become an integral aspect of polymer chemistry and materials science due to their multiresponsive abilities to external stimuli such as temperature, light, pH, electric and magnetic fields. The special interest in these classes of polymers has grown significantly due to their high level of sensitivity and wide range of application that cuts across many multidisciplinary fields including industries, biotechnology, medicine and engineering, and nanoscience [8].

11.2 Polymeric ionic liquids (PILs): preparation strategies

PILs are species of ionic liquid wherein the repeating monomer units are interconnected via covalent linkage to form macromolecular architecture [9]. This new class of solvents that reflects the combination of the unique properties of ILs and the monomeric molecules (Figure 11.1) has been used in the fabrication of novel materials with enhanced mechanical durability and functionality with dimensional control over the polymerization process [10]. Different polymerization processes have been employed for the preparation of PIL. These include:

11.2.1 Homopolymerization

Homopolymerization involves the polymerization of a single type of monomer to form a homopolymeric ILs. Based on homopolymerization and anion exchange reactions, Li et al. [11] prepared a thermally stable gel polymer electrolyte membrane with excellent electrochemical properties based on the PILs as polymer host by incorporating *N*,*N*-dimethyl-*N*-methyl-*N*-(2-methylethyl) ammonium bis(trifluoromethane sulfonyl)imide (DEME-TFSI) IL and nanosize SiO_2 for lithium batteries (Figure 11.2). In an experimental study, Kong and Jiang [12] showed that the radical branching polymerizations of two asymmetrical divinyl monomers, allyl methacrylate (AMA) and furfuryl methacrylate (FMA) produced PILs (PAMA and PFMA) with high molecular weights (10^6–10^7).

11.2.2 Copolymerization

In the copolymerization technique, a copolymeric IL is obtained from more than one species of the monomeric unit. In a typical reaction, Zhou et al. [13] prepared copolymeric quaternary ammonium-typed IL based on 1-allyl-methylimidazolium chloride

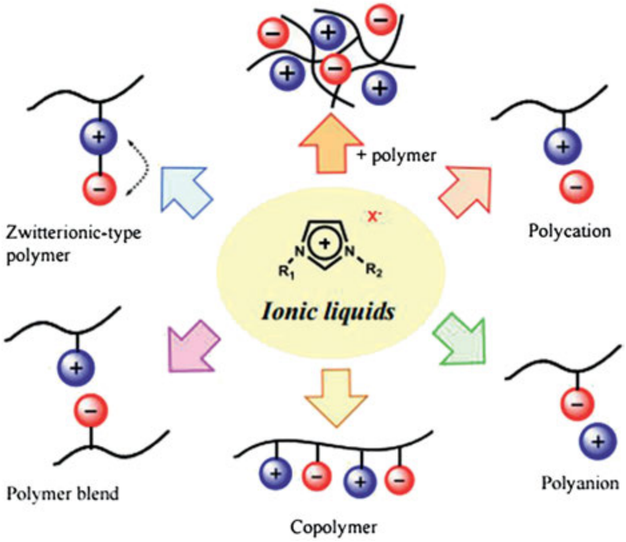


Figure 11.1: Preparation strategies of PILs with different types of monomers. Reproduced from Ref. [2] Copyright 2014 Elsevier Ltd.

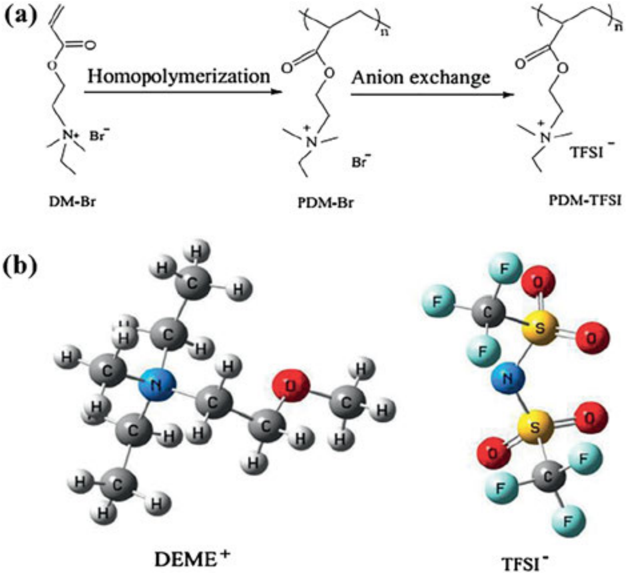


Figure 11.2: (a) An illustration of the homopolymerization of PILs (b) molecular structure of conformer of the IL, DEME$^+$ TFSI$^-$ for density functional theory (DFT) calculations. Reproduced from Ref. [11] Copyright 2013 Elsevier B.V.

(AlMeIm$^+$ Cl$^-$), styrene (IL-styrene), and ethylene dimethacrylate (EDMA) that displayed a brilliant performance in capillary electrochromatography-mass spectroscopy (CEC-MS) analysis of amino acids and peptides and parabens with stable separation and electrospray ionization. Mao et al. [14] prepared a novel IL, AlMeIm$^+$ Cl$^-$ polymer monolith poly(ionic liquid-*co*-ethylene dimethacrylate) incorporated with zeolitic imidazolate framework-8 (ZIF-8-poly(IL-co-EDMA)) by one-step copolymerization for the enhanced selective separation of four alkyl-chained benzenes in reversed-phase CEC (Figure 11.3a). Moreover, Kuzmicz et al. [15] introduced a single-pot solvothermal copolymerization of a PIL-based porous network (PILPNs) based on divinylbenzene and monomeric IL. The PILPNs was employed for organo-catalysis and production of microporous carbon monoliths (Figure 11.3b).

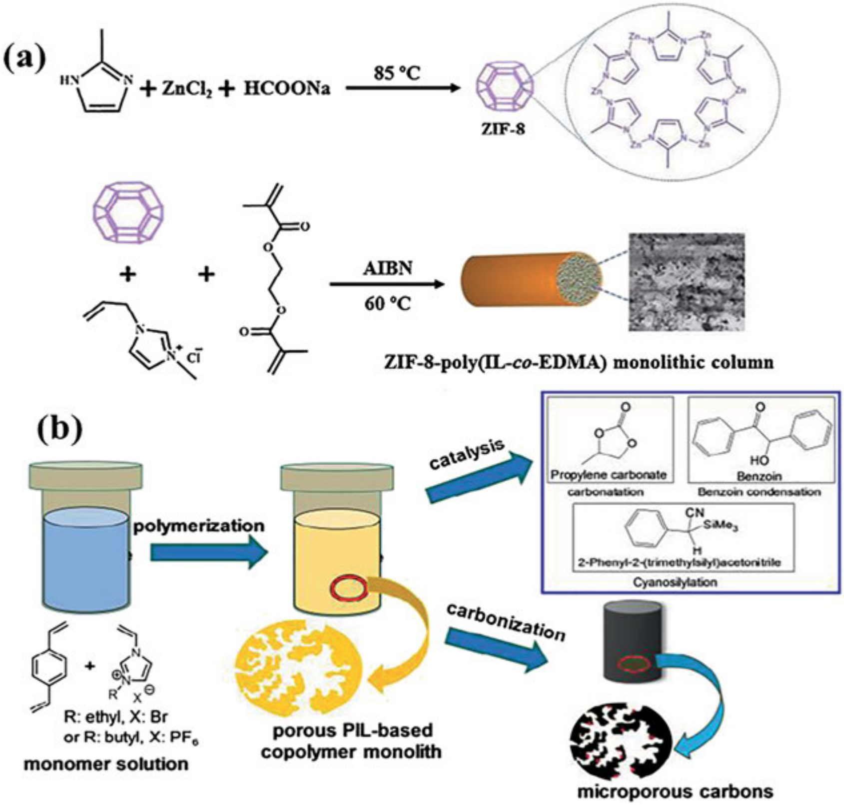


Figure 11.3: (a) Schematics for the preparation of IL-copolymerized monolith incorporated with ZIF-8. Reproduced from Ref. [14] Copyright 2018 Elsevier B.V. (b) Syntheses route for the fabrication of mesoporous PIL copolymer networks for application in organocatalysis and microporous carbon production. Reproduced from Ref. [15] Copyright 2014 Elsevier Ltd.

11.2.3 Free radical polymerization (FRP)

FRP is a paramount synthetic pathway for the fabrication of numerous polymers and polymeric composite materials. It is a versatile and nonspecific form of polymerization reaction that allows the facile reactions of polymeric free-radical chain ends and other chemicals or substrates such as enzymes and catalytic proteins [16]. In a study, Aquil et al. [17] synthesized a novel PIL consisting of polyvinylimidazolium and pendent nitroxide radical on each monomer unit by FRP at 40 °C. The process which was initiated with 2,2′-azobis(4-methoxy-2,4-dimethyl valeronitrile) displayed promising potentials as the cathode in a lithium-ion battery (Figure 11.4). Based on one pot conventional radical polymerization reactions, Vanti et al. [18] prepared different ionically-conducting polymer electrolytes that comprise side-chain liquid crystal terpolymers with liquid crystallinity over a wide range of compositions, light-responsive properties and ionic conductivities in the range of 10^{-8}–10^{-4} S cm^{-1}. Additionally, Pantazidis et al. [19] kinetically studied the synthesis of potassium 4-styrenesulfonyl (trifluoromethylsulfonyl) imide (STFSIK) monomer as well as its controlled/living nitroxide-mediated radical polymerization (NMRP) for water dialysis, using *N*-tert-butyl-*N*-(2-methyl-1-phenylpropyl)-o-(1-phenylethyl) hydroxylamine as the initiator in 50% w/v solutions of DMF at 125 °C.

11.2.4 Atom transfer radical polymerization (ATRP)

ATRP is an example of a reversible-deactivation radical polymerization that usually involves a catalytic system based on transition metal and an alkyl halide (R-X) as the

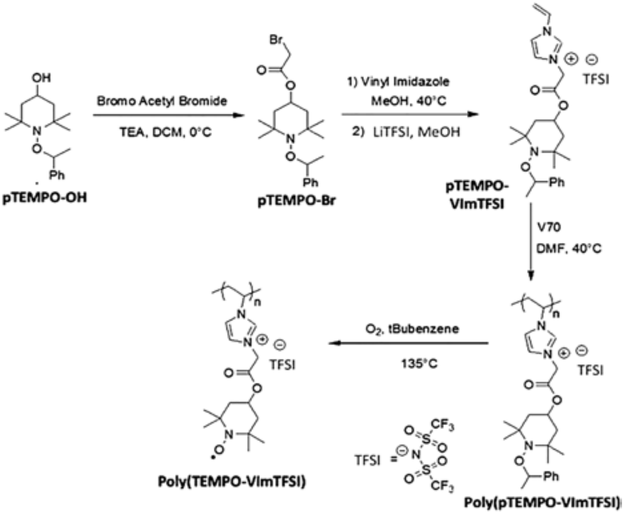


Figure 11.4: Synthesis route of the PIL-bearing nitroxide free-radicals. Reproduced from Ref. [17] Copyright 2018 Elsevier Ltd.

initiator (Figure 11.5a). This technique favors the fabrication of polymeric materials with low dispersity, afore-known molecular weight (MW) and well-preserved chain-end functional properties [20]. For example, Guo et al. [21] reported an electrochemically-mediated ATRP of methyl acrylate (MA) in 1-butyl-3-methylimidazolium hexafluorophosphate ($BMIM-PF_6$) IL in which the plotted kinetics suggests very fast polymerization rates with good control over MW and dispersity coupled with over 90% monomer conversion within a period of 300 s (Figure 11.5b). In another PIL medium, Tang et al. [22] prepared microcrystalline cellulose by grafting polymethylmethacrylate (MCC-*g*-PMMA) using ethanediamine as the ligand in an IL solution of 1-allyl-3-methylimidazolium chloride ([AMIM]Cl). The PMMA covalently bonded to the cellulose backbone with increased molecular weight and low polydispersity. The studies of Xue et al. [23] revealed that in an IL system, 1-(triethylene-tetramine)ethyl-3-methyl chloride ($[N_4MIM]Cl$) could be prepared to replace the organic ligand coordinating with CuBr to catalyze the ATRP. These were further employed for the ATRP of MMA in the IL system of 1-allyl-3-methylimidazolium chloride ([AMIM]Cl) with improved catalytic performance (Figure 11.5c).

Additionally, star-shaped PIL-3 and PIL-4 based on poly(2-(dimethyl-ethylamino)ethyl methacrylate) bis(trifluoromethylsulfonyl)imide (P(EtDMAEMA-TFSI)) with three-arm and four-arm architectures were prepared through ATRP and ion exchange with brilliant performances of the materials in lithium metal batteries by

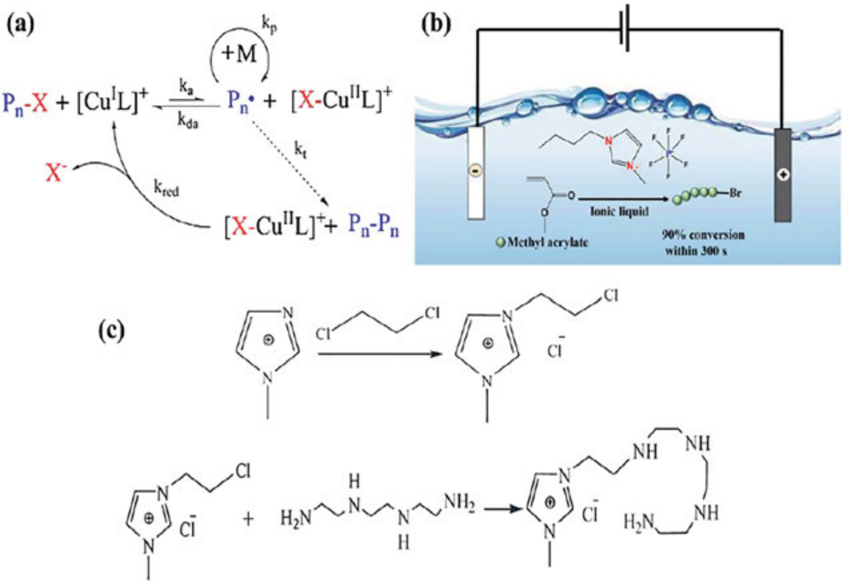


Figure 11.5: (a) Mechanism of ATRP with activator regeneration (b) eATRP of MA in $BMIM-PF_6$. Reproduced from Ref. [21] Copyright 2019 Elsevier B.V. (c) Synthetic route to coordinating $[N_4MIM]Cl$. Reproduced from Ref. [23] Copyright 2018 Elsevier Ltd.

Zhou et al. [24]. Meanwhile, Chen et al. [25] employed ATRP using activators generated by electron transfer (AGET ATRP) of acrylonitrile for the preparation of 1-methylimidazolium acetate ([mim][AT]), 1-methylimidazolium propionate([mim][PT]), and 1-methylimidazolium butyrate ([mim][BT]) ILs respectively with the aid of ascorbic acid, ethyl 2-bromoisobutyrate (EBiB), and $FeBr_3$ as a reducing agent, initiator, and catalyst respectively without any additional ligand.

11.2.5 Reversible addition fragmentation chain transfer (RAFT) polymerization

RAFT polymerization is one in which a chain transfer agent usually in the form of a thiocarbonylthio compound is introduced to provide control over the molecular weight and polydispersity of the polymer during a FRP process. Kumar et al. [26] investigated the effect of ILs on the RAFT polymerization of butyl methacrylate (Figure 11.6a). It was gathered that the ILs substantially increased the rate of polymerization, and the RAFT agents contributed to the molecular mass control and narrow dispersity of the

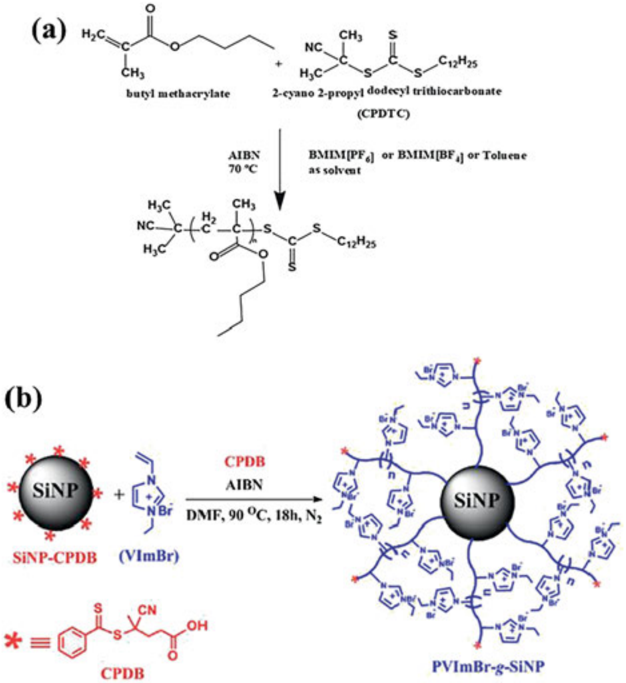


Figure 11.6: (a) Polymerization of butyl methacrylate with RAFT agent in 3-butyl-1-methyl imidazolium hexafluorophosphate BMIM[PF_6] as IL. Reproduced from Ref. [26] Copyright 2018 Elsevier Ltd. (b) Synthesis of PVImBr grafted SiNP. Reproduced from Ref. [27] Copyright 2020 Elsevier Ltd.

corresponding polymer. In another study, Koyilapu et al. [27] recorded success in the grafting of poly(vinylimidazolium)bromide (PVImBr) PIL brush polymers onto the surface of silica nanoparticles (SiNPs) using metal-catalyst-free and a facile RAFT technique to develop new membranes with improved functional and mechanical properties (Figure 11.6b). Chen et al. [28] developed a strategy to facilely prepare an IL-like inimer made up of a styryl group and trithiocarbonate moiety using the neutralization reaction involving a monomeric unit of an alkaline IL and a carboxyl-bearing chain transfer agent (Figure 11.7).

11.2.6 Photopolymerization

Photopolymerization is a technique that utilizes ultraviolet or visible light to initiate and propagate a polymerization reaction leading to the formation of a linear or crosslinked polymeric architecture. Based on photocuring protocols, Stepniak et al. [29] prepared IL gel polymer electrolyte (IL-GPE) *in situ* containing a mixture of *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl)imide, lithium bis(trifluoromethanesulphonyl) imide, and ethoxylated bisphenol A diacrylate as promising electrolyte candidates for flexible lithium-ion batteries. Furthermore, Li et al. [30] employed a facile thiol-ene photopolymerization method to rapidly design an IL-functionalized hybrid monolithic

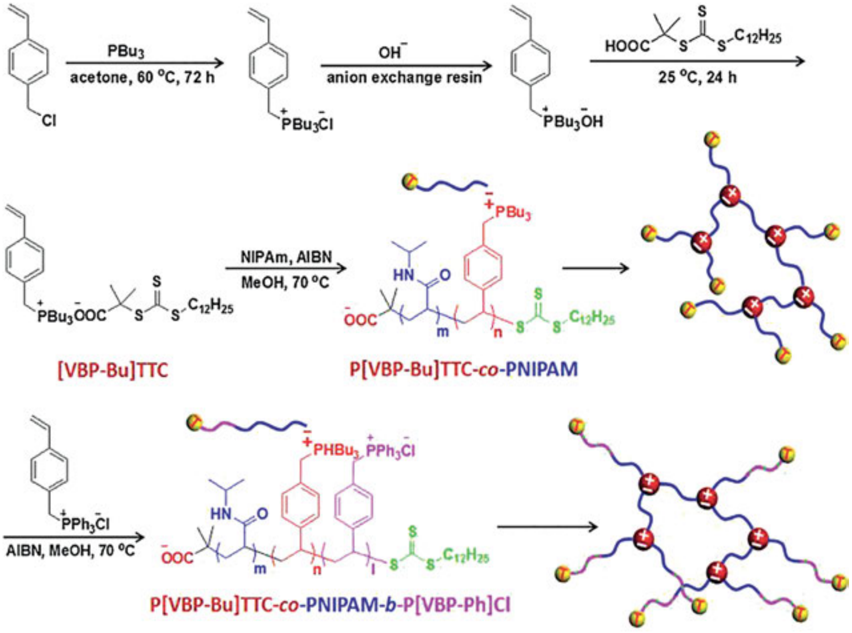


Figure 11.7: Detailed synthesis route for IL-like inimer and the branched polymers. Reproduced from Ref. [28] 2018 Elsevier Ltd.

column based on polyhedral oligomeric silsesquioxane (POSS) in a UV-transparent fused-silica capillary (Figure 11.8). The thiol–vinyl–methacrylate ternary system displayed a substantial separation ability toward the analysis of small molecules.

11.3 Applications of smart/intelligent polymers based on PILs

Smart/intelligent materials are specially designed to change their performance property in the presence of an external stimulus. These materials can be extremely sensitive to environmental conditions of temperature, pH, light, chemicals, electromagnetic fields; hence, they are otherwise called stimuli-responsive materials [31, 32]. Additionally, these materials can retain special features such as shape memory, self-healing, wound dressing and conductivity in different media. Thus, these multifunctional abilities of smart materials have attracted considerable interest for application in many multidisciplinary fields. As polymeric composites, they can be prepared by one or more of the polymerization reactions highlighted above. Due to the fascinating properties of PILs, some researchers have attempted to synthesize smart polymeric materials based on PILs. Studies have shown that the diverse chemical structures and ionic characteristics of PIL afford them the vast ability to interact via covalent linkage, electrostatic interaction, hydrogen bonding, van der Waals interaction, spatial confinement and π → π interaction with other molecules to form a polymeric composite membrane with smart and tunable properties [33]. For example, Correia et al. [34] developed magnetic ionic liquid (MIL) composite of 1-butyl-3-methylimidazolium tetrachloroferrate, ([Bmim][$FeCl_4$]) and electroactive polymer poly(vinylidene fluoride-trifluorethylene) (P(VDF-TrFE)) at different evaporation temperatures of solvent and different MIL contents (Figure 11.9). The strategy

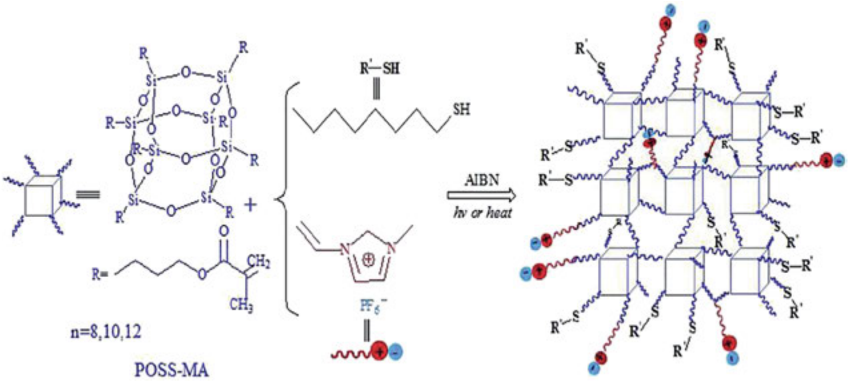


Figure 11.8: Preparation strategy of ILs functionalized POSS hybrid monoliths. Reproduced from Ref. [30] Copyright 2019 Elsevier B.V.

produces a new material with improved and controlled physicochemical properties for industrial applications. Zhao et al. [35] prepared PIL enveloped nanosilica composite by Pickering emulsion polymerization as stimuli-responsive electrorheological particles (Figure 11.10a). The material displayed greater electro-responsive ability and temperature stability. Moreover, Yang et al. [36] synthesized a hybrid organic–inorganic material based on f-PMMA-silica by polymerization of MMA monomer and tetraethoxysilane precursor aided by 3-trimethoxysilyi-propyl-methacrylate as a coupling agent combining both the mechanical properties as well as the functional properties of both the hybrid and IL (Figure 11.10b). Pipertzis and coworkers [37] showed that PILs bearing a polythiophene backbone are unique and can simultaneously conduct electronic charge and ions at the nanoscale, therefore, possessing tunable functional properties.

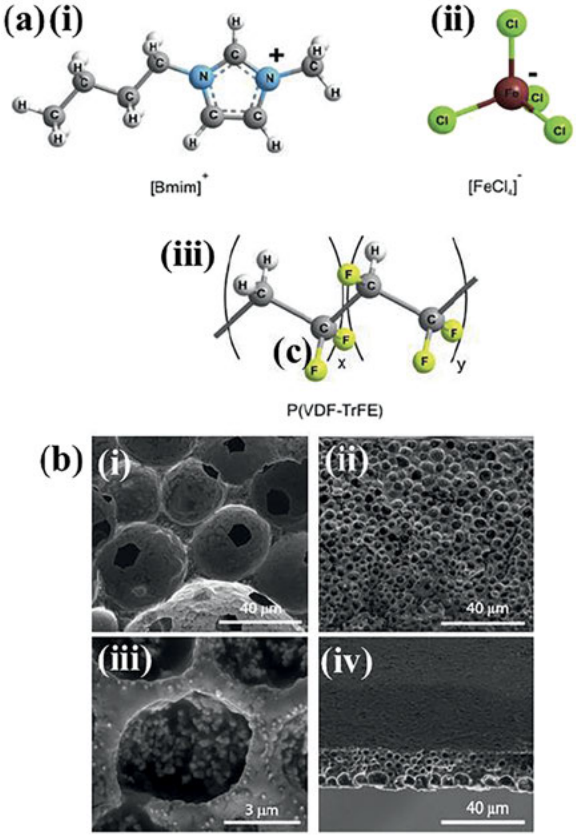


Figure 11.9: (a) Structural representation of MIL (i) cation (ii) anion (iii) and of P(VDF-TrFE) (b) Scanning electron micrograph of P(VDF-TrFE)/[Bmim][FeCl$_4$] composite films with 40% wt. of MIL synthesized at (i) 25 °C (ii) and (iii) 90 °C (iv) 210 °C. Reproduced from Ref. [34] Copyright 2019 Elsevier Ltd.

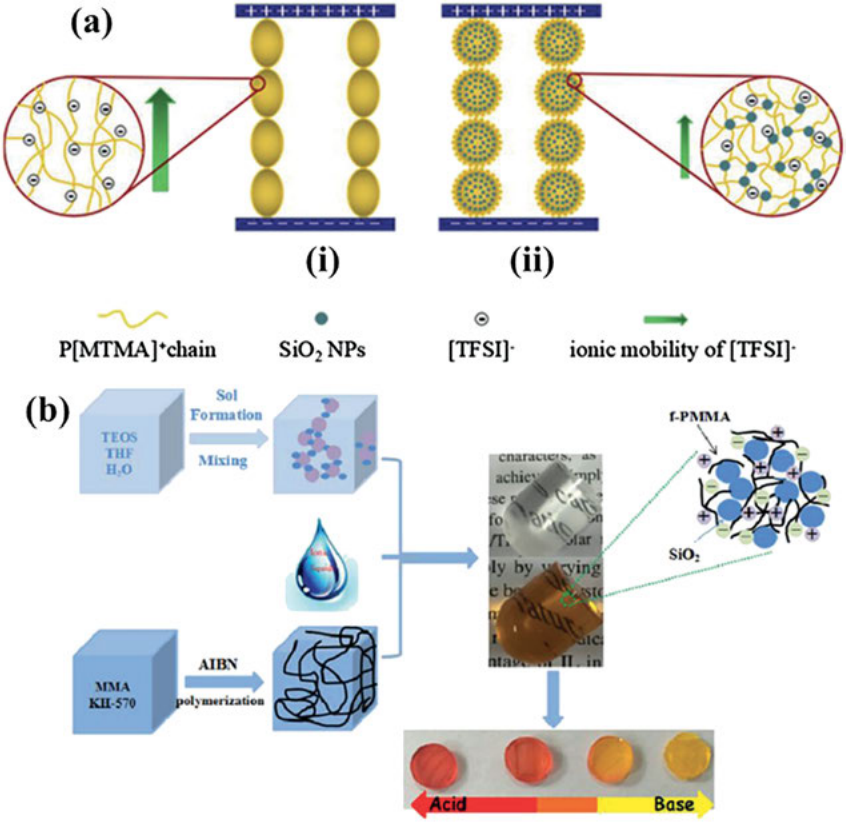


Figure 11.10: (a) Formation of P[MTMA][TFSI]/silica composites (ii) the composites viewed under electric fields at high temperature. Reproduced from Ref. [35] Copyright 2018 Elsevier Ltd. (b) Synthetic pathway of transparent HOI ionogels and their response to different pH. Reproduced from Ref. [36] Copyright 2017 Elsevier B.V.

Furthermore, Nagy et al. [38] reported the fabrication of resorcinol-formaldehyde polymer gels at various room temperature ionic liquid (RTIL)-water mixtures. Low-temperature nitrogen adsorption revealed that the sizes of both the cations and anions influence the pore morphology of the aerogel. The study shows that the state of the synthesis of the gel depends on the intrinsic pH sensitively due to the anion of the IL. In another study, Guo et al. [39] developed PIL-based membranes by *in situ* photo-cross-linking of an IL monomer and anion-exchange with amino acids. The new robust compounds displayed significant antibacterial properties with no significant hemolysis and cytotoxicity toward human red blood and skin fibroblast cells. Wei et al. [40] prepared a new IL skeleton typed magnetic core–shell molecularly imprinted polymers (Fe_3O_4-COOH@IL-MIP) for the adsorption of lysozymes. The

MIP adsorbent displayed an adsorption capacity of 166.36 mg/g, an imprinting factor of 2.67, and multiple reusabilities without obvious loss of rebinding ability, while the lysosomes conformation remained intact after elution whose rate was as high as 74%.

11.4 Conclusion and prospects

The chapter explored the progress in the preparation of PILs as an emerging substrate for developing novel smart/intelligent composite materials. Owing to the prominent feature of ILs, which is the presence of mobile electrons, this specific feature can be channeled for making new stimuli-responsive materials. Although a lot of research has focused on the preparation of stimuli-responsive materials based on existing polymerization protocols with which PILs are been generated such as copolymerization, FRP, ATRP, RAFT, and photopolymerization reaction. Besides, some efforts have been channeled to the fabrication of porous polymeric materials, metal-organic frameworks, and polyoxometalate composites. However, the literature survey shows a scanty approach of fabricating stimuli-responsive composite (macro-/nano-composite) directly by utilizing PILs. Thus, in selecting monomers for the preparation of PILs, properties such as response to pH, light, temperature, magnetic field, and conductivity are necessary to be considered. Therefore, combining the intriguing properties of the PILs (tunability, conductivities, improved thermal and chemical stability, improved processability, and flexibility) with suitable monomers will proffer new avenues for the fabrication of smart polymers for targeting specific aspects of industrial, biological or environmental applications.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.
Research funding: None declared.
Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Mogurampelly S, Ganesan V. Ion transport in polymerized ionic liquid-ionic liquid blends. Macromolecules 2018;51:9471–83.
2. Nishimura N, Ohno H. 15th Anniversary of polymerised ionic liquids. Polymer (Guildf) 2014;55: 3289–97.
3. Ghandi K. A review of ionic liquids, their limits and applications. Green Sustain Chem 2014;04: 44–53.
4. Shamsuri AA. Ionic liquids: preparations and limitations. MAKARA Sci Ser 2011;14:101–6.
5. Cheng Y, Yang J, Hung JH, Patra TK, Simmons DS. Design rules for highly conductive polymeric ionic liquids from molecular dynamics simulations. Macromolecules 2018;51:6630–44.

6. Shaplov AS, Vlasov PS, Lozinskaya EI, Ponkratov DO, Malyshkina IA, Vidal F, et al. Polymeric ionic liquids: comparison of polycations and polyanions. Macromolecules 2011;44:9792–803.
7. Obadia MM, Drockenmuller E. Poly(1,2,3-triazolium)s: a new class of functional polymer electrolytes. Chem Commun 2016;52:2433–50.
8. Mecerreyes D. Polymeric ionic liquids: broadening the properties and applications of polyelectrolytes. Prog Polym Sci 2011;36:1629–48.
9. Yuan J, Mecerreyes D, Antonietti M. Poly(ionic liquid)s: an update. Prog Polym Sci 2013;38: 1009–36.
10. Kausar A. Research progress in frontiers of poly(ionic Liquid)s: a review. Polym Plast Technol Eng 2017;56:1823–38.
11. Li M, Yang B, Wang L, Zhang Y, Zhang Z, Fang S, et al. New polymerized ionic liquid (PIL) gel electrolyte membranes based on tetraalkylammonium cations for lithium ion batteries. J Membr Sci 2013;447:222–7.
12. Kong L, Jiang B. Free radical branching homopolymerization of asymmetrical divinyl monomers in isopropyl alcohol. Polymer (Guildf) 2018;151:316–24.
13. Zhou W, Sun W, Liu Y, et al. Ionic liquid-copolymerized monolith based porous layer open tubular column for CEC-MS analysis. Talanta 2020;209:120556.
14. Mao Z, Bao T, Li Z, Chen Z. Ionic liquid-copolymerized monolith incorporated with zeolitic imidazolate framework-8 as stationary phases for enhancing reversed phase selectivity in capillary electrochromatography. J Chromatogr A 2018;1578:99–105.
15. Kuzmicz D, Coupillaud P, Men Y, Vignolle J, Vendraminetto G, Ambrogi M, et al. Functional mesoporous poly(ionic liquid)-based copolymer monoliths: from synthesis to catalysis and microporous carbon production. Polymer (Guildf) 2014;55:3423–30.
16. Zavada SR, Battsengel T, Scott TF. Radical-mediated enzymatic polymerizations. Int J Mol Sci 2016; 17:1–27.
17. Aqil M, Ouhib F, Aqil A, El Idrissi A, Detrembleur C, Jérôme C. Polymer ionic liquid bearing radicals as an active material for organic batteries with ultrafast charge-discharge rate. Eur Polym J 2018; 106:242–8.
18. Vanti L, Mohd Alauddin S, Zaton D, Aripin NFK, Giacinti-Baschetti M, Imrie CT, et al. Ionically conducting and photoresponsive liquid crystalline terpolymers: towards multifunctional polymer electrolytes. Eur Polym J 2018;109:124–32.
19. Pantazidis C, Andreou S, Glynos E, Sakellariou G. Synthesis of a well-defined polyelectrolyte by controlled/“living” nitroxide-mediated radical polymerization. Kinetic study. Eur Polym J 2020: 109815. https://doi.org/10.1016/j.eurpolymj.2020.109815.
20. Matyjaszewski K. Atom transfer radical polymerization (ATRP): current status and future perspectives. Macromolecules 2012;45:4015–39.
21. Guo JK, Zhou YN, Luo ZH. Electrochemically mediated ATRP process intensified by ionic liquid: a “flash” polymerization of methyl acrylate. Chem Eng J 2019;372:163–70.
22. Tang E, Yuan M, Li L, Bian F, Zhao D. Synthesis of microcrystalline cellulose grafting poly (methyl methacrylate) copolymers by ATRP in 1-allyl-3-methylimidazolium chloride. Adv Mater Res 2013; 621:157–61.
23. Xue T, Tang E, Guo X, Wang R, Zhao L, Zhou J, et al. CuBr coordinated by the ionic liquid [N_4MIM]Cl as a catalyst for biphasic ATRP in 1-allyl-3-methylimidazolium chloride ionic liquid. Eur Polym J 2018;106:182–7.
24. Zhou N, Wang Y, Zhou Y, Shen J, Zhou Y, Yang Y. Star-shaped multi-arm polymeric ionic liquid based on tetraalkylammonium cation as high performance gel electrolyte for lithium metal batteries. Electrochim Acta 2019;301:284–93.
25. Chen H, Liang Y, Liu D, Tan Z, Zhang S, Zheng M, et al. AGET ATRP of acrylonitrile with ionic liquids as reaction medium without any additional ligand. Mater Sci Eng C 2010;30:605–9.

26. Santha Kumar ARS, Roy M, Singha NK. Effect of ionic liquids on the RAFT polymerization of butyl methacrylate. Eur Polym J 2018;107:294–302.
27. Koyilapu R, Singha S, Kutcherlapati SNR, Jana T. Grafting of vinylimidazolium-type poly(ionic liquid) on silica nanoparticle through RAFT polymerization for constructing nanocomposite based PEM. Polymer (Guildf) 2020;195:122458.
28. Chen X, Liu X, Miao C, Song P, Xiong Y. Ionic liquid-like inimer mediated RAFT polymerization of *N*-isopropylacrylamide. Eur Polym J 2018;107:229–35.
29. Stepniak I, Andrzejewska E, Dembna A, Galinski M. Characterization and application of *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl)imide ionic liquid-based gel polymer electrolyte prepared in situ by photopolymerization method in lithium ion batteries. Electrochim Acta 2014;121:27–33.
30. Li M, Lei X, Huang Y, Guo Y, Zhang B, Tang F, et al. Ternary thiol-ene photopolymerization for facile preparation of ionic liquid-functionalized hybrid monolithic columns based on polyhedral oligomeric silsesquioxanes. J Chromatogr A 2019;1597:167–78.
31. Liu YD, Choi HJ. Recent progress in smart polymer composite particles in electric and magnetic fields. Polym Int 2013;62:147–51.
32. Yarimaga O, Jaworski J, Yoon B, Kim JM. Polydiacetylenes: supramolecular smart materials with a structural hierarchy for sensing, imaging and display applications. Chem Commun 2012;48: 2469–85.
33. Zhang SY, Zhuang Q, Zhang M, Wang H, Gao Z, Sun JK, et al. Poly(ionic liquid) composites. Chem Soc Rev 2020;49:1726–55.
34. Correia DM, Fernandes LC, García-Astrain C, Tariq M, Esperança JMSS, de Zea Bermudez V, et al. Magnetic ionic liquid/polymer composites: tailoring physico-chemical properties by ionic liquid content and solvent evaporation temperature. Compos B Eng 2019;178:107516.
35. Zhao J, Liu Y, Zheng C, Lei Q, Dong Y, Zhao X, et al. Pickering emulsion polymerization of poly(ionic liquid)s encapsulated nano-SiO_2 composite particles with enhanced electro-responsive characteristic. Polymer (Guildf) 2018;146:109–19.
36. Yang F, Wu D, Luo Z, Tan B, Xie Z. Hybrid organic-inorganic dyeionogels: reversibly pH-responsive materials based dye-ionic liquids with improved structural stability and flexibility. Sensor Actuator B Chem 2017;249:486–92.
37. Pipertzis A, Mühlinghaus M, Mezger M, Scherf U, Floudas G. Polymerized ionic liquids with polythiophene backbones: self-assembly, thermal properties, and ion conduction. Macromolecules 2018;51:6440–50.
38. Nagy B, Geissler E, László K. Room temperature ionic liquids to tailor resorcinol – formaldehyde polymer gels. Microporous Mesoporous Mater 2020;294:1–10.
39. Guo J, Xu Q, Zheng Z, Zhou S, Mao H, Wang B, et al. Intrinsically antibacterial poly(ionic liquid) membranes: the synergistic effect of anions. ACS Macro Lett 2015;4:1094–8.
40. Wei X, Wang Y, Chen J, Ni R, Meng J, Liu Z, et al. Ionic liquids skeleton typed magnetic core-shell molecularly imprinted polymers for the specific recognition of lysozyme. Anal Chim Acta 2019; 1081:81–92.

Index

https://doi.org/10.1515/9783110726145-012