



Removal of heavy metals (Cu^{2+} and Cd^{2+}) from wastewater using chemically activated watermelon peels

Shehu A^{1*} and M. B. Ibrahim²

¹Departments of General Studies Federal College of Agricultural Produce Technology, Kano, Nigeria

²Department of Pure and Industrial Chemistry, Bayero University, P.M.B3011, Kano-Nigeria

Corresponding author Email:

Received 18 Apr 2023, Revised 21 May 2023, Accepted 25 May 2023

Cited as: Shehu A. and Ibrahim M. B. (2023), Removal of heavy metals (Cu^{2+} and Cd^{2+}) from wastewater using chemically activated watermelon peels Arabian Journal of Chemical and Environmental Research, 10 Issue 1, 27–34

Abstract

Activated Carbon of high adsorption efficiency and highly active surface properties were prepared from water melon fruits peels, then carbonized using muffle furnace at 300°C for 30 minutes, 1M H_2SO_4 solution was used to activate the samples. The adsorption efficiency of the activated carbon is considered on the following; the effect of contact time, adsorbent dosage, and concentration. The adsorptive efficiency of the adsorbent in removing Cadmium (Cd^{2+}) and Copper (Cu^{2+}) ions from wastewater were compared. The Cu^{2+} and Cd^{2+} adsorption isotherm on activated orange peels impregnated corresponded with the Langmuir isotherm ($R^2 = 0.958$). However, the Freundlich adsorption isotherm was a superior ($R^2 = 0.9767$). On the whole a chemically activated watermelon peel was a good adsorbent for the treatment of wastewaters, for a cleaner and healthier environment.

Keywords: wastewaters, activated carbon, adsorption efficiency, water melon

*Corresponding author.

E-mail address: akchemist88@gmail.com

1. Introduction

Lack of clean water for drinking is an enormous challenge in most of the developing countries of the world due to daily contamination by excessive release of heavy metals into the environment as a

result of industrialization and urbanization which Nigeria is not exceptional (Agbaire *et al.*, 2014; El Hammari *et al.*, 2022; Ikpe *et al.*, 2022). Industrial uses of metals and other domestic processes have introduced substantial amounts of potentially toxic heavy metals into the atmosphere and into the aquatic and terrestrial environments. Heavy metals are elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0 (Ubong *et al.*, 2023; Srivastava & Majumder, 2008). They are generally referring to the elements such as Cd (cadmium), Cr (chromium), Cu (copper), Hg (mercury), Ni (nickel), Pb (lead), Fe (iron) and Zn (zinc) which are commonly associated with pollution and toxicity problems (Ad *et al.*, 2015; Belbachir *et al.*, 2013). Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless final products (Elmouaden *et al.*, 2015; Ikpe *et al.*, 2017). They occur naturally in rock formation and ore minerals and so a range of normal background concentration is associated with each of these elements in soils, sediments, waters and living organisms (Uwantae *et al.*, 2023; Kierczak *et al.*, 2021; Jodeh *et al.*, 2015; Ukpong *et al.*, 2013). In small quantities, certain heavy metals are nutritionally essential for healthy life, some of these are referred to as the trace elements (e.g., iron, copper, manganese, and zinc). These elements, or some form of them, are commonly found naturally in foodstuffs, in fruits, fishes and vegetables, and in commercially available multivitamin products (Imoisi *et al.*, 2020; Karim *et al.*, 2015). Heavy metals are also common in industrial applications such as in the manufacture of pesticides, batteries, alloys, electroplated metal parts, textile dyes, steel, mining, refining ores, fertilizers industries, and paper industries (Ubong *et al.*, 2020; Jadaa *et al.*, 2023). Many of these products are in our homes and actually add to our quality of life when properly used.

Water pollution by heavy metals is one of the most important environmental problems today because they do not degrade into harmless products, tend to accumulate and are toxic to human beings. Among the heavy metals, cadmium is one of the extremely toxic and has been classified as a human carcinogen and teratogen impacting lungs, liver and kidney (Charkiewicz *et al.*, 2023; Ikpe *et al.*, 2020). The main contamination sources of this element are anthropogenic: industry wastewaters, mining operations, waste incineration as well as the combustion of some coals and oils. Increasing global emission of cadmium compounds into the atmosphere, together with aqueous and solid emission lead to local contamination problems. An additional problem of Cd²⁺ toxicity is its accumulative character. The US Environmental Protection Agency (USA EPA) has established a maximum contaminant level of 0.005 mg/L for cadmium in drinking water, while the World Health Organization (WHO) has set a maximum guideline concentration of 0.003 mg/L (Krystyna *et al.*, 2019).

Given widespread Cadmium (Cd²⁺) and Copper (Cu²⁺) ions contamination and the low drinking water guideline, there is considerable interest to remove it before discharge wastewaters. Several

treatment methods can be used for this purpose, such as filtration, chemical precipitation, coagulation, solvent extraction, ion exchange, adsorption, membrane process, and bioremediation (Akpakpan *et al.*, 2018; Abidi *et al.*, 2022).

Among these techniques, adsorption has been recognized as one of the most popular methods due to its simplicity of operation, high efficiency, easy recovery and cost-effectiveness. An ideal adsorbent for this purpose should have high surface area, high adsorption capacity, mechanical stability and be easily regenerated. The process parameters such as solution pH, temperature, contact time and dosage of adsorbent also have significant impacts on the adsorption effectiveness. The aim of the study is to determine the adsorption efficiency of chemically activated water melon peel

2. Materials and methods

2.1 Sample Collection and Treatment

Water melon fruit were purchased from Monday market, Borgu local government, New Bussa Niger State, Nigeria. Thereafter, the water melons were washed and the peels collected. The water melon peels were then sun dried for one month to remove the moisture using standard analytical method described by (Huang *et al.*, 2017). The water melon peels were ground into smaller bits using an electronic blender. The water melon peels were then carbonized using a muffle furnace at 300°C. The carbonized water melon peels were then activated with 1M conc. H₂SO₄. Thereafter, it was washed with distilled water until the pH of the adsorbent was brought to neutral. The adsorbent was then dried at 105°C using an oven for 3 hours in order to evaporate the water used in washing the water melon peels.

2.2 Adsorbate Preparation

Copper (Cu²⁺) solution was prepared from its salt of Copper nitrate Cu (NO₃)₂ and Cadmium (Cd²⁺) solutions was as well prepared from its salt of Cadmium chloride (CdCl₂.21/2H₂O). The stock solutions were prepared taking 1 g of each salt and dissolved in 1000 ml volumetric flasks separately and then diluted with deionized water to the mark which gave a concentration of 1000 ppm. Thereafter, Serial dilution was prepared from the stock solutions of Cu²⁺ and Cd²⁺ where concentrations of 50 ppm, 75 ppm, 90 ppm, 115 ppm and 140 ppm were prepared by diluting 5 ml, 7.5 ml, 9 ml, 11.5 ml and 14 ml in 100 ml of deionized water respectively (Ikpe *et al.*, 2017).

2.3 Contact Time

Varying time of 20, 25, 30, 35 and 40 min was used during the study of the effect of contact time on adsorption of the heavy metals. A fixed mass of 2.5 g of adsorbent was placed into several bottles of 50 ml of 50 ppm of solutions added. Mechanical Orbital Shaker was used in shaking the solutions for

various times of 20, 25, 30, 35 and 40 min before they were filtered and the filtrate analyzed using the Atomic Absorption Spectrophotometer (Ikpe *et al.*, 2022).

2.4 Dosage

Adsorbent Dosage of 1 g, 1.5 g, 2 g, 2.5 g and 3g were placed into different 100 ml polyethylene bottles with 50 ml of 50 ppm of the solutions of copper nitrate and Cadmium chloride respectively. The solution was shaken using a Mechanical Orbital Shaker for 20 min, then the filtrate of the mixture was analyzed using Atomic Adsorption Spectrophotometer (Ikpe *et al.*, 2020).

2.5 initial metal Concentration

2.5 g of adsorbent was placed into several 100 ml polyethylene bottles, 50 ml solutions with concentrations of 50, 75, 90, 115 and 140 ppm of Cu^{2+} and Cd^{2+} obtained from 1000 ppm stock solutions was added and shake for 20 min using Mechanical Orbital Shaker. An atomic adsorption spectrophotometer was used to analyze the filtrate obtained from the mixture (Huang *et al.*, 2007).

3. Results and discussion

3.1 Effect of contact time

The figure 1 shows, with increasing in contact time, the amount adsorbed increases, as there is enough time for interaction and efficient contact time between the adsorbent and adsorbate. The patterns of the curve established that the adsorption is time dependent in which adsorption efficiency was proportionally related to time (Ukpong *et al.*, 2013).

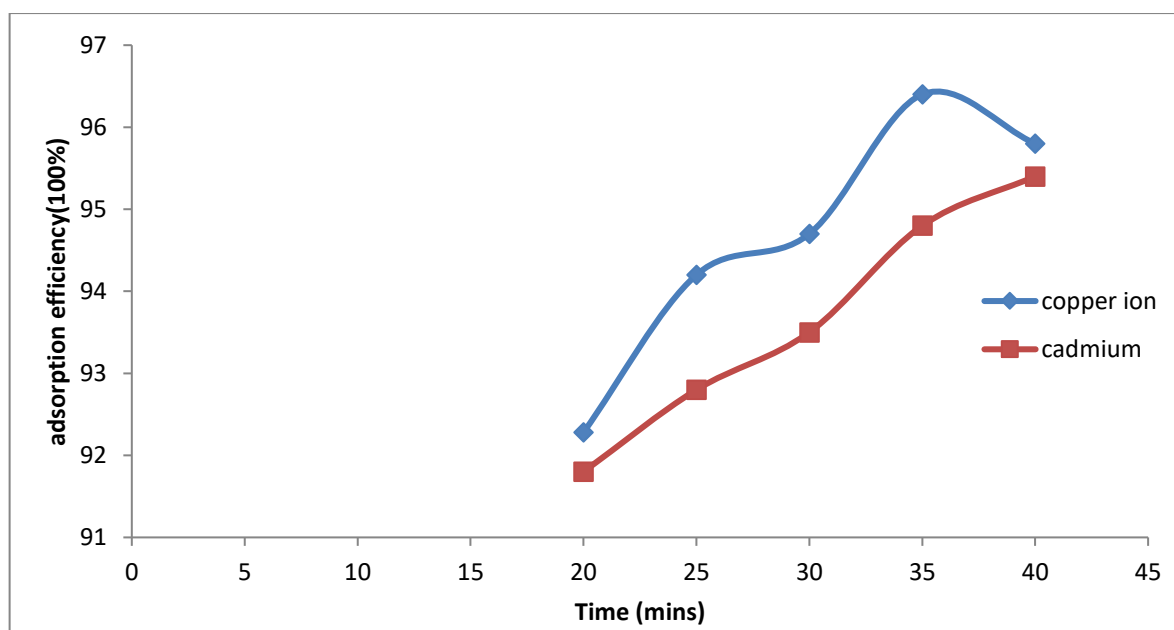


Figure 1 Effect of contact time on adsorption of Cu^{2+} and Cd^{2+}

The result indicates that adsorption efficiency for Cu^{2+} increased from 92.28% with a contact time of 20 mins to a maximum point of 96.80% with a contact time of 20 mins while in case of Cd^{2+} the adsorption efficiency was increased from 95.40% at 20 mins to 95.40% at 40 mins.

3.1 Effect of adsorbent dosage

The rate of adsorption was found to increase with increase in the adsorbent dosage from 1 to 3 g for each of the test carried out. The availability and accessibility of adsorption site is controlled by adsorbent dosage. At constant initial concentration of 50 mg/l, a constant time of 20 minutes (Othman *et al.*, 2013).

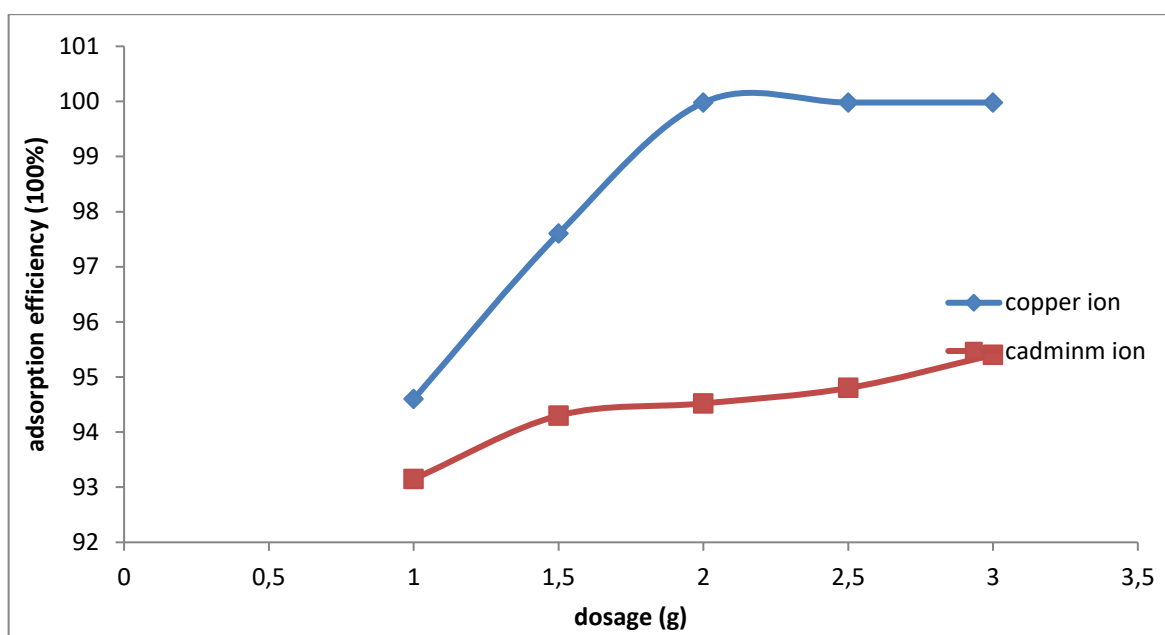


Figure 2 Effect of adsorbent dosage on adsorption of Cu^{2+} and Cd^{2+}

Effect of initial concentration

The efficiency of metal uptake by an adsorbent is highly dependent on the initial metal ion concentration of the solution. Figure 1 showed the initial metal ion adsorbed onto the chemically activated carbon decreases as the initial metal ion concentration increases. The reason for the decrease in adsorption efficiency is due to the relatively smaller number of active sites available on adsorbent. The decrease in adsorption efficiency can be explained by the fact that as the concentration of the adsorbate increases so does the metal loading on the adsorbent (McKay *et al.*, 1995), so when the concentration is higher, more ion will be competing for the same adsorption sites and go through without being adsorbed. The results indicated that there is a great interaction between the adsorbent and adsorbate in solutions of lesser initial concentration in Cu^{2+} with adsorption of 99.96% and 99.90% at 50 mg/l compared to Cd^{2+} with adsorption efficiency of 98.81% and 98.64% at 140 mg/l.

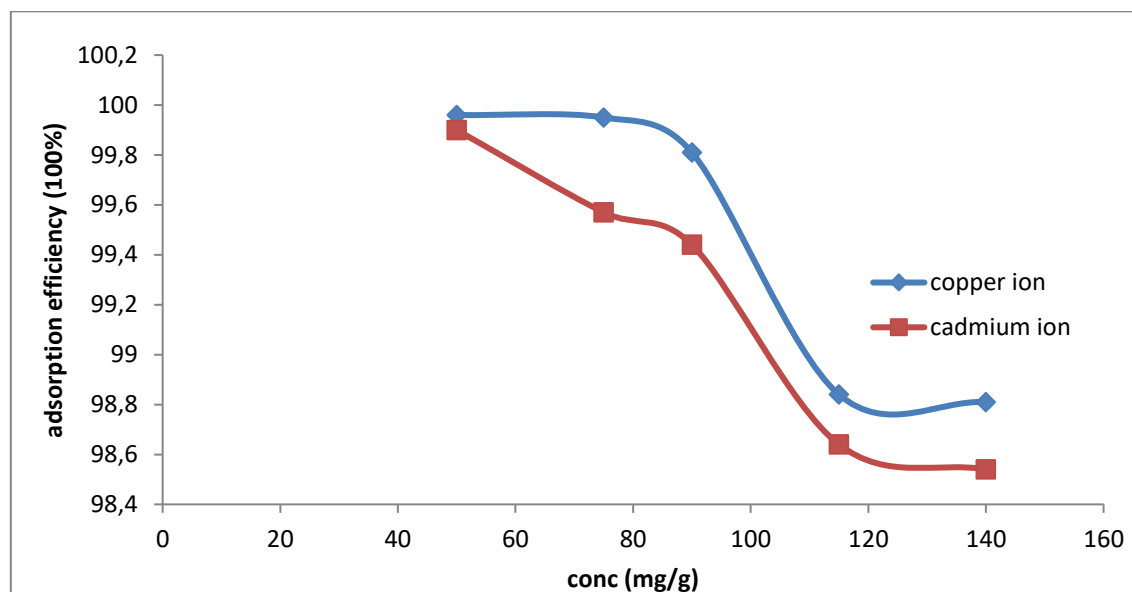


Figure 3. Effect of initial concentration on Adsorption of Cu^{2+} and Cd^{2+}

3.3 Adsorption isotherm

In successful representation of equilibrium adsorption behaviour, it is important to have a satisfactory description of the equation between the various phases composing the adsorption systems. The equilibrium data obtained for copper and cadmium for their adsorption using chemically activated water melon peel was analyzed using the Langmuir and Freundlich Adsorption Isotherm (Ahmadi *et al.*, 2022; Roy *et al.*, 2022).

Adsorption isotherm studies were carried out to determine the approximate estimation of adsorption capacity of an adsorbent and the intensity of heavy metal ions uptake using adsorbent dosage at constant concentration of 50 mg/l of metal ion. With the Langmuir's equation to analyze copper and cadmium adsorption isotherm, at regression value ($R^2 = 0.958, 0.9767$) and the graph shows the relationship between c_e/q_e in the y-axis and c_e in the x-axis while the Freundlich equation shows the relationship between $\log c_e$ on the x-axis and $\log q_e$ on the y-axis.

Conclusion

- Activated Carbon were prepared from water melon fruits peels and carbonized using muffle furnace at 300°C.
- Excellent adsorption efficiency and highly active surface were provided
- The Activated Carbon served to remove Cadmium (Cd^{2+}) and Copper (Cu^{2+}) from wastewater.
- Langmuir and Freundlich adsorption isotherms were discussed.

Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

- Abidli A., Huang Y., Ben Rejeb Z., *et al.* (2022), Sustainable and efficient technologies for removal and recovery of toxic and valuable metals from wastewater: Recent progress, challenges, and future perspectives, *Chemosphere*, 292, 133102, doi.org/10.1016/j.chemosphere.2021.133102
- Ad C., Benalia M., Laidani Y., Elmsellem H., *et al.* (2015) Adsorptive removal of cadmium from aqueous solution by *Luffa Cylindrica*: Equilibrium, dynamic and thermodynamic, *Der Pharma Chemica*, 7N°12, 388-397
- Agbaire P. O., Akporid S. O., Akporhonor E. E. (2014). Water Quality Index Assessment of Borehole water in the Hostels in One of the Higher Institutions Delta State. *Research Journal of Chemical Sciences*, Department of Chemistry, Delta State University, Abraka, Nigeria. 4(7), 78-81.
- Ahmadi H., Hafiz S.S., Sharifi H., Rene N.N., Habibi S.S., Hussain S. (2022), Low cost biosorbent (Melon Peel) for effective removal of Cu (II), Cd (II), and Pb (II) ions from aqueous solution, *Case Studies in Chemical and Environmental Engineering*, 6, 100242, ISSN 2666-0164, <https://doi.org/10.1016/j.cscee.2022.100242>
- Akpakpan, A.E., Nsi, E.W., Ekpenyong, A., and Ikpe, E.E. (2018) Equilibrium, kinetics and Isotherm studies on the Adsorption of Eosin and Malachite green using activated carbon from *Huracrepitans* seed shells. *AASCIT Journal of Environment* 3(2), 24 -28.
- Belbachir C., Aouniti A., Khamri M., Chafi A., Hammouti B. (2013) Heavy metals (copper, zinc, iron and cadmium) in sediments and the small clam (*Chamelea gallina*) of the coastal area north-east of Morocco, *J. Chem. Pharm. Res.*, 5 N(12), 1307-1314
- Charkiewicz A.E., Omeljaniuk W.J., Nowak K., Garley M., Nikliński J. (2023) Cadmium Toxicity and Health Effects-A Brief Summary. *Molecules*, 28(18), 6620. [doi: 10.3390/molecules28186620](https://doi.org/10.3390/molecules28186620)
- El Hammari L., Latifi S., Saoiabi S., Saoiabi A., *et al.* (2022), Toxic heavy metals removal from river water using a porous phospho-calcic hydroxyapatite, *Mor. J. Chem.* 10(1), 62-72, <https://doi.org/10.48317/IMIST.PRSM/morjchem-v10i1.31752>
- Elmouaden K., Chaouay A., Oukhrib R., O. Jbara, S. Jodeh, R. Salghi, O. Hamed, M. Hilali, L. bazzi, B. Hammouti, S. Radi, (2015) Microbiological Pollution of Marine Environment of the Coastal of Agadir. Impact on the Corrosion of Mild Steel, *Int. J. Electrochem. Sci.*, 10N°10, 7955-7965
- Ikpe, E.E., Ubong U.U., and Archibong U. (2022). Proximate analysis, heavy metals and total hydrocarbon content of *Callinectes sapidus* obtained from Ibaka River, Akwa Ibom State, Nigeria. *REJOST*. 1-43.
- Ikpe, E.E., Esua E., Ekwere, I., Willie, I., Olumide, A. (2017) Analytical assessment on the removal of phenol from aqueous solution using orange peel based activated –carbon. *American Journal of Engineering Research*. 6 (12) 129 – 133.
- Ikpe, E.E., Ekwere I.O., Ukpong E.G., Effiong J.O., Okon O.E. (2020) Assessment of heavy metals and hydrocarbons in *Rhizophora mangle*, *Callinectes sapidus*, and sediment in Qua-Iboe River, Akwa Ibom State, Nigeria. *Global Journal of Advanced Engineering Technology*. 7(3), 1-8
- Imoisi, O.B., Ukhun, M.E., Ikpe, E.E. (2020) Quality parameter of olein, palm kernel oil and its blends subjected to thermal stress using photometric technology. *Eur. J. Agric. Food Sci.*, (2) 5, 1-18.
- Jadaa W., Mohammed H.K. (2023). Heavy Metals – Definition, Natural and Anthropogenic Sources of Releasing into Ecosystems, Toxicity, and Removal Methods – An Overview Study. *Journal of Ecological Engineering*, 24(6), 249-271. <https://doi.org/10.12911/22998993/162955>

- Jodeh S., Odeh R., Sawalhi M., *et al.* (2015), Adsorption of lead and zinc from used lubricant oil using agricultural soil: equilibrium, kinetic and thermodynamic studies, *J. Mater. Environ. Sci.* 6(2), 580-591
- Huang, Y. H. (2007). Thermodynamics and kinetics of adsorption of Cu (II) onto waste iron oxide. *Journal of hazardous materials.* 144(1), 406-411
- Karim S., Aouniti A., El hajjaji F., *et al.* (2016), Bioaccumulation of heavy metals in commercially important marine fishes (*Palaemon Serratus* and *Solea Vulgaris*) caught in the Mediterranean coast from the North East of Morocco, *Der Pharma Chemica*, 8(19), 515-523
- Kierczak J., Pietranik A., Artur Pędziwiatr A. (2021), Ultramafic geoecosystems as a natural source of Ni, Cr, and Co to the environment: A review, *Science of The Total Environment*, 755, Part 1, 142620, ISSN 0048-9697, <https://doi.org/10.1016/j.scitotenv.2020.142620>
- Krystyna, P. (2019) Removal of Cadmium from wastewaters with low-cost adsorbents. *Journal of Environmental Chemical Engineering.* 7(1), 102795.
- McKay, G. (1995). Use of Adsorbents for the Removal of Pollutants from Wastewaters. CRS Press, Boca Raton, FL.
- Othman N., Azhar N., Megat Abdul Rani P. S, and Zaini H. M. (2016). Metal Removal and Antimicrobial Properties of Watermelon rind modified with clove, *MATEC Web of Conferences* 7, 01028 (2016) DOI: [10.1051/mateconf/20167801028](https://doi.org/10.1051/mateconf/20167801028)
- Roy DC *et al* (2020) Isolation and characterization of two bacterial strains from textile effluents having malachite green dye degradation ability. *bioRxiv*, 2020, 1–15
- Srivastava N.K., Majumder C.B. (2008), Novel biofiltration methods for the treatment of heavy metals from industrial wastewater, *Journal of Hazardous Materials*, 151, Issue 1, 1-8, ISSN 0304-3894, <https://doi.org/10.1016/j.jhazmat.2007.09.101>
- Ubong, U.U., Ikpe, E.E., Ekanem, A.N., Jacob, J.N., and Archibong U.D. (2023) Heavy metals profile of the proposed dumpsite at Ntak- Inyang Itam, Akwa Ibom State, Nigeria *Journal of Geography, Environment and Earth Science International* 27(2), 17 -28.
- Ukpong, E. C. and Okon, B. B. (2013). Comparative Analysis of Public and Private Borehole Water Supply Sources in Uruan Local Government Area of Akwa Ibom State. *International Journal of Applied Science and Technology*, Department of Civil Engineering, Faculty of Engineering, University of Uyo, Akwa Ibom State, Nigeria, 3(1), 30-45.
- Uwanta, E.J., Nicholas, E.S., Ikpe, E.E., Ocheni, A. (2023) Comparative spectrophotometric determination of Neodymium(III), Samarium(III) and Terbium(III) in aqueous and micelle media. *Science Journal of Chemistry* 11(2), 64-76.
- Ubong, U.U., Ekwere, I.O., Ikpe, E.E. (2020) Risk and toxicity assessment of heavy metals in *Tympanotomus fuscatus* and sediment, Iko River, Akwa Ibom State, Nigeria. *International journal of environment and climate change.* 10(3), 1-10.

(2023); www.mocedes.org/ajcer