

Removal of Toxic Metals from Aqueous Solution Using Isolated Chitin (*Poly [β -(1 \rightarrow 4)-N-acetyl-D-glucosamine]*)

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-----ABSTRACT-----

Aqueous media containing heavy metals from industries are directly or indirectly discharged into the environment to cause pollution and threat to human life. The bio-polymer chitin was synthesised using local snail shell to study the adsorption of lead, zinc and nickel from aqueous solution. The synthesis of chitin involves the following stages: (i) pre-concentration, (ii) demineralization, (iii) deprotonization and (iv) deacetylation. Chitin is characterized using analytical technique such as Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron microscope (SEM) and X-ray fluorescence (XRF) to confirm the presence of chitin. This study shows the effect of pH, time, and adsorbent dosage removal efficiency of the metals in solution. The concentrations of Pb^{2+} , Ni^{2+} and Zn^{2+} absorbed under different conditions was evaluated using atomic adsorption spectroscopy (AAS). The result shows that the optimum pH adsorption for Pb^{2+} , Ni^{2+} and Cu^{2+} using chitin was found to be at pH 2 for the all metals (Pb^{2+} , Ni^{2+} and Zn^{2+}) with percentage removal efficiency (92.5%, 82.4%, 80%). The synthesized chitin has a potential of an adsorbent for the removal of heavy metals in aqueous solution.

Keywords: Heavy metal, chitin, characterization, adsorption, atomic adsorption spectroscopy

Date of Submission: 27-03-2021

Date of Acceptance: 10-04-2021

I. INTRODUCTION

Toxic metal is relatively dense metal or metalloid that is potentially toxic especially to humans and the environment (Tchounwu, *et al.*, 2012). These heavy metals have polluted the atmosphere, water, soil and food chain [Hernandez-Montoya, *et al.*, 2013]. Heavy metals like arsenic, copper, cadmium, chromium, nickel, zinc, lead, and mercury are major pollutants of fresh water reservoirs because of their toxic, non-biodegradable, and persistent nature in the environment. The industrial growth which is the major source of heavy metals which leads to the introduction of such pollutants into different segments of the environment including air, water, soil, and the biosphere. Heavy metals are easily absorbed by fishes and vegetables due to their high solubility in the aquatic environments. Human beings are often exposed to heavy metals in various ways either through the inhalation of metals in the work places or polluted neighbourhoods or through the ingestion of food particularly sea food that contains high levels of heavy metals or paint chips that contain lead (Jarup 2003). These metals pose toxicity threat to human beings and animals even at low concentration level (Roberts *et al.*, 2011). Generally, heavy metal pollution originates from natural sources such as mining, weathering of rocks, refinery, and anthropogenic sources, such as untreated domestic and industrial wastewater discharges, accidental chemical spillage, direct soil waste dumping, and residues from some agricultural inputs (Lone *et al.*, 2003 and Faisal *et al.*, 2004) and are present in air, sediments, and water. These elements are associated with environmental degradation, poor water quality (Sadeghi *et al.*, 2006) and different human diseases (Micó *et al.*, 2006) due to their toxicity at very low doses/concentrations. They can enter the body through food chain, air, and water, and bio-accumulate over a period of time (Frías-Espéricueta *et al.*, 2006). Metals in the environment are present in the solid, liquid or gaseous states. They may be present as individual elements and as organic and inorganic compounds. The geosphere is the source of all metals except those that enter the atmosphere from space in form of meteorites and cosmic dust. Within the geosphere, metals are present in minerals, glasses and melts. In the hydrosphere, metals occur as dissolved ions and complexes, colloids and suspended solids and in the atmosphere, metals are present as gaseous elements and compounds and as particulates and aerosols [Merzouk 2011]. The gaseous and particulate metals may be inhaled, while solid and liquid metals may be ingested or absorbed thereby entering the biosphere. The movement of metals from one site to another depends on the linear and temporal scale of observation. For example, the oceans are vast reservoir for a variety of

chemical elements. They also serve as a conduit for elements derived from weathering of rocks to return to the geosphere through sedimentation. A reservoir may act as a catalyst for change in the states of metals and metal compounds without actually having incorporated those metals, as in the case of some biologically mediated reactions. Heavy metals are important components of building materials, vehicles, appliances, tools, computer and are essential in infrastructures including; highways, bridges, railroads, electrical utilities. Civilization discovered metals of antiquity such as gold, copper, silver, lead, tin, iron, zinc and mercury. Different methods of approach have been proposed with the regard of removal of heavy metal ions from wastewaters. Some conventional methods used to remove heavy metals include: electro dialysis, ion exchange, membrane separation, reverse osmosis, ultra filtration, activated carbon, adsorption and chemical precipitation [Igwe *et al.*, 2006 and Merzouk 2011].

II. MATERIALS AND METHODS

2.1 Sampling Method

The snail shell samples were purchased randomly from the local market at Ojo, Iyana-Oba, Ojo Local Government, Lagos State, Nigeria. The snails were preserved in a conducive environment until they are required for pre-treatment and synthesis of chitin. Random Sampling was used when the snail shells sample was collected from the Market at a particular point in time.

2.2 Study Area

The sample which was used as the adsorbent (snail shells synthesized to chitin) was collected from different snail sellers Iyana-Iba Market, Lasu Road, Lagos State.



Figure 1: Map of Ojo Local government of Lagos State, Nigeria

2.2 Pre-treatment of the snail shell samples

Snail pre-conditioning process was introduced as the first step to the common procedure of snail shells extraction, the snail shells were washed thoroughly and rinsed with tap water and with distilled water in order to remove sand debris, dust and other impurities. At the preconditioning stage, snail shells were soaked in 0.05 M acetic acid solution for 24 hours. The shells were washed thoroughly with distilled water and dried to remove excess water. The dried shell was pulverized to powdery form to ensure a large surface area was achieved using mortar and pestle. The grinded shell was sieved using a set of sieve with mesh size 30 μm in order to obtain finely powdered particles. The powdered shell was oven dried for 4 days at 60 $^{\circ}\text{C}$ and kept in a desiccator in order to prevent moisture from the sample. Then dried shells were demineralized using 0.68 M HCl (1:10 w/v) at ambient temperature (approximately 30 $^{\circ}\text{C}$) for 6 hours. The residue was washed with distilled water until PH in the range of 6.5 -7.5 was obtained and then the residue was dried. After that the demineralized snail shells were deproteinized using 0.62 M NaOH solution (1:10 w/v) at ambient temperature (approximately 30 $^{\circ}\text{C}$) for 16 hours. Then residue was washed thoroughly with water followed with distilled water until PH in the range of 6.5 - 7.5 was obtained. The chitin was dried and ground and screened with 150 μm sieve. The chitin obtain from the above process was deacetylated in 25 M and NaOH (1:10 w/v) for 20 hours at 65 $^{\circ}\text{C}$. After deacetylation, the

chitin was washed thoroughly with water followed with distilled water until PH in the range of 6.5 -7.5 was obtained.

2.3 Synthesis of Chitin (adsorbent)

A preconditioning process was introduced as the first step as the common procedure of snail shells extraction; the snail shells were washed thoroughly, rinsed with tap water, and then with distilled water in order to remove sand debris, dust, and other impurities. The snail shells were soak in 0.05 M acetic acid solution and allowed for 24 hours. Then shells were washed thoroughly with water and dried to remove excess water. The dried shell was pulverized to powdery form to ensure a large surface area using mortar and pestle. The grinded shell was sieved using sieve with mesh size 30 μ m in order to obtain finely powdered particles. The powdered shell was oven dried for 4 days at 60 $^{\circ}$ C and kept in a desiccator in order to prevent moisture from the sample. Then dried shells were demineralized using 0.68 M HCL (1:10 w/v) at ambient temperature (approximately 30 $^{\circ}$ C) for 6 hours. The residue was washed with distilled water until PH in the range of 6.5 -7.5 was obtained and then the residue was dried. After that the demineralized snail shells were deproteinized using 0.62 M NaOH solution (1:10 w/v) at ambient temperature (approximately 30 $^{\circ}$ C) for 16 hours. Then residue was washed thoroughly with water followed with distilled water until pH in the range of 6.5 -7.5 was obtained. The chitin was dried and ground and screened with 150 μ m sieve. The chitin obtain from the above process was deacetylated in 25 M and NaOH (1:10 w/v) for 20 hours at 65 $^{\circ}$ C. After deacetylation, the chitin was washed thoroughly with water followed with distilled water until pH in the range of 6.5 -7.5 was obtained.

2.4 Characterization

The synthesized chitosan was characterized by Fourier transformed infrared (FT-IR) spectroscopy (Perkinsin Elmer) in the range of 400 to 4000 cm^{-1} . The crystallinity of chitin in powder form was studied by X-ray diffraction method using Cu K radiation generated at 40 kV and 40 mA at scanning speed of 0.3 2 θ / min within a range of 50 to 350.

2.5 Adsorption Studies

A stock solution of Pb^{2+} , Ni^{2+} and Cu^{2+} (1000mg / L) were prepared from $\text{Pb}(\text{NO}_3)_2$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ salts respectively in which the solutions were all soluble in water to form colourless, green and colourless solutions respectively. The stock solution of the metals was diluted appropriately for the different metal concentration required for the adsorption studies. $\text{Pb}(\text{NO}_3)_2$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ solution was taken and 50mg of 150 μ m particle size chitin was added. Then the mixture was continuously stirred using magnetic stirrer for 6 hours at room temperature (30 $^{\circ}$ C). After that solution was filtered and filtrate and 3mg/L of $\text{Pb}(\text{NO}_3)_2$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ solution were analyzed using atomic adsorption spectroscopy to determine amount of Pb^{2+} , Ni^{2+} and Cu^{2+} absorbed by chitin. The effect of temperature was studied by changing only reaction temperature to 50 $^{\circ}$ C and keeping other parameters constant. Effect of particle size of chitin powder on amount of metal uptake was studied by increasing the particle size of powder to 355 μ m and repeated the above mentioned procedure. pH of Pb^{2+} , Ni^{2+} and Cu^{2+} solution was adjusted to 5.7 by using 1M NaOH solution.

III. RESULTS AND DISCUSSION

3.1 Characterization

3.1.1 FTIR

Figure 2: FTIR spectra of chitin derived from the above mentioned process. It represents all the relevance peaks of chitin compared to standard FTIR spectrum of chitin. (Zouhour et al., 2010). The uptake Pb^{2+} , Ni^{2+} and Zn^{2+} metals was mainly affected via coordination with the amine groups ($-\text{NH}_2$) on chitosan. This is illustrated by the FT-IR spectra presented in Figure 2. Chitin charged with metal ion forms a new energy band at 1768 cm^{-1} . This band corresponds to the bending of plane of N-H. The infrared spectrum for (*Poly [β -(1 \rightarrow 4)-N-acetyl-D-glucosamine]*) before adsorption was presented in Figure 2.

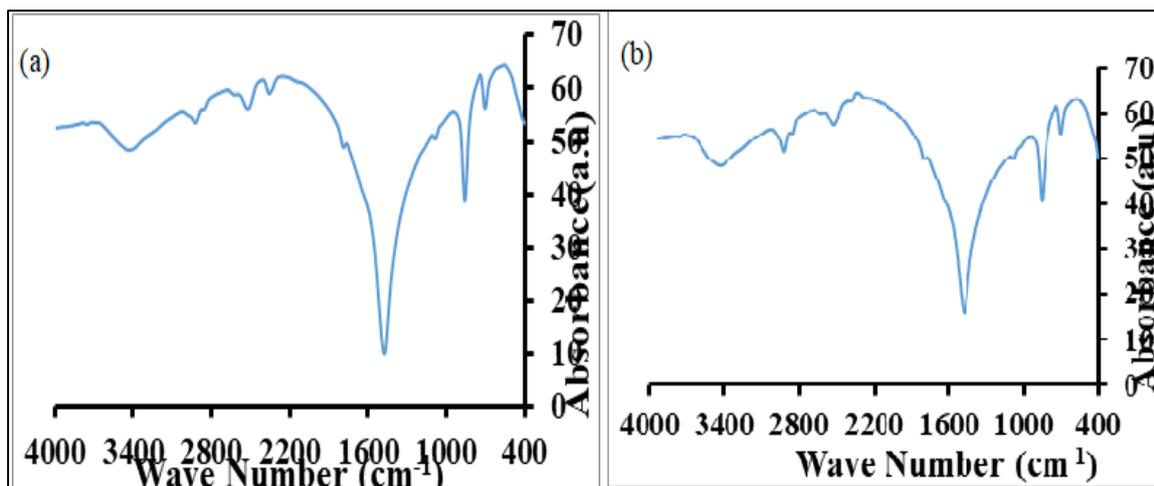


Figure 2: FTIR absorption peaks of Poly [β -(1 \rightarrow 4)-N-acetyl-D-glucosamine] before adsorption process and (b) shows chitin - Pb²⁺, Ni²⁺ and Zn²⁺

The peak at 1768 cm⁻¹ shows C=O stretch. The sharp at 1462 cm⁻¹ shows strong bands in for amines. The wavenumber between 1068 cm⁻¹ and 698 cm⁻¹ are representative of (C-O). The band at 3442 cm⁻¹ refers to group O-H (hydroxyl group), C-H group, C=O (carbonyl group), CH₃ bending, C-O group and N-H (amino group) respectively. After adsorption was shown in Fig2 (b), were the spectrum was taken at 3420 cm⁻¹, 2912 cm⁻¹, 1784 cm⁻¹. The peak in region 1468cm⁻¹ shows the presence (C=C) ring stretch of aromatic ring, 1060 cm⁻¹ and 690 cm⁻¹ which refers to group O-H (hydroxyl group), C-H group, C=O (carbonyl group), CH₃ Bending C-O group and N-H (amino group) respectively (Pavia et al., 2008).

3.1.2 Scanning Electron Microscopy

SEM was used to determine the morphology in (Poly [β -(1 \rightarrow 4)-N-acetyl-D3 n -glucosamine]). The SEM image in Fig 3 (a) and (b) indicates the morphology of adsorbent before and after adsorption which reveals the porous structure on the surface of chitin. The morphology on (b) after adsorption is due to the presence of the metals adsorption which implies the activation process and this was effective.

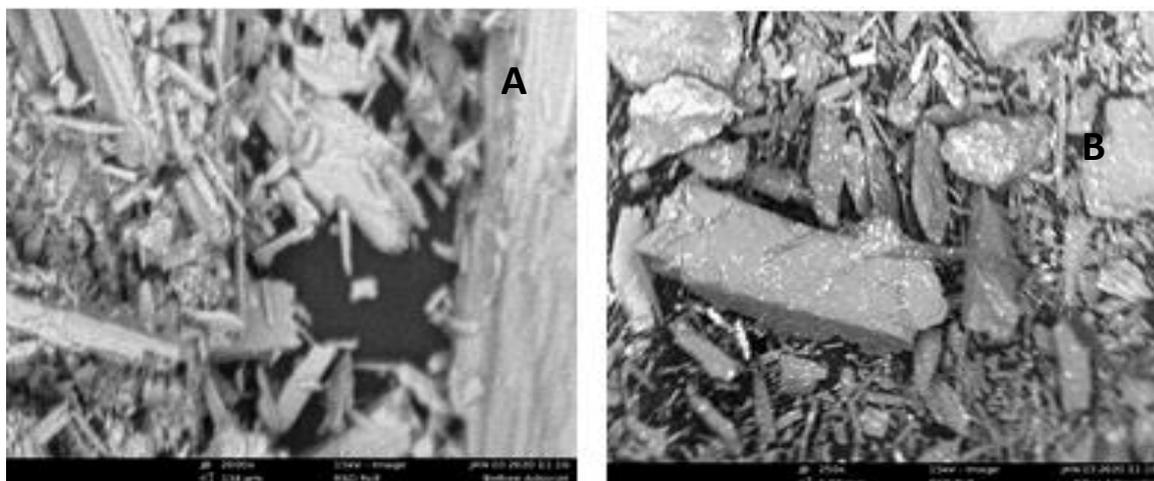


Figure 3: SEM images of chitin adsorbent (a) before and (b) after adsorption

3.1.3 FTIR Spectroscopy

The XRF analysis of the synthesised chitin powder shows the strong reflection peaks which indicate that calcium, iron, copper, lead and strontium are present before and after adsorption (Jolanta et al., 2010). The spectra of synthesized chitin before and after adsorption are presented in Figure 4.

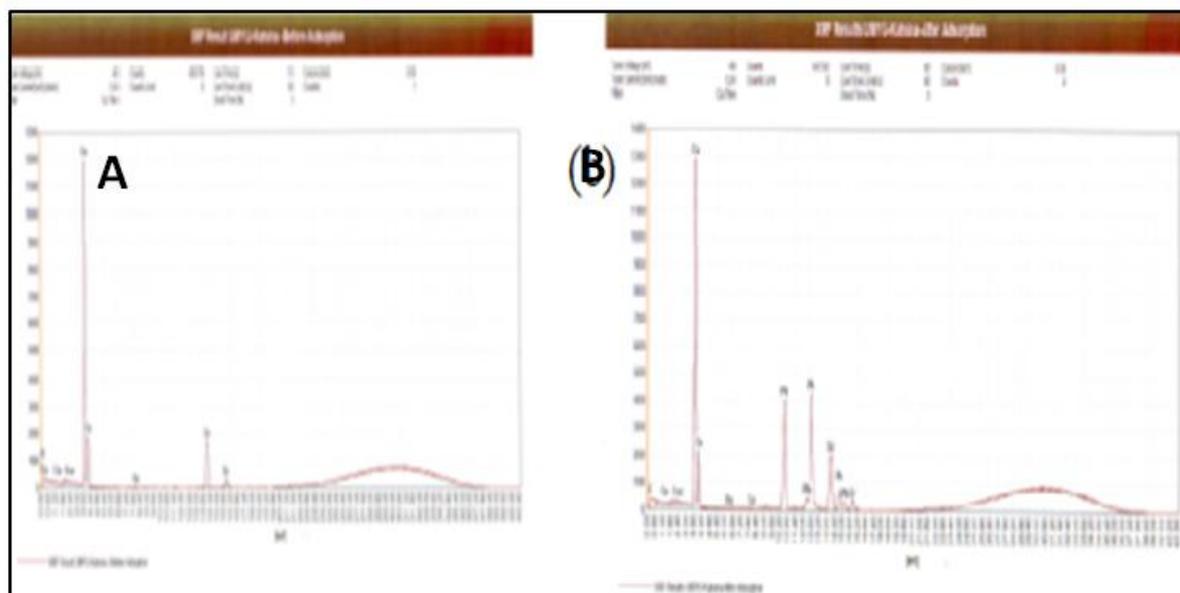


Figure 4: XRF Image of Chitin (a) before adsorption and (b) after adsorption

3.2 ADSORPTION STUDIES

The adsorption of metals from aqueous solution was conducted by optimizing the pH, contact time, and dosage of adsorbent to determine their effect in the removal of metals.

3.2.1 pH Effect on The Removal of Metals

The pH range studied was from pH 2.0 to pH 10.0 and the ability of removing Pb^{2+} , Zn^{2+} and Ni^{2+} ions by adsorbent depends on the pH solution. The optimum pH for the removal of Pb^{2+} , Zn^{2+} and Ni^{2+} ions using *Poly [β -(1 \rightarrow 4)-N-acetyl-D-glucosamine]* was determined. There was decrease in sorption with an increase in pH due to the weakening of electrostatic force of attraction between the positively charged adsorbate and adsorbent and finally caused reduction in sorption (REF). Increase in pH tends to precipitate biosorbent as insoluble hydroxides or hydrated oxide, thereby lowering its ability for biosorption (Byramoglu et al., 2006). The optimum pH for the *Poly [β -(1 \rightarrow 4)-N-acetyl-D-glucosamine]* was found to be at pH 2 for Pb^{2+} , Zn^{2+} , Ni^{2+} (92.5%, 82.4%, 80s%). The pH effect on the removal of metals from the test solution is presented in Figure 5.

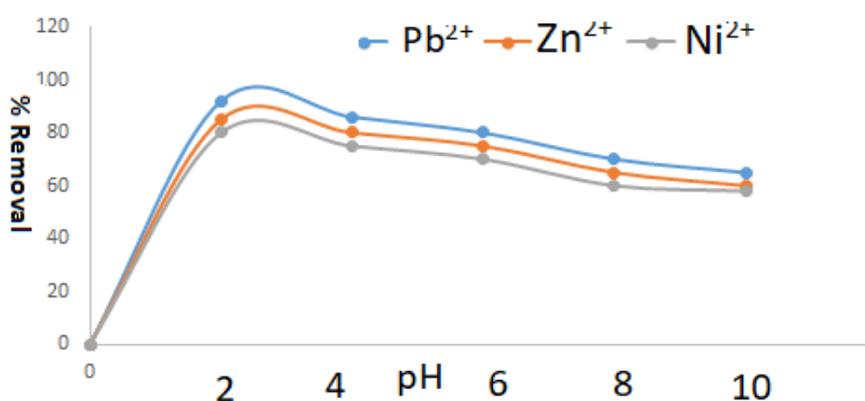


Figure 5: Effect of pH on the removal of Pb^{2+} , Zn^{2+} and Ni^{2+} using *Poly [β -(1 \rightarrow 4)-N-acetyl-D-glucosamine]*

3.2.2 CONTACT TIME EFFECT ON THE REMOVAL OF METALS

Figure 6 shows the biosorption efficiency Pb^{2+} , Zn^{2+} and Ni^{2+} removal and uptake capacity of synthesised chitin as a function of contact time. Increase in contact time leads to increase in % extraction efficiency. The optimum percentage removal for Pb^{2+} , Zn^{2+} and Ni^{2+} are (92 %, &70 % and 64 %) is achieved at 150 min respectively. The contact time effect on metal removal from the aqueous solution is presented in Figure 5.

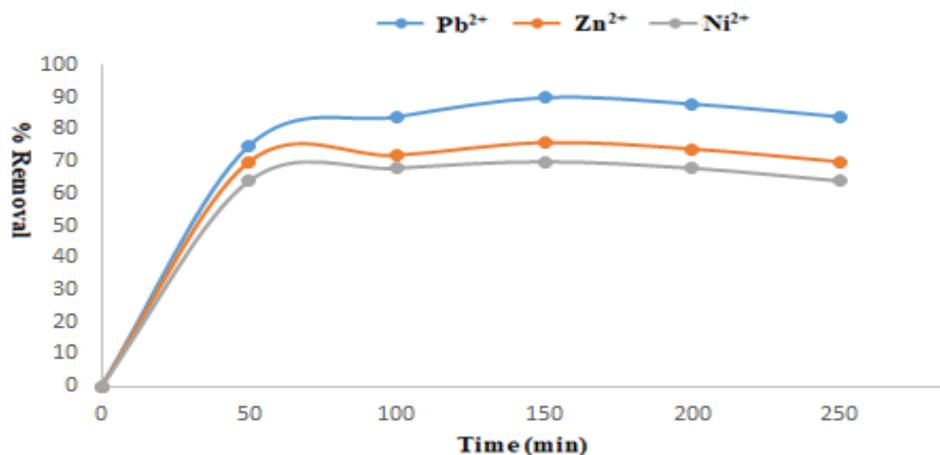


Figure 6: Effect of contact time of Pb²⁺, Zn²⁺ and Ni²⁺ removal using Poly [β -(1 \rightarrow 4)-N-acetyl-D-glucosamine]

3.2.2 ADSORBENT DOSAGE EFFECT OF THE REMOVAL OF METALS

Figure 6 shows the biosorption efficiency of Pb²⁺, Zn²⁺ and Ni²⁺ ions in aqueous media depends on the quantity of biosorbent. The dosage studied was between (20 and 100) mg / g with 92 %, 74 % and 68% respectively. Percentage removal of metals increased, as the dosage increases and remains constant as it reaches equilibrium. This is due to the greater availability of the exchangeable functional groups at higher concentration of the sorbent (Yu et al.; 2000). The adsorbent dosage effect on metal removal from the aqueous solution is presented in Figure 6.

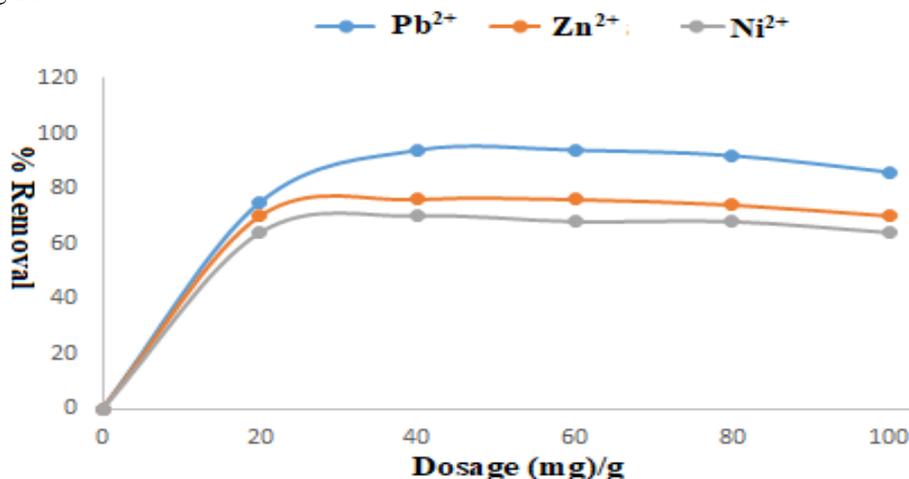


Figure 6: Effect of dosage (mg/g) on the removal Pb²⁺, Zn²⁺ and Ni²⁺ using Poly [β -(1 \rightarrow 4)-N-acetyl-D-glucosamine]

3.3 ADSORPTION ISOTHERMS

3.3.1 Langmuir Isotherm

In 1916, Langmuir derived an adsorption isotherm based on theoretical considerations, which was named after him. Langmuir adsorption theory explained that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface, the energy of adsorption is constant and there is no interaction between the adsorbed molecules. The mathematical representation of this model is given in linear form as:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}K_L} + \frac{C_e}{q_{\max}}$$

Where q_e is the metal adsorption capacity of the adsorbent, q_{\max} (mg/g) is the maximum adsorption capacity, K_L is the adsorption energy and C_e is the final concentration. The disadvantage of Langmuir isotherm is that it is only limited to monolayer adsorption and reversible process when no interaction occurs between the molecules adsorbed on the active site and the neighbouring sites. This isotherm is useful for representing chemisorption. The value of adsorption energy (K_L) is -52.63 and the maximum adsorption capacity q_{\max} is 0.3105.

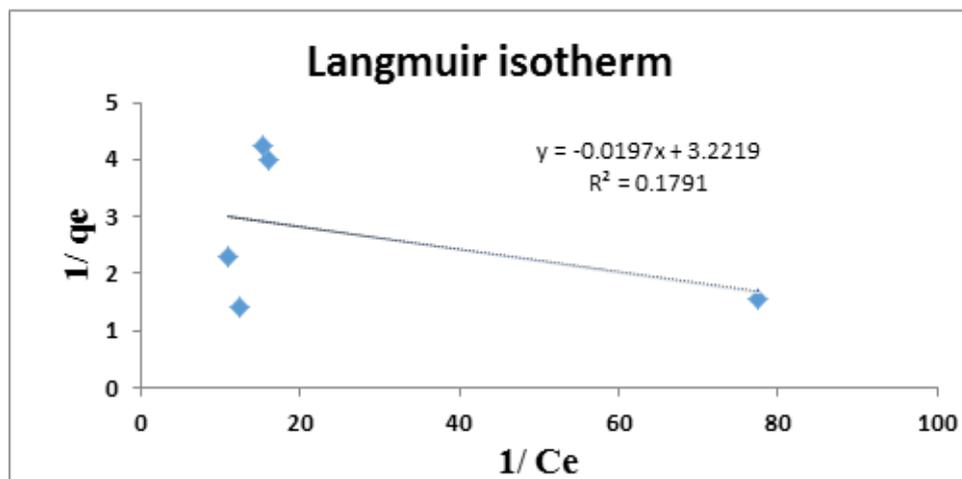


Figure 7: Graphical representation of Langmuir adsorption Isotherm

3.3.2 Freundlich Isotherm

Freundlich Isotherm model describes the adsorption on heterogeneous surfaces with interactions occurring between the adsorbed molecules and is not restricted to the formation of monolayer. This Isotherm is suitable for describing the adsorption of solutes from liquid to solid surface using different varieties of adsorbents. The equation of this model is given in linear form by:

$$\text{Log } q_e = \log K_F + \frac{1}{n} \log C_e$$

Where q_e (mg/g) is the metal adsorption capacity of the adsorbent, K_F is the bond energy while $1/n$ is the heterogeneity factor that is related to the adsorption capacity and intensity and C_e is the equilibrium concentration (mgL^{-1}). In this model, it is assumed that when the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases and the sorption energy exponentially decreases over the completion of the sorption centre of the adsorbent.

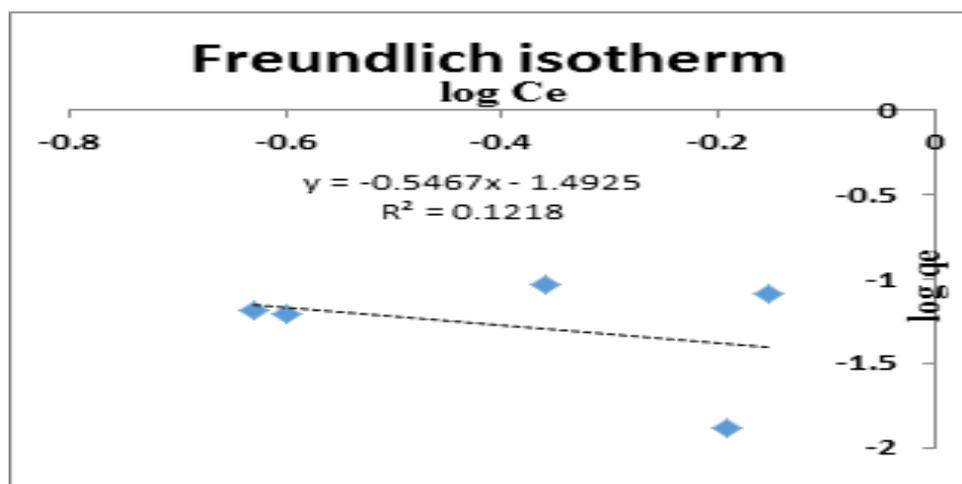


Figure 8: representation of Freundlich Isotherm

The obtained data may be perfectly fit on the Langmuir isotherm model since the regression coefficient (R^2) is higher than the regression coefficient obtained for the Freundlich isotherm model. The value of the bond energy (K_F) is 0.0322 and the heterogeneity factor (n) is -1.83.

IV. CONCLUSION

The synthesized chitin has a potential of an adsorbent for the removal of heavy metals in aqueous solution. Lead has the highest extraction removal with 94 % and was achieved at pH 2.2, bio-sorbent dosage of 60 mg/g, 150 min contact time

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Moronkola, B.A, et. al. "Removal of Toxic Metals from Aqueous Solution Using Isolated Chitin (Poly [β -(1 \rightarrow 4)-N-acetyl-D-glucosamine])." *The International Journal of Engineering and Science (IJES)*, 10(04), (2021): pp. 01-08.