**Jewel Journal of Scientific Research (JJSR) 7(1): 51–58, 2022**
**©Federal University of Kashere-Nigeria (Print ISSN: 2384 – 6267, Online ISSN 2756-651X)**
**jjsr.fukashere.edu.ng**

# Utilization of Bio-adsorbents for the adsorption of heavy metals in wastewater: Effect of kinetic parameters

**F. U. Mukhtar [1], A. L. Yaumi [1]*, A. S. Girei [1], H. Umar, [1] and I. A. Usman[2]**
[1]Department of Chemical Engineering, University of Maiduguri, P.M.B 1069, Borno State
[2]Department of Physics, Federal University of Kashere, P.M.B 182, Gombe State
***Corresponding Author**: aliyaumi@unimaid.edu.ng; +2348037387456

**Abstract**

A new and novel Bioadsorbent was obtained from the blend of Moringa, Okra and Pumpkin, (MOP). Moringa, Okra and Pumpkin seed (MOP) were used as a toxin-free, locally available material and economically adsorbent in the present study. This study focuses on the adsorption of Cr, Cd, Zn, Pb, and Fe from an aqueous solution. The adsorption experiment was performed using a series of flasks containing 50 ml solutions of wastewater at desired concentration with the mass of the adsorbent. Atomic Adsorption Spectrophotometer (AAS) was used to determine the concentration of the heavy metals. The results revealed that a pH of 6, reaction temperature of 35 ˚C, 90 minutes contact time and 0.5 g adsorbent dosage were the optimum reactive condition of the process having 4.1, 3.6, 4.3, 3.5 and 4.0 mg/g maximum adsorption capacity for Cr, Fe, Pb, Zn, and Cd respectively. Therefore, it is evident that Moringa, Okra and Pumpkin seeds can be effectively utilized to reduce the concentration of heavy metals in wastewater.

**Keywords:** Heavy Metals, Bioadsorbents, Adsorption, Kinetic parameters, Moringa

*Received:* 2nd Nov., 2021 *Accepted:* 24th Mar., 2022 *Published Online:* 7th April, 2022

## Introduction

Rapid Industrialization and the release of harmful effluent from the industries into the water bodies affect the quality of water making it poor for utilization. Heavy metals are one of the pollutants that affect the quality of water (Malik *et al*., 2020). Their existence in the water body's cause's contamination in the food chain destroys aquatic lives. There is evidence that shows even at a lower concentration, heavy metals are capable of producing illnesses such as various types of cancers, vascular disease, kidney damage, diarrhea, dermatitis and brain damage (Babel and Kuniawan, 2003). Based on the fact that 59 elements are classified as heavy metals due to their specific density higher than 5 g/cub.cm and their high atomic weight (Al-Qahtani, 2015). Heavy metals such as Zinc (Zn), Cadmium (Cd), Lead (Pb), Chromium (Cr) and Iron (Fe) are highly toxic and hazardous (Ebrahimi *et al.*, 2012; Babel and Kuniawan, 2003). There are several methods of removing heavy metals from wastewater like the Ion-Exchange, membrane filtration, adsorption and chemical precipitation were used to expel the metal pollutants from wastewater (Ghaedi *et al*., 2012). However, the Adsorption process has great advantages in the removal of heavy metals in an aqueous solution due to its simplicity in design, low energy requirement and effectiveness. The Adsorption process largely depends on the type of material used to remove the desired adsorbate.

Numerous natural-based materials were studied as an alternative for the adsorption of heavy metals from aqueous solutions such as zeolite (Taamneh & Sharadqah, 2017), Fibers (Coşkun *et al.,* 2006), and nanocrystals (Abiaziem *et al*., 2019). However, these methods have high energy requirements. Bioadsorbent derived from agro-waste are low-cost materials with excellent elemental composition and good surfaces which can be utilized for the removal of heavy metals in an aqueous solution (Jain & Prasad, 2008). Moringa seed is a shrub mostly grown in Africa and the Asian region (Parrotta, 2018). The seed of Moringa, Okra and Pumpkin are mostly considered as waste in the developing country, therefore there is a need to find a means of harnessing these materials to combat the problem of waste in the environment (Sulyman, 2017). Hence, this study is aimed at utilizing this bioadsorbents for the removal of heavy metals in wastewater. The effect of kinetic parameters on the adsorption process will also be examined.

## Materials and Methods

### Precursor Preparation

The Moringa, (MO), Okra, (OK) and Pumpkin, (PM) were obtained from the local market in Maiduguri, Borno State, Nigeria. The seeds of the bioadsorbent were washed severally with water, dried in an oven, sorted to remove bad ones and was grinded with high speed electric blender and stored in an air-tight container APHA (2005).

### Adsorption of Bioadsorbent

The experiment for the adsorption and kinetic studies were carried out by preparing a stock solution of the Cr, Fe, Zn, Pb and Cd by dissolving the quantity of the annular grade salts in 1000 mL of de-ionized water. The stock solution was further diluted using distilled water to obtain the solutions of the various known concentration. The adsorption was carried out in batch using a series of flasks containing 50 ml solutions of waste water at desired concentration with the mass of adsorbent. The mixture was mixed at different ratios 2:1:1 (Moringa, Okra and Pumpkin respectively) at 250 rpm using a shaker (jar test equipment). Atomic Adsorption Spectrophotometer (Edibon) was used to determine the concentrations of the heavy metals. The effect of dosage was studied from 0.1- 0.8 g. The initial concentrations used was 10 mg/l. The effect of dosage was studied from 0.1- 0.8 g at concentration of 10 mg/L by adsorption. The effect of concentration was investigated between the range of 50 - 400 mg/L, the contact time was varied from 10 - 120 min, pH between the range of 6 - 8 and the effect of temperature was studied from 25 - 55 $^0$C respectively. At equilibrium, the adsorption $q_e$ (mg/g), was calculated by Equation 1:

$$q_e = \frac{(C_o - C_e)V}{\mathrm{m}} \qquad 1$$

Where $C_o$ and $C_e$ (mg/l) are the concentrations of the heavy metals at initial and at equilibrium, V is the volume of the solution (L) and m is the mass of the adsorbent used (g). The heavy metal removal percentage was calculated using Equation 2:

$$\%\ Heavy\ metal\ removal\ = \frac{(C_o - C_e)}{C_o}\ x\ 100 \qquad 2$$

## Results and Discussion

### Effect of Moringa, Okra and Pumpkin Seeds Dosage on Metal Ion Adsorption

The adsorbent dose is one of the most important factors that determine the adsorption capacity of adsorbent for a given initial concentration. The effect of the adsorbent dose on the adsorption of five heavy metals (Fe, Cr, Cd, Zn and Pb) is shown in Figure 1. As the dosage was increased from 0.1 - 0.8 g, the percentage removal of chromium concentration was increase from 58 % to 92.2 %. There was a rapid increase from 0.1 - 0.4 which was due to the unsaturated sites available during the adsorption reaction and the number of sites available for the adsorption sites increases by increasing the adsorbent dosage. Moreover, after the dosage of 0.5 g, there was insignificant change in the percentage removal of chromium concentration. This is as a result of the overlapping of the active site at a higher dosage as reported by Manzoor *et al.* (2013).

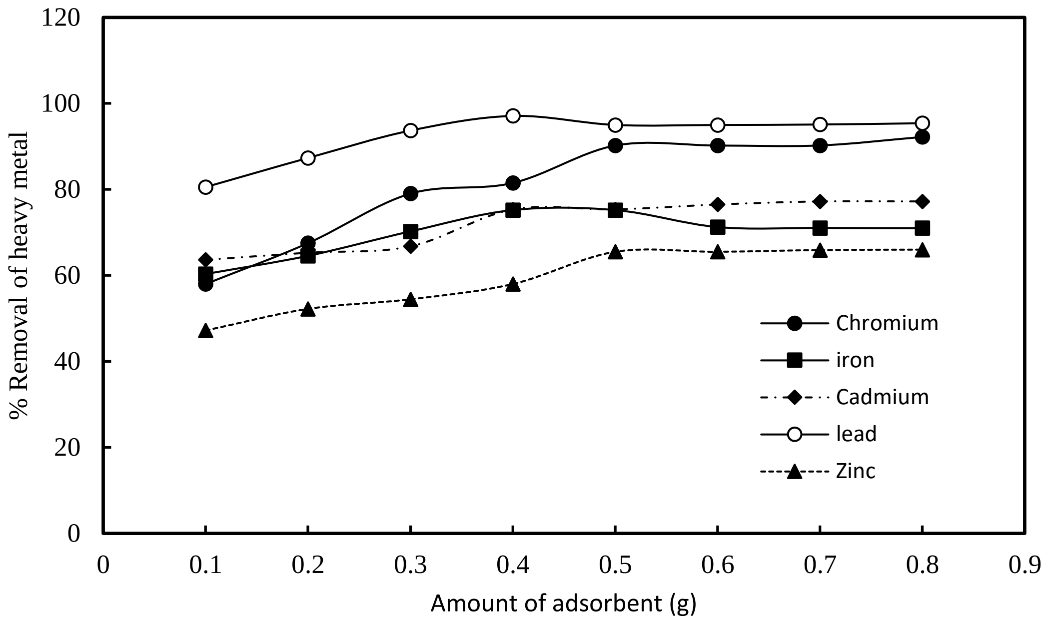


**Figure 1:** Effect of dosage on the adsorption of heavy metals

Furthermore, as the dosage was increase from 0.1 - 0.5 g, the rate of adsorption of iron concentration was increased from 60.33 % to 75.2066 %, this is due to the unsaturated active sites available during the adsorption process and the number of adsorptions increases with increase of the adsorbent dosage. However, at 0.4 - 0.5 g, the percentage removal of the heavy metal was stable. At 0.6 - 0.8 g, the adsorption drops slightly, this is due to the overlapping of active site as a result of higher dosage as reported by Manzoor *et al.*, (2013).

For cadmium, there is high rate of adsorption from 0.1 - 0.4 g of the adsorbent dosage. This is due to the high active site occupied by the adsorbent dosage. The adsorption rate has increased from 63.66 % to 75.362 %. At the dosage of 0.5 - 0.8 g it attends equilibrium due to the saturation of the active site on the adsorbent. As the dosage was increased from 0.1 - 0.8 g, there was a rapid respond in the heavy metals removal of lead from 80.55 % to 95.4 %. Which means Moringa, Okra and Pumpkin Seeds has a high rate of removal of lead ion concentration more than Chromium, Iron, Zinc and Cadmium.

Zinc is one of the heavy metals found in Wastewater. Their high concentration is toxic to human health and environment. The zinc concentration can be reduced using a cheap locally available bioadsorbent (Moringa, Okra and Pumpkin Seeds). It was observed that increase of the dosage from 0.1 - 0.5 g increases the removal of zinc concentration from 47.2 % to 65.5 %. This is due to the number of active sites which increases with the number of dosages. With further increase of the dosage from 0.6 - 0.7 g, it still maintains a removal of 65.5 % which is due to the saturation of the active sites. Further increase to 0.8 g increases the removal uptake to 66 %. The increase in adsorption percentage with increasing adsorbent dose arises because of the availability of the active site or exchange sites at higher concentrations of adsorbents (Al-Qahtani *et al.*, 2016).

**Effects of Contact Time and Initial Metal Ion Concentrations**

One of the most important parameters used in the design of adsorption is the equilibrium time. Contact time was optimized from (10 – 120 min) for the maximum removal of heavy metals with the initial concentrations of 50 - 500 mg/L for Cr, Fe, Pb, Zn and Cd. The effect of contact time and initial concentration on the removal of Fe, Cr, Cd, Zn and Pb by Moringa, Okra and Pumpkin seeds adsorbents is given in Figure 2(a-e).

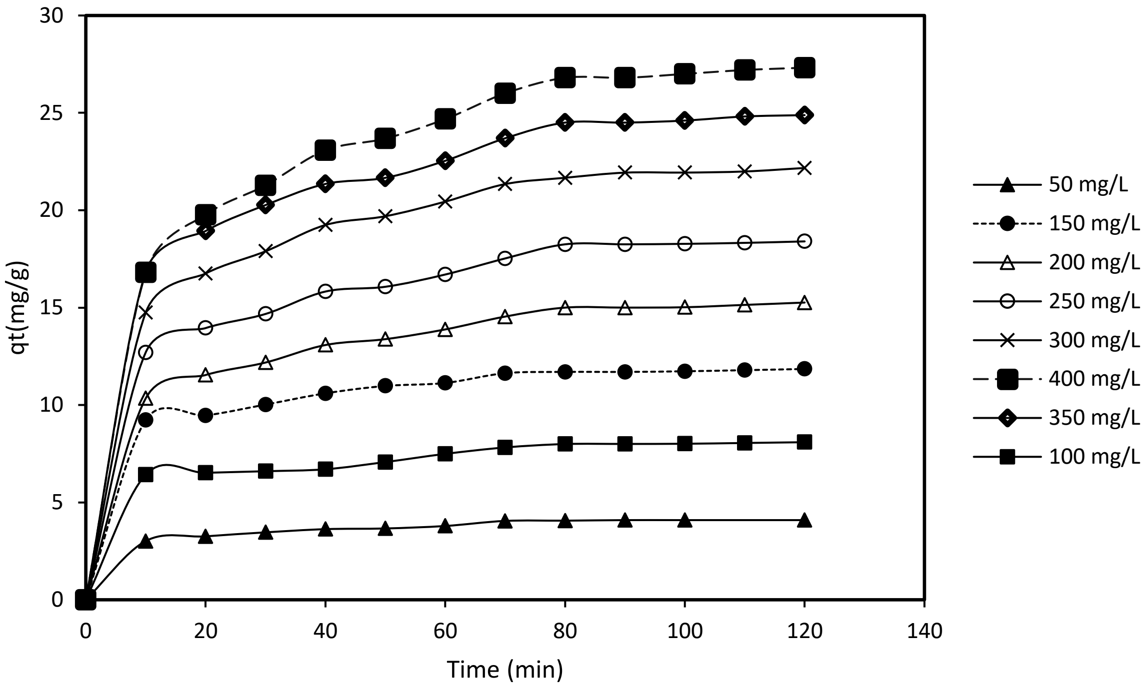


**Figure 2(a):** Effect of Contact Time and Initial Concentration of Chromium

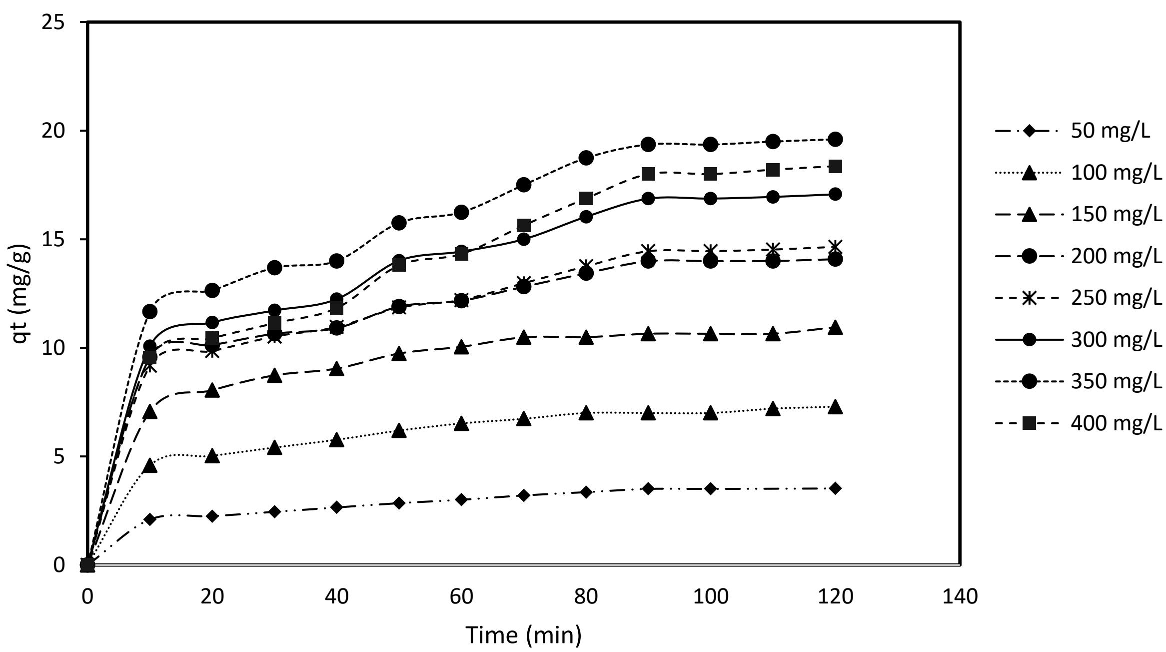


**Figure 2(d):** Effect of Contact Time and Initial Concentration of Lead

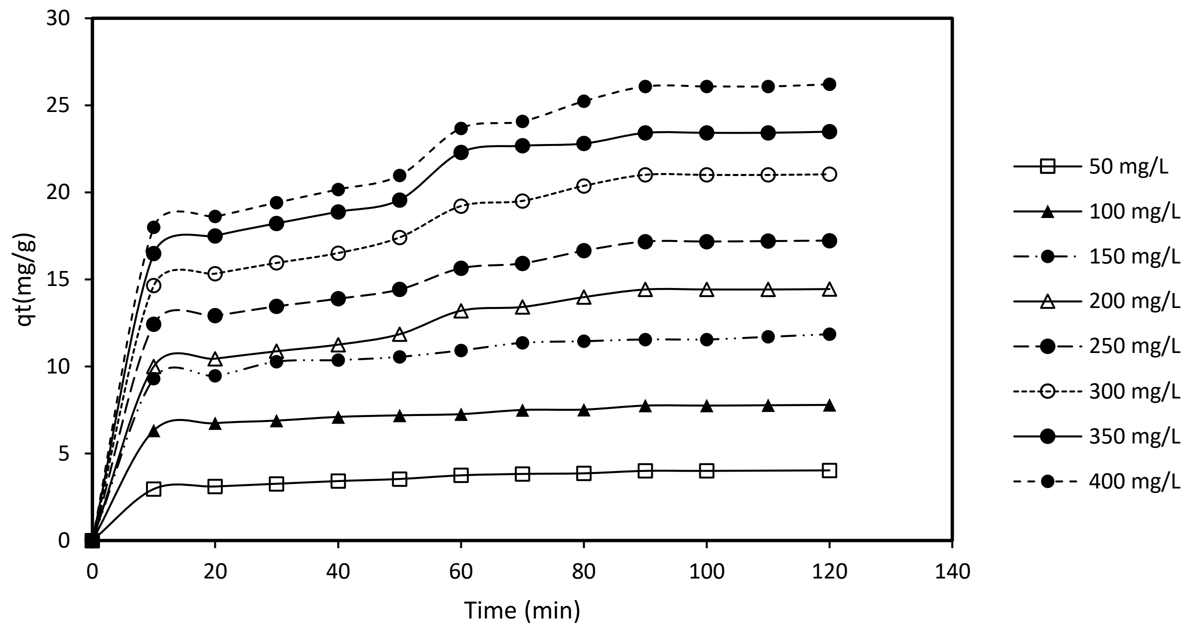


**Figure 2(e):** Effect of Contact Time and Initial Concentration of Cadmium

In Figure 2(a-e), it shows that there was a very fast adsorption of the Chromium ion, Iron, Lead, Zinc and cadmium ion in the fast 10 minutes and more than 60 % of the chromium was adsorbed (3.0 mg/g); 70 % of the Lead was adsorbed (3.5 mg/g); 59 % of the Cadmium was adsorbed (2.5 mg/g); 46 % of the Cadmium was adsorbed (2.3 mg/g); 41 % of the Cadmium was adsorbed (2 mg/g) at initial concentration. The rapid initial sorption was likely due to extra-cellular binding and the slower sorption likely resulted from intracellular binding (Okoye *et al*., 2010). Equilibrium were reached at 80, 90, 70, 90 and 90 min for, $Fe^{+}$, $Pb^{+}$, $Zn^{+}$ and $Cd^{+}$ respectively and at later stages the percentage increment is very slow across the times. Similar results have been reported by Al-Anber, (2011) evaluated the effect of contact time by varying the times in minutes. In his work, it was also discovered that the rate of adsorption was rapid in the first ten minutes where the maximum adsorption was achieved and at later stages, there was a minimum adsorption across the increment in contact times. At the initial stage, the rapid increase on the uptake of the metals ion is due to the availability of the uncovered surface and also the active sites on the surface of the adsorbents (Zou *et al.,* 2006). With increase in contact time the pores were filled and the rate became slower (Chowdhury *et al.,* 2011). It was observed that with increase of the initial concentration of Fe, Cr, Cd, Zn and Pb from 50 to 400 mg/L, the maximum adsorption took place at 50 mg/L, the percent removal of Chromium (Cr), Iron (Fe), Lead (Pb), Zinc (Zn) and Cadmium (Cd) by the adsorbent (Moringa, Okra and Pumpkin seeds) decreased from 81 % to 68.88 %, 87.78 to 25 %, 86.6 to 22.53 %, 77.4 to 67.42 %, and 83.56 to 71.75 % respectively. This means that the highest adsorption affinity occurred at lower concentrations of the heavy metals and this was agreed with the results obtained by (Chowdhury *et al.,* 2011). This result may be explained by limited availability of active sites on the adsorbent surface (Rashed, 2006). Dada *et al*. (2012) indicated that the adsorption capacities of the heavy metals on local clay increased with the increase of initial metal ion concentration. The experimental data of Xuejiang *et al.* (2006); Kilic *et al.* (2008) and Al-Qodah (2006) revealed that the adsorption capacity of Pb, Cd, and Cu on activated sewage sludge increases with the increase in initial metal concentration. The results obtained in this study agreed with previous literatures.

**The Effect of pH**

The pH is an important factor that plays a vital role in the adsorption process. The pH of the solution determines the degree of ionization of the adsorbate molecule, the surface charge of the adsorbent, and the extent of dissolution of the functional groups on the active site of the adsorbent. In this study, the effect of pH value on the adsorption of heavy metal ion was investigated and the result of the percentage removal of Fe, Cr, Cd, Zn and Pb in relation to the pH is shown in Figure 3. The removal efficiency of Cr, Fe, Pb, Zn and Cd reached maximum of 94.1 %, 79.4 %, 93.5 %, 74.3 % and 77.2 % respectively at a pH of 6. However, removal efficiency for the Fe, Cr, Cd, Zn and Pb decreased when the pH is above 6 (Figure 3). This shows that the removal efficiency decreases with increase in the pH value from 6 to 8. The increase in the percentage removal of the heavy metal (pH 6) is attributed to the limited competition between the metal ion and $H_3O$, the $H_3O^+$ is low due to decrease in $H_3O^+$ concentration and the adsorbent surface was negatively charged, promoting stronger affinity towards the metal ions. Therefore, the force of attraction was high for the cationic Cr, Fe, Pb, Zn and Cd high adsorption was observed. After pH 6, the adsorption of Cr, Fe, Pb, Zn and Cd by the adsorbent was decreased because at pH > 6.0, the Cr, Fe, Pb, Zn and Cd gets precipitated due to hydroxide anions forming a lead hydroxide precipitate. These results can be further proven by the results of previous research for the adsorption of Pb (II) from aqueous solution using new adsorbents prepared from agricultural waste (Ghasemi *et al*., 2014) which indicates the decrease in the percentage removal of heavy metals when the pH < 6. In this work, the maximum removal efficiency of Lead ion as observed at a pH of 6 and decreases with increase in the pH. Dongxiao *et al.* (2019) also found that pH of 6 is the optimum condition for the adsorption of $Cu^{2+}$, $Cd^{2+}$ and $Pb^{2+}$ using silicate tailing as an adsorbent.

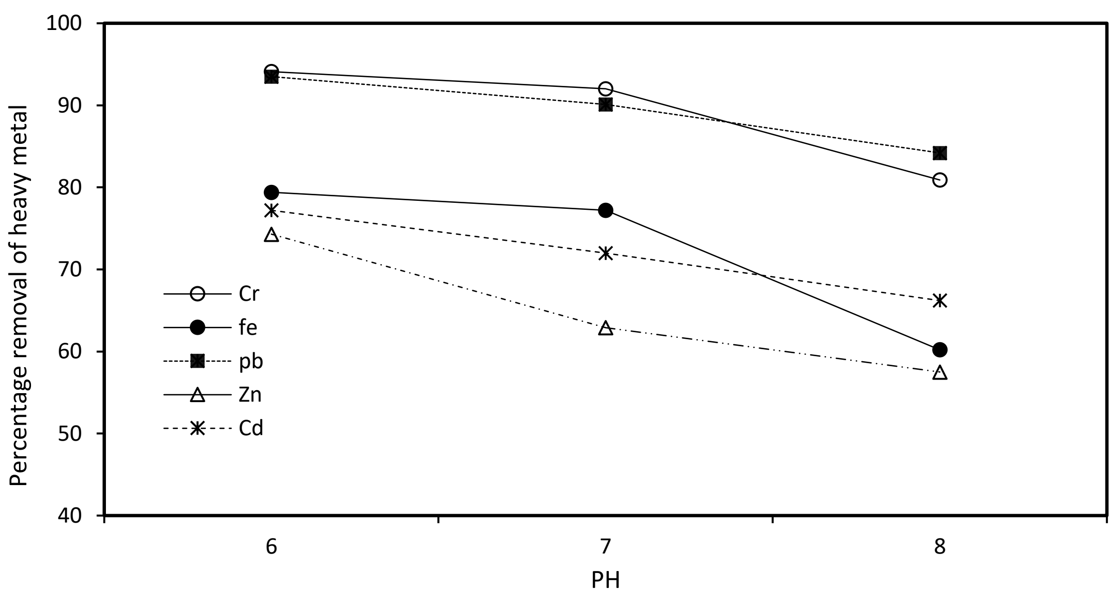


**Figure 3:** Effect of pH

**Effect of Temperature**

Figure 4 shows the effect of solution temperature on the adsorption capacity on Moringa, Okra and Pumpkin seeds (MOP) for the removes of heavy metals. The effect of temperature on the adsorption of heavy metals (Cr, Fe, Pb, Zn and Cd) on MOP were carried out at 25 - 55 $^0$C for all the metals, this can be attributed to strength of the attraction and binding between the metal ions and the active site on the surface of the adsorbent. The rate of the metal ion removal decreases with further increase in temperature from 35 - 55 $^0$C. The decrease in metal ion adsorption with rise in temperatures may be due to the weakling of the forces between the adsorbate and the adsorbent (Asuquo, 2017). The decrease in adsorption capacity as the temperature increases from 35 - 55 $^0$C indicates an exothermic reaction process.

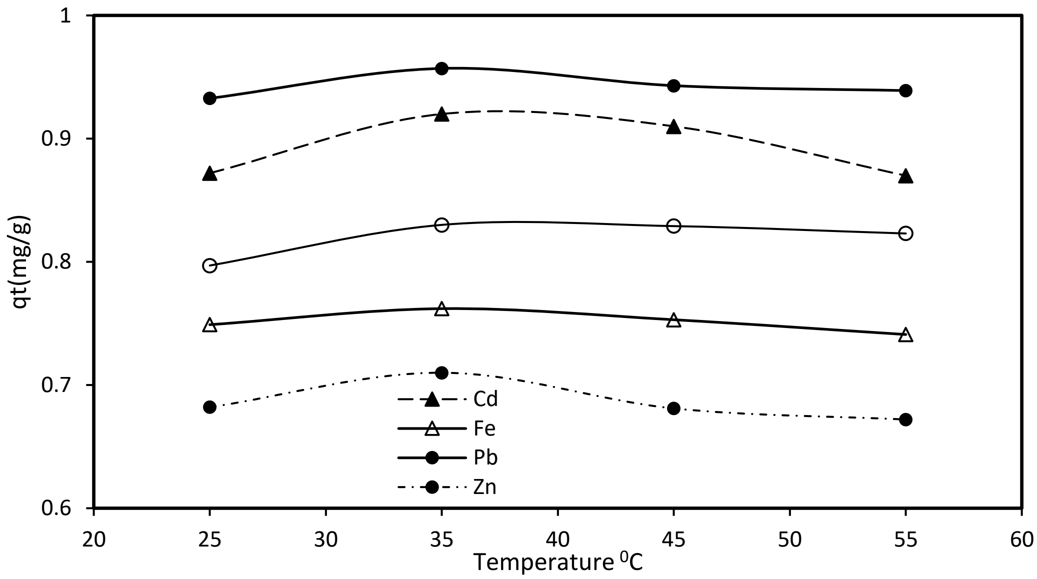


**Figure 4:** Effect of Solution Temperature

**Conclusion**

The present study explores new approach for the utilization of bioadsorbents for the removal of heavy metals in waste water. The effects of concentrations showed that the highest adsorption affinity occurred at a lower concentration of 50 mg/L for all the metals. The pH decreases with increase in pH from 6 – 8, temperature has an insignificant effect on adsorption capacity with the maximum adsorption at 35 ̊C indicating a physical adsorption. Contact time increases the rate of Chromium, Iron, Zinc, Lead and Cadmium uptake. Therefore, kinetic parameters showed that the optimum pH obtained was 6, Temperature 35℃, contact time of 90 min and adsorbent dosage of 0.5 g. Therefore, the seeds of these bioadsorbent can be effectively utilized for the adsorption of Cr, Fe, Zn, Pb and Cd in waste water.

**References**

Abiaziem, C. V., Williams, A. B. and Ibijoke, A. (2019). Adsorption of lead ion from aqueous solution unto cellulose nanocrystal from cassava peel. *Journal of Physics*, 1299: 1-17 https://doi.org/10.1088/1742-6596/1299/1/012122

Al-Anber, M. A. (2011). Thermodynamics approach in the adsorption of heavy metals. In: Moreno-Pirajan, J.C (Ed.), Thermodynamics-Interaction Studies-Solids, Liquids and Gases. InTech,Rijeka, pp 737-764.

Al-Qahtani K.M. (2015). Assessment and Treatment some of the Local Seeds used in Removal of Heavy Metals, *Journal of American Science*, 3: 198-203.

Al-Qahtani, K.M. (2016). Water purification uses different waste fruit cortexes for the removal of heavy metals. *Journal of Taibah University of Science* 10(5): 700-708.

Al-Qodah Z (2006). Biosorption of heavy metal ions from aqueous solutions by activated sludge. *Desalination*, 196(1-3): 164-176.

Asuquo, J.E. (2017). Effect of Temperature on the Adsorption of Metallic Soaps of Castor Seed Oil onto Haematite. *International Journal of Advanced Research in Chemical Science*, 4(6): https://doi.org/10.20431/2349-0403.0406005

APHA (2005) SM 3111B. Standard Methods for Examination of Water and Waste Water. Analytical Public Health Association, Centennial Edition, Washington DC.

Babel, S. and Kurniawan, T. A. (2003). 'Low-cost adsorbents for heavy metals uptake from contaminated water: A review' *Journal of Hazardous Materials*, 97: 219-243.

Coşkun, R., Soykan, C. and Saçak, M. (2006). Removal of some heavy metal ions from aqueous solution by adsorption using poly(ethylene terephthalate)-g-itaconic acid/acrylamide fiber. *Reactive and Functional Polymers*, 66(6): 599–608.

Ebrahimi, A., Pourgheysari, H. and Moazeni, M. (2012). Heavy metal content in edible salts in Isfahan and estimation of their daily intake via salt consumption. *International Journal of Environmental Health Engineering*, 1(1): 8. https://doi.org/10.4103/2277-9183.94392

Ghasemi M., Naushad M, Ghasemi N, and Khosravi-fard Y. (2014). Adsorption of Pb(II) from aqueous solution using new adsorbents prepared from agricultural waste: Adsorption isotherm and kinetic studies. *Journal of Industrial and Engineering Chemistry*,125 (20): 2193–2199.

Ghaedi, M., Sadeghian, B., Pebdani, A.A., Sahraei, R., Daneshfar, A., Duran, C. (2012). Kinetics, thermodynamics, and equilibrium evaluation of direct yellow 12 removals by adsorption onto silver nanoparticles loaded with activated carbon. *Chem. Eng. J.* 187: 133–141.

Jain, N. and Prasad, S. (2008). Agricultural and agro-processing wastes as low-cost adsorbents for metal removal from wastewater : A review. *Journal of Scientific and Industrial Research*, 67: 647-658.

Kilic M, Keskin ME, Mazlum S and Mazlum N. (2008). Effect of conditioning for Pb (II) and Hg (II) biosorption on waste-activated sludge. *Chemical Engineering and Processing*, 47(1), 31-40.

Malik, D. S., Sharma, A. K., Sharma, A. K., Thakur, R. and Sharma, M. (2020). A review on impact of water pollution on freshwater fish species and their aquatic environment. *Advances in Environmental Pollution Management: Wastewater Impacts and Treatment Technologies*, *December*, 10–28. https://doi.org/10.26832/aesa-2020-aepm-02

Manzoor, Q., Nadeem, R., Iqbal, M., Saeed, R. and Ansari, T.M. (2013). Organic Acids Pretreatment Effect on *Rosa bourbonia* Phyto-Biomass for Removal of Pb(II) and Cu(II) from Aqueous Media. *Bioresource Technology*, 132(5): 446-452.

Rashed, M. N. (2006). Fruit stones from industrial waste for the removal of lead ions from polluted water. *Environmental Monitoring and Assessment*, 119(1-3): 31-41.

Sulyman, M., Namiesnik. J. and Gierak. A. (2017). Low-cost adsorbents derived from agricultural by-products/wastes for enhancing contaminant uptakes from wastewater: a review. *Polish Journal of Environmental Studies*, 26(2): 479–510.

Taamneh, Y. and Sharadqah, S. (2017). The removal of heavy metals from aqueous solution using natural Jordanian zeolite. *Applied Water Science*, 7(4): 2021–2028.

Xuejiang W., Chen L., Xia S., Zhao J. and Jean, M. C. (2006). Biosorption of Cu (II) and Pb (II) from aqueous solutions by dried activated sludge. *Minerals Engineering*, 19(9): 968-971.

Zou, W, R.; Han, Z.; Chen, Z. and Jinghua, J. S. (2006). Kinetic study of adsorption of Cu(II) and Pb(II) from aqueous solutions using manganese oxide-coated zeolite in batch mode. *Colloids and Surfaces*, 279(1): 238–246.