

Effect of Chitosan Powder Prepared from Snail Shells to Remove Lead (II) Ion and Nickel (II) Ion from Aqueous Solution and Its Adsorption Isotherm Model

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Abstract: The toxic effects of heavy metals have remained a major source of concern globally because of their non-biodegradable nature which makes heavy metal pollution a serious environmental problem. The extents of removal for two heavy metals were investigated on adsorbent dose, temperature, pH, contact time and initial metals ion concentration. Maximum adsorption was obtained at pH 5 for Pb²⁺ ion and pH 7 for Ni²⁺ ion with 82.1% and 68.28%, at maximum adsorption temperature 335K and 355K for both metal ions with 87% and 80% metal removal respectively. The study shows that initial metal ion concentration and adsorbent dose on metals adsorption increases for both metal ions having a maximum adsorption dose at 99.93% and 70.58% removal at 180mins contact time for both metal ions with 99.83% and 70.37%. FTIR spectrum of raw chitosan showed the following peaks; 3263cm⁻¹, 3109.25cm⁻¹, 1627cm⁻¹ and 2854cm⁻¹ denoting -NH₂/-NH asymmetric stretching, -OH stretching, -C=O stretching and -CH group showing that binding process for both metal ions onto chitosan bands at 3109.25cm⁻¹ and 2854cm⁻¹ in the spectrum. The spectra indicated -NH group was involved in the binding process due to substantial changes in absorption intensity of -NH stretching after adsorption and peak 1627cm⁻¹ assigned to C=O occurred before the binding process. The two peaks in the 2800-2900 cm⁻¹ region was observed in Pb²⁺ ion which disappear in the Ni²⁺ ion laden spectrum, the spectrum for Ni²⁺ ion has only one peak observed in this region while the Pb²⁺ ion has two and in the finger print region, 600-1000 cm⁻¹, the spectra of Ni²⁺ ion and Pb²⁺ exhibited two and one peaks respectively. This supported the higher sorption capacity of Pb²⁺ ion over Ni²⁺ ion. The data were evaluated using Langmuir, Freundlich and Temkin isotherms, the data complied with Freundlich isotherm with high R² values 0.984 and 0.971 for both metal ions while Temkin isotherm shows high R² values 0.991 and 0.981 for both Pb²⁺ and Ni²⁺ ions respectively.

Keywords: Adsorption, pH, Chitosan, Heavy Metals, Snail Shells

1. Introduction

With the growth of industry, there has been a drastical increase in the discharge of industrial waste to the environment, chiefly soil and water, which has led to the accumulation of heavy metals, especially in urban areas. The indiscriminate release of heavy metals into the soil and waters is a major health concern worldwide, as they cannot be broken down to non-toxic forms and therefore have

long-lasting effects on the ecosystem [1]. Likewise, the heavy metals present in this wastewater are persistent and non-degradable in nature. Moreover, they are soluble in aquatic environment and thus can be easily absorbed by living cells. Thus, by entering the food chain, they can be bioaccumulated and biomagnified in higher trophic levels also. The heavy metals, if absorbed above the permissible labels, could lead to serious health disorders. These heavy metals are widely generated as a wastewater or waste product in the industries like textiles, leather, paper,

plastics, electroplating, cement, metal processing, wood preservatives, paints, pigments and steel fabricating industries during production which are not been treated or check the pollutant load before discharge to waterways and open lands [2]. These industries discharge large quantities of toxic wastes and the untreated effluents from these industries causes environmental and industrial pollution [3]. In light of the facts, treatment of heavy metals containing industrial effluent becomes quite necessary before being discharged into the environment. A wide range of physical and chemical processes are available for the removal of these metals from waste waters, such as precipitation, ultrafiltration, adsorption, ion-exchange, reverse osmosis, oxidation, ozonation, coagulation, flocculation and membrane filtration processes [4]. But most of these techniques become ineffective when the concentrations of heavy metals are less than 100 mg/L [5]. These methods are not very effective, are costly and require high energy input. They are associated with generation of toxic sludge, disposal of which renders it expensive and non-ecofriendly in nature and in the recent past, number of approaches has been investigated for safe and economical treatment of heavy metal laden wastewater. Adsorption has emerged out to be better alternative treatment methods and offering a wide advantage over other conventional processes. It is said to be effective and economical because of its relatively low cost [6]. Also low residual generation, ease of heavy metal removal and possibility for the reuse of the adsorbent makes adsorption an economical and favorable technology for heavy metal removal from wastewater.

However, many reports have been published on the low-cost adsorbents for heavy metals removal from aqueous solutions [7, 8, 9, 10], which has been found to be economically appealing for the removal of toxic metals from wastewater by choosing a perfect adsorbents under optimum operating conditions [11, 12] and in recent time, chitosan has been used for adsorption of heavy metals due to the attribution of exposed free amino groups, which chelates five to six times greater than chitin [13] and also possession of its wide excellent properties such as abundance, non-toxicity, biodegradability, hydrophilicity and adsorption property [14]. Hence the objective of this work is to investigate effect of chitosan powder (size < 80 micrometer) prepared from snail shells to remove Pb^{2+} ion and Ni^{2+} ions from wastewater, characterization of the used chitosan using Fourier Transform Infrared Spectroscopy (FTIR) and its adsorption isotherm model.

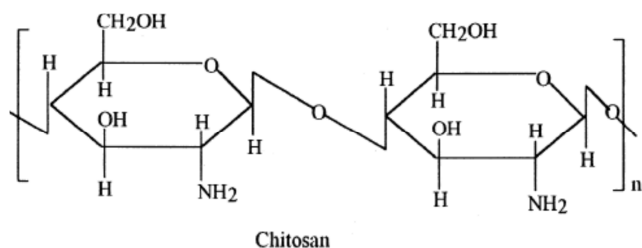


Figure 1. Structure of chitosan.

Chitosan is a unique basic polysaccharide and partially deacetylated polymer of glucosamine obtained after alkaline deacetylation of the chitin [15, 16, 17]. It consists of mainly of β - (1-4-2- acetamido-2-deoxy-D-glucose) units and is the second most abundant biopolymer on earth after cellulose, widely distributed in crustacean shells and cell walls of fungus [16, 17, 18 and 19]. Chitosan is soluble in dilute acids and solubilisation occurs by the protonation of the $-NH_2$ function on the C-2 position of the D-glucosamine repeat unit, where by the polysaccharide is converted to a polyelectrolyte in acidic media. Chitosan are widely used for waste water treatments of polymers experimentally proven that decrease the chemical oxygen demand, total nitrogen and destroy the microbial population [20]. The high porosity of this natural polymer results in novel binding properties for metal ion such as cadmium, copper, lead, nickel uranyl, mercury and chromium etc., [21]. Water purification plants throughout the world use chitosan to remove oil, grease, heavy metals, and the fine particulate matter that cause turbidity in wastewater streams [16]. However, with the use of synthetic polymer; the low metallic strength, low thermal, mechanical stability and flexibility behavior of chitosan can be increase [22] and can also help chitosan to be modified physically and chemically [23, 24, 25]. It has been used widely as an adsorbent for transition metal ions and organic species because the amino ($-NH_2$) and hydroxyl ($-OH$) groups on chitosan chains can serve as the coordination and reaction sites [26, 27]. It is also reported that chitosan has the highest chelating ability in comparison to other natural polymers obtained from seafood wastes and natural substances like bark, activated sludge and the synthetic polymer poly (4-aminostyrene) which is used in commercial chelating ion-exchange resins [28, 29].

2. Materials and Methods

2.1. Materials

All chemicals used in the study were of analytical grade obtained from Chemistry Department, Federal University of Technology Akure, Ondo State, Nigeria. Aqueous solutions of lead and nickel were prepared from lead nitrate and nickel sulphate respectively. Subsequent concentrations needed for the experiments were prepared by diluting the stock solutions to desired concentrations with de-ionized water. De-ionized water was used throughout the study and all glassware and other containers were thoroughly cleaned by soaking in detergent followed by soaking in 10% Nitric acid for 48hrs and finally rinsed with de-ionized water several times prior to use.

2.2. Preparation of Chitosan

The chitosan used were prepared based on the method proposed by Wan Ngah and Fatinathan [19, 30]. Chitosan used was synthesized from snail shells purchased from a local market in Akure South Local Government Area, Ondo State, Nigeria. The shells were washed, dried and pulverized into fine powder using mechanical grinding machine, the

sample was deproteinised using 1.2M NaOH, boiled at 70°C for one hour, washed severally with de-ionized water, then obtained sample was demineralized using 0.7M HCl, boiled at 70°C for 15mins, wash severally with de-ionized water. The resulting sample was deacetylated using 50% NaOH, boiled at 100°C for 3hrs, washed and filtered repeatedly until the filtrate became neutral, oven-dried, cooled and sieved to obtain 280-300 micrometre mesh size.

2.3. Methods

Adsorption experiments were conducted in Erlenmeyer flasks with ground-glass stoppers. 30ml of each metal ion solution were transferred to different 100ml flasks together with 0.3g of snail shell derived chitosan, and placed in a water bath shaker maintained at 25°C. Accurately weighed 0.3g of chitosan was added to each of the beaker, The mixtures were stirred continuously and allowed to stand for 6hrs, then the mixtures were then filtered using Whatman number 4 filter paper and the filtrates taken for metal ion analysis using Atomic Absorption Spectrometer (Model: buck scientific VPG210). The extent of removal of the two metals was investigated separately on the effect of adsorbent dose, effect of temperature, effect of pH of the solution, effect of contact time in shaking the adsorbent metal solution mixture and effect of metals ion concentration by varying needed parameters and keeping other parameters constant [31]. The pH (Mudder 0.01 readout accuracy digital pocket pen type, Backlit LCD. 0.00-14.00 pH meter) of each solution was adjusted to different values with either NaOH or HCl in duplicate.

2.4. Factors Influencing Adsorption Process

2.4.1. Effect of Adsorbent Dose

The effect of adsorbent weight on the adsorption was studied by using 30ml of each metal ion solution were transferred to different 100ml flasks together with 0.3g of snail shell derived chitosan, and placed in a water bath shaker maintained at 298K for suitable time with different weigh of adsorption dose (0.25, 0.5, 0.75, 1.00, 1.25, 1.50 g).

2.4.2. Effect of Temperature

Adsorption process was performed in the same manner as mentioned in the above paragraph at temperature 305, 315, 325, 335, 345 and 355K to estimate the thermodynamic behavior of adsorption process, this depends if the adsorption decreases with increasing temperature then the process is exothermic and vice versa.

2.4.3. Effect of Contact Time

Effect of contact time on adsorption was studied by using 30ml of each metal ion solution were transferred to different 100ml flasks together with 0.3g of snail shell derived chitosan, and placed in a water bath shaker maintained at 298K for suitable time with a time range of 5, 15, 30, 60, 90, 120, 150, 180, 240, 300 and 360 mins.

2.4.4. Effect of pH

The effect of adsorbent weight on the adsorption was

studied by using 30ml of each metal ion solution were transferred to different 100ml flasks together with 0.3g of snail shell derived chitosan, and placed in a water bath shaker maintained at 298K for suitable time with different pH-media. NaOH (0.1 N) and (0.1 N) HCL were used to adjust the pH 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0 and the concentration of the adsorbent was measured by UV-visible spectrophotometer.

2.4.5. Effect of Metals Ion Concentration

Adsorption process was performed in the same manner as mentioned in the above paragraph at with initial metal ion concentrations ranging from 100, 200, 300, 400 and 500 mg/l with a fixed adsorbent dose of 0.3g at the optimum pH and contact time.

The removal efficiency (E) was calculated using;

$$E (\%) = [(C_0 - C_1) / C_0] \times 100 \quad (1)$$

Where C_0 and C_1 denote the initial concentration and final residual concentration of metal ion in mg/l respectively.

3. Results and Discussion

3.1. FTIR Analysis of the Biosorbent and Biosorbent-Metals

Chitosan as a biomaterial that contains several active binding sites. The active groups of the derived chitosan powder before and after metal ion removal were analysed using FTIR spectrometer. Figure 2. Shows the spectrum of raw chitosan while Figure 3 and Figure 4 show the spectra of Pb^{2+} ion laden chitosan and Ni^{2+} ion laden chitosan respectively. FTIR spectroscopy provides information through bonding properties, frequencies and intensities, and can therefore be used to identify species and predict chemical processes involved. FTIR spectrum of raw chitosan in Figure 2 shown a broad absorption band in the range 3000 to 3500 cm^{-1} which is attributed to O-H stretching vibrations and the 3263 cm^{-1} to vibration of NH. The stretching vibrations of methylene C-H at 2854 cm^{-1} , absorption peak at 1558 cm^{-1} correspond to the NH_2 . The amide II band is used as the characteristic band of N-acetylation [32]. The spectra of raw chitosan showed the different vibration that occurs after deacetylation process, which was not the emergence of vibration C = O at 1627 cm^{-1} region which indicates the vibration of C = O has been reduced on chitosan as well as the emergence of absorption at 894 cm^{-1} on chitosan which was the vibration of NH_2 . Raw Chitosan showed no amide band, but hydroxyl and, amino bands at the ranged spectra up to 3500 cm. In terms of chemical properties, raw chitosan is more applicable, due to its molecular structure as a high molecular weight polymer, being a linear polyamine whose amino groups are readily available for chemical reactions and salt formation with acids.

FTIR analysis of Pb^{2+} laden Chitosan and Ni^{2+} laden Chitosan.

The spectrum for Pb^{2+} ion laden Chitosan in figure 3 shown the presence of the following functional groups O-H stretching

vibrations (3466), C-H stretching vibrations (2921, 2853), C-H first stretch overtone (1734; 1643), CH₂ bending (1456; 1401), C-O valence vibration (1036). While the spectrum for Ni²⁺ ion laden Chitosan shown in Figure 4 shows the presence of O-H stretching vibrations (3344.5, 2360.6), (2340.1), (1636.4), C = O and COOH overtones (668.1, 620.1). The spectra indicated that -NH group was involved in the binding process because there were substantial changes in the absorption intensity of the -NH stretching after adsorption. Vibration shift was observed for the possible O-H, N-H absorption peaks. This could be possibly attributed to the interaction of the functional group with metal ions. The two peaks in the 2800-2900 cm⁻¹ region observed in Pb²⁺ ion

disappear in the Ni²⁺ ion laden spectrum. Another spectral shift is observed in the 1600-1700 cm⁻¹ region for the Pb²⁺ ion laden spectrum. The spectrum for Ni²⁺ ion has only one peak observed in this region while the Pb²⁺ ion has two. In the finger print region, 600-1000 cm⁻¹, the spectra of Ni²⁺ ion and Pb²⁺ exhibited two and one peaks respectively. This supported the higher sorption capacity of Pb²⁺ ion over Ni²⁺ ion [33]. The information observed from FTIR spectral data has shown that the -OH and possibly the -NH₂ groups were present on the surface of chitosan and may have been responsible for the uptake of Pb²⁺ ions on the chitosan. These functional groups are known to act as very active legends and therefore, tend to bind readily with metals ions.

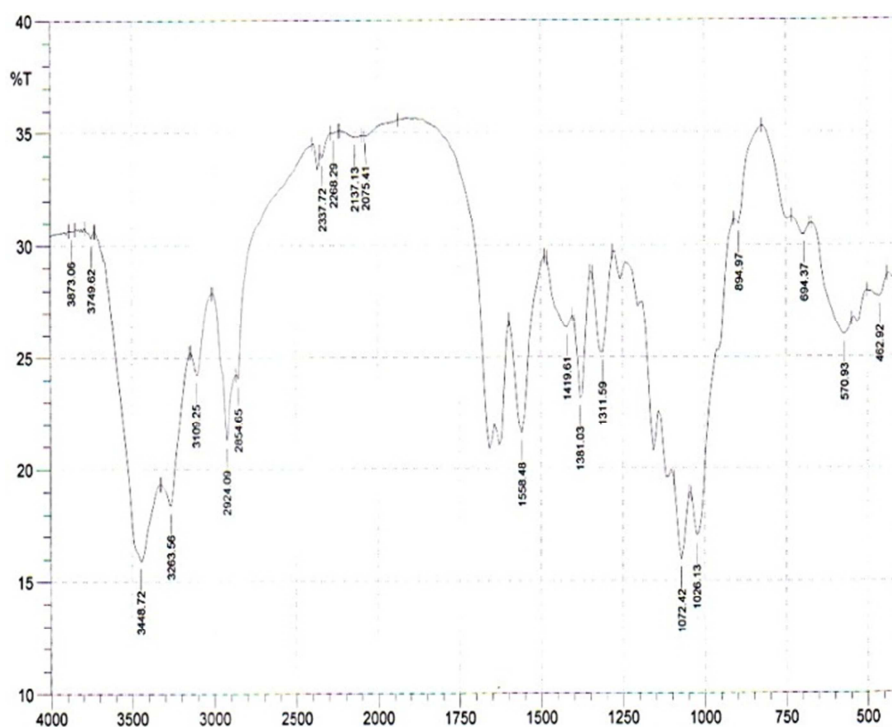


Figure 2. FTIR Spectrum of Raw Chitosan.

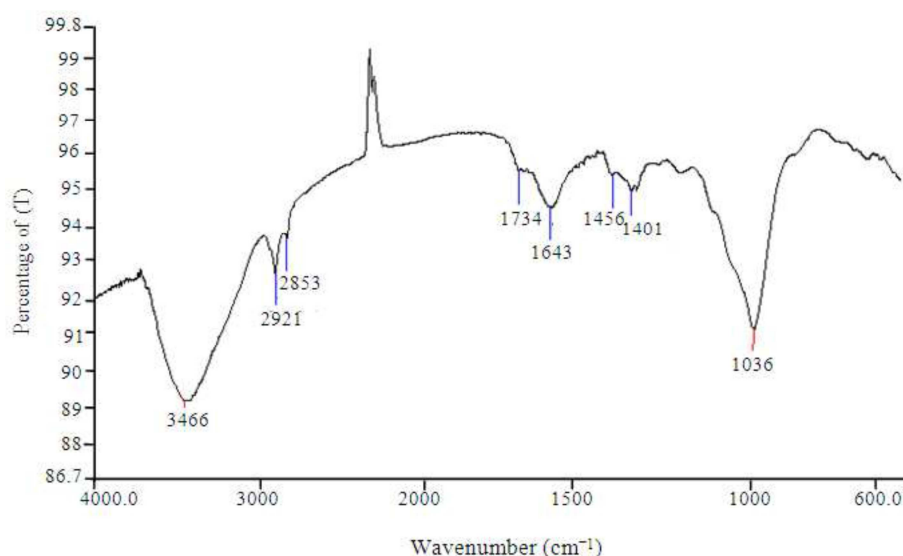


Figure 3. FTIR Spectrum of Pb²⁺ ion laden Chitosan.

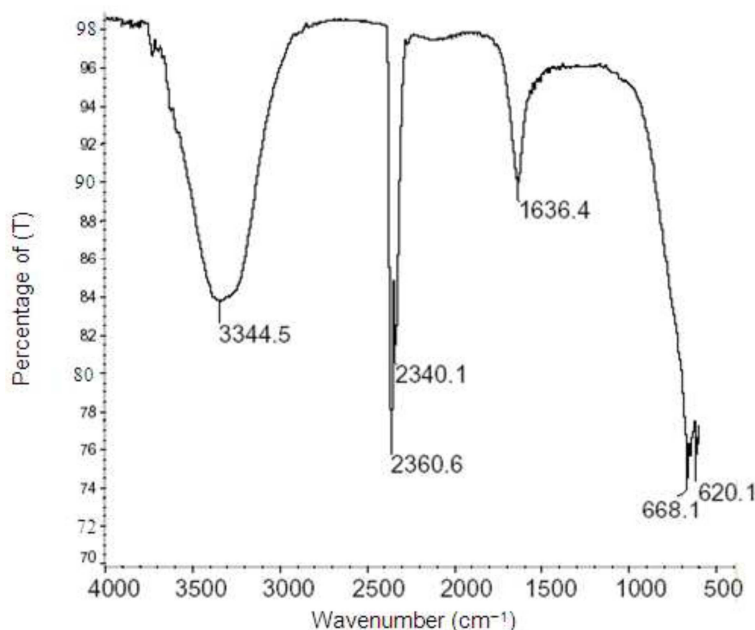


Figure 4. FTIR Spectrum of Ni^{2+} laden Chitosan.

3.2. Result of Analysis on Factor Influencing Adsorption Process

3.2.1. Result of Analysis on Effect of Adsorbent Dose on the Adsorption of Pb^{2+} and Ni^{2+} (II) Ions

Adsorbent provides binding sites for the sorption of metal ions, and hence its concentration strongly affects the sorption of metal ions from the solution [34]. The amount of adsorbent used for the treatment studies is an important parameter, which determines the potential of adsorbent to remove metal ions at a given initial concentration [35]. The study effect of adsorbent dose on metal adsorption has shown that adsorption had increased for both the metals with increase in amount of chitosan derived from snail shell. The effect of the amount of adsorbent for the removal of Pb^{2+} and Ni^{2+} ions was depicted in the Figure 5. It was shown that the removal of Ni^{2+} ions increases with an increase in the amount of adsorbent until record the highest value then decreased while for Pb^{2+} ion there is no dramatically increase in adsorption rate as the adsorbent dosage increases.

The amount of adsorbent dose varied ranging from 0.25g to 1.50g and For Pb^{2+} ion, minimum percentage removal was 99.81% for the dose of 0.25g to maximum value of 99.93% for the dose of 0.5g, therefore for Pb^{2+} ion it can be observed that removal efficiency of the adsorbent generally improved with increasing dose due to availability of more binding sites in the surface of the adsorbent as the dosage increases [22, 36, 37, 38]. This is expected due to the fact that the higher dose of adsorbents in the solution, the greater availability of exchangeable sites for the ions [39]. It showed no further increase in adsorption after a certain amount of adsorbent was added (1.00 - 1.50g). This suggests that after a certain dose of adsorbent, the maximum adsorption sets in and hence the amount of metal ions bound to the adsorbent and the amount of free ions remain constant even with further addition of adsorbent

dose [40]. Whereas for Ni^{2+} ion, minimum percentage removal was 40.61% for the dose of 1.50g to maximum value of 70.58% for the dose of 0.75g. This shows that there was a dramatically increase in the rate of adsorption of Ni^{2+} ion from 0.25 - 0.75g of the adsorbent dose due the active sites on an adsorbent get deprotonated [13, 41] causing an increase in the rate of adsorption dose and also decreases from 0.75 - 1.50g of the adsorbent dose due to the fact that the active site on the adsorbent dose get protonated as the adsorbent dose increases, the adsorbent is positively charged and hence offers repulsive force to approaching the metal ions, therefore leading to a decrease in the adsorption of Ni^{2+} ion at higher adsorbent dose [42]. However, the percentage adsorption of metal ions was higher for Pb^{2+} ion as compared to the Ni^{2+} ion and likewise this result showed that the adsorbent dose chitosan was efficient for maximum removal of Pb^{2+} and Ni^{2+} ions.

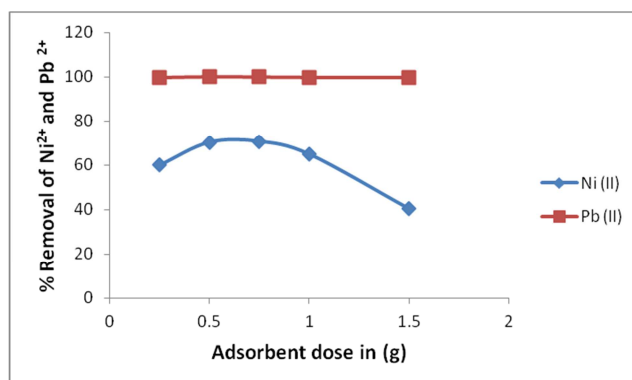


Figure 5. Effect of adsorbent dose on the adsorption of Pb^{2+} and Ni^{2+} ions.

3.2.2. Result of Analysis on Effect of Temperature on the Adsorption of Pb^{2+} and Ni^{2+} Ions

Temperature change affects the stability of the metal ion species initially placed in solution. Increase in temperature

increases the rate of adsorbate diffusion across external pore at the adsorbate particles because liquid viscosity decreases as temperature increases [43]. It can be seen in Figure 6 that for Pb^{2+} ion there is increase in the adsorption rate as the temperature increases from 305 – 325K and decreases as the temperature increases from 325 - 355K and maximum adsorption was observed at 335K for Pb^{2+} ion showing 87% removal and at over 335K adsorption decreased to 45% removal of the Pb^{2+} ion, as seen in Figure 6 below, with an increase in temperature, adsorption capacity decreases due to fact that as decrease in activity surface brings about adsorption between Pb^{2+} ion and chitosan adsorbent leading to an exothermic process [44]. Also, with increasing temperature, the forces of attraction between the chitosan surface and Pb^{2+} ion get loosen and weakened and bring about weak binding interaction between the active sites metal ion which set in decrease in sorption rate to support physiosorption which is exothermic process [45]. Likewise for Ni^{2+} ion, there is increase in the adsorption rate as the temperature increases from 305 – 355K and maximum adsorption occur at 355K showing 80% removal of Ni^{2+} ion which suggesting that adsorption between Ni^{2+} ion and chitosan was an endothermic process, the increase in temperature not only increases the rate of diffusion of the metal ions present but also increases the rate of complexation with the functional groups present in the adsorbent [46]. Therefore Pb^{2+} has 87% removal with an exothermic process and Ni^{2+} has 80% removal with an endothermic process.

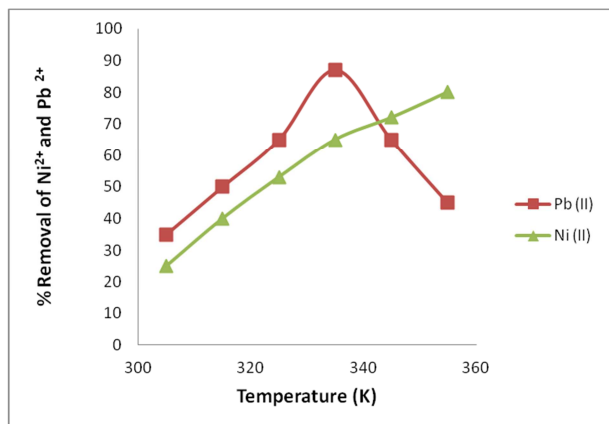


Figure 6. Effect of Temperature on the adsorption of Pb^{2+} and Ni^{2+} ions.

3.2.3. Result of Analysis on Effect of Contact Time on the Adsorption of Pb^{2+} and Ni^{2+} Ions

In batch adsorption experiments, the determination of the optimum contact time required to achieve the highest removal of metal ions is one of the key factors usually assessed. Equilibrium time is one of the important parameters for selecting a wastewater treatment system [47]. Effect of contact time on adsorption was studied and the results are shown in Figure 7. This result indicated that metal ions removal was increased with an increase in contact time before equilibrium was reached [15]. Other parameters such as dose of adsorbent and pH of solution were kept constant. Increase in removal efficiency with increase in time of

contact can be attributed to the fact that more time becomes available for metal ions to make an attractive complex with chitosan [48]. Likewise, the rate of percentage metal removal is higher in the beginning due to a larger surface area of the adsorbent being available for the adsorption of the metals. The metal uptake by the sorbent surface will be rapid initially, and then slow down as the active site get adsorbed by the heavy metals remaining in solution [49].

From the obtained result, it was shown that the removal of metal ions increased as contact time increases from 5 - 120 mins for both Pb^{2+} and Ni^{2+} ions while there is no appreciable change in the adsorption rate for both Pb^{2+} and Ni^{2+} ions as they tend to attained equilibrium at 180 -360 mins contact time with Pb^{2+} recording 99.83% removal and Ni^{2+} ion showing a recording 70.37% removal. This plots indicated that the remaining concentration of metal ions becomes asymptotic to the time axis such that there is no appreciable change in the remaining metal ion concentration after 180 mins for both metal ions. This time (180mins) represent the equilibrium time at which an equilibrium metal ion concentration (C_e) is presume to have been attained for both Pb^{2+} and Ni^{2+} ions. It is evident that the adsorption of the two metal ions unto chitosan follows two phases, a linear phase of adsorption and then an almost flat plateau section. This may be attributed to the instantaneous utilization of the most readily available adsorbing sites on the adsorbent surface, which go in line and the same with work published by [50].

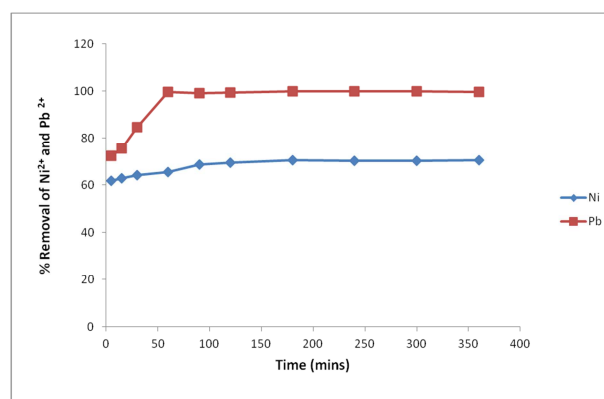


Figure 7. Contact Time Studies of the adsorption of Pb^{2+} and Ni^{2+} ions.

3.2.4. Result of Analysis on Effect of pH on the Adsorption of Pb^{2+} and Ni^{2+} Ions

The solution pH is one of the parameters having considerable influence on the adsorption of metal ions, because the surfaces charge density of the adsorbent and the charge of the metallic species present on the pH [51]. Also pH can affects concentration of the counter ions on the functional groups of the adsorbent, surface charge of the adsorbent, equilibrium of the system, metal chemistry of solution, and the degree of ionization of the of the adsorbate during reaction [52, 53, 54]. The adsorption of Pb^{2+} and Ni^{2+} ions on snail shell derived chitosan was studied over a pH range 1.0 – 9.0 by using a fixed concentration at 298K. The role of hydrogen ion concentration was examined in solutions at different pH. From Figure 8, it can be explained by the following facts that at

lower pH values, H^+ in the solution will compete strongly with heavy metals ion for the active sites due to the fact that the adsorbent is positively charged and hence offers repulsive force to approaching the metal ions therefore, it reduces heavy metal ion binding on the adsorbent surface [55]. When pH increases, the electrostatic repulsion between heavy metals ions and surface sites and the competing effect of H^+ decrease and consequently the heavy metals ion adsorption increases [56]. The result in Figure 8 showed an increase in adsorption with increasing pH of solution for both metals ions. For Pb^{2+} ion showing the removal efficiency from 55.48% to 82.1% over a pH range of 1.0 - 5.0 and then decline at higher pH 5.0 - 9.0 showing a decrease in the removal efficiency 82.1% to 42.68% and likewise for Ni^{2+} ion, showing an increase in the removal efficiency from 9.12% to 68.26% over a pH range of 1.0 - 7.0 and drastically decrease at higher pH 7.0 - 9.0 showing a decrease in the removal efficiency from 68.28% to 58.5%. This result explain that Pb^{2+} ion show that maximum removal were obtained at pH 5 with little significance to pH 4 while Ni^{2+} ion show that maximum removal were obtained at pH 7. Beyond this optimum pH, the results showed a decrease in adsorption for both metal ions due to formation precipitates or metal hydroxides as $Pb(OH)_2$ and $Ni(OH)_2$. Hence 82.1% removal of Pb^{2+} ion was achieved even at a low pH of 5 because of the low concentration of Pb^{2+} ion present in the wastewater. The increase in percentage removal of the metal ions may be explained by the fact that at higher pH the adsorbent surface is deprotonated and negatively charge; hence attraction between the positively metal cations occurred [57]. Likewise Increases in metal removal with increase pH can be explained on the basis of a decrease in competition between proton and metal cations for same functional groups and by decrease in positive surface charge, which results in a lower electrostatic repulsion between surface and metal ions and brings about decrease in adsorption at higher pH is due to formation of soluble hydroxyl complexes [15, 58] These Similar trend was observed with the adsorption of lead and Nickel from aqueous solution by chitosan [59, 60, 61].

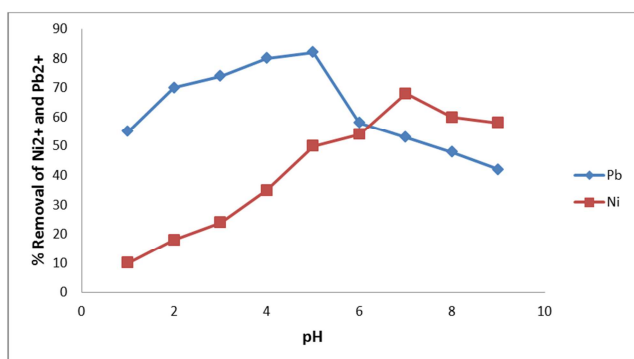


Figure 8. pH Profile Studies of the adsorption of Pb^{2+} and Ni^{2+} .

3.2.5. Result of Analysis on Effect of Initial Metal Ion Concentration on the Adsorption of Pb^{2+} and Ni^{2+} Ions

Initial ion concentration has a significant effect on the adsorption of heavy metals ions from wastewater through

ability of surface functional groups to bind metal ions and provide a driving force to overcome the mass transfer resistance of metal between the aqueous and solid phases [62, 63]. As initial metal ion concentration increases, there is an increase in the amount of metal ions bound but the percentage quantity adsorbed decreases [64, 65]. From the study, it was shown that effect of initial metal ion concentration (C_0) on the adsorption behaviour of Pb^{2+} and Ni^{2+} metal ions samples, ranging from 100 to 500 mg/ l with a fixed adsorbent dose of 0.3g at the optimum pH and contact time. Figure 9 showed that Pb^{2+} has optimum adsorption at 75mg/L with 7.48mg/g metal removal corresponding to 99.97% metal bound; Ni^{2+} showed optimum adsorption at 10mg/L with 0.85mg/g metal removal corresponding to 84.74% metal bound. The adsorbed metal ion for Pb^{2+} and Ni^{2+} ions values increased with increase in initial ion concentration (C_0), this increase is probably due to a high driving force for mass transfer, therefore when the concentration of metal ions in solution was higher, the adsorption capacity also increases [66].

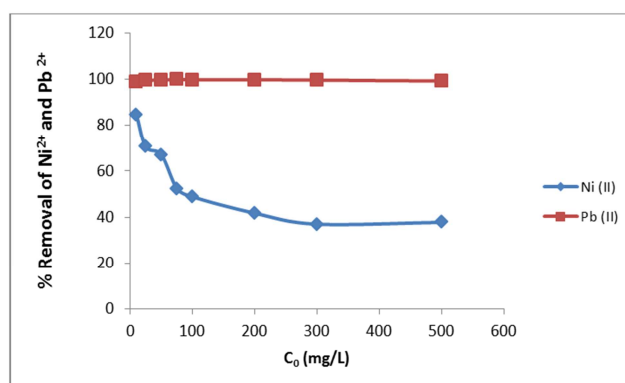


Figure 9. Initial Metal ion Concentration Study of the adsorption of Pb^{2+} and Ni^{2+} ions.

4. Adsorption Model

4.1. Adsorption Isotherm

The adsorption isotherms are one of the most useful data to understand the mechanism of the adsorption and the characteristics of isotherms are needed before the interpretation of the kinetics of the adsorption process. It is also to examine the relationship between sorbed (q_e) and aqueous concentration C_e at equilibrium, sorption isotherm models are widely employed for fitting the data, of which the Langmuir and Freundlich equations are most widely used to describe the equilibrium sorption of metal ions [59]. Several equilibrium data are usually verified using adsorption isotherms to study the nature of adsorption process. These include Langmuir, Freundlich and Temkin isotherm models.

4.2. The Langmuir Isotherm

The Langmuir isotherm model assumes a surface with homogeneous binding sites, equivalent sorption energies, and no interaction between sorbed species [67]. The Langmuir model assumes that the uptake of metal ions occurs on a

homogenous surface by monolayer adsorption without any interaction between adsorbed ions [68]. In this model once a site is filled, no further sorption can take place at that site. As such, the surface will eventually reach a saturation point where the maximum adsorption of the surface will be achieved [69]. The Langmuir equation has been frequently used to give the sorption equilibrium. The Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases. To get the equilibrium data, initial metal concentrations were varied while the adsorbent mass in each sample was kept constant. The linearised Langmuir isotherm allows the calculation of adsorption capacities and Langmuir constant by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_o b} + \frac{C_e}{q_o} \quad (2)$$

Where C_e is the equilibrium concentration (mg/L), q_e is the amount adsorbed at equilibrium; q_o and b is Langmuir constants related to the adsorption capacity and energy respectively. The essential characteristic of the Langmuir isotherm may be expressed in terms of dimensionless separation parameter $R_L = 1/(1 + b C_0)$, which is indicative of the isotherm shape that predicts whether an adsorption system is favourable or unfavourable [70]. The adsorption process as a function of R_L may be described as: Unfavorable when $R_L > 1$; Linear when $R_L = 1$; Favorable when $0 < R_L < 1$; Irreversible when $R_L = 0$. The plots of C_e/q_e vs C_e for both Pb^{2+} and Ni^{2+} ions were presented in Figure 10 and 11 respectively. R^2 values of 0.752 for Ni^{2+} suggested that the Langmuir isotherm provided a fairly favourable model for the sorption process, whereas Pb^{2+} ion with R^2 value of 0.125 indicated that the data did not fit into Langmuir Isotherm.

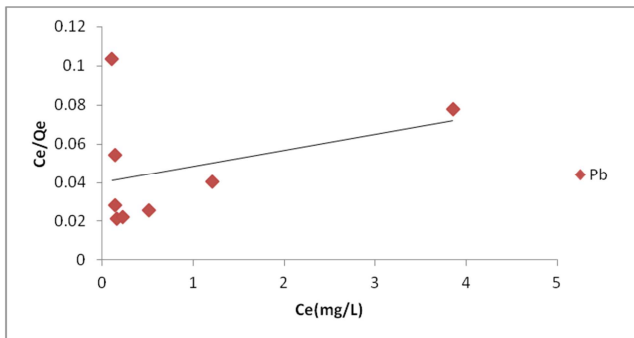


Figure 10. Plot of Langmuir Isotherm for Pb^{2+} Ion.

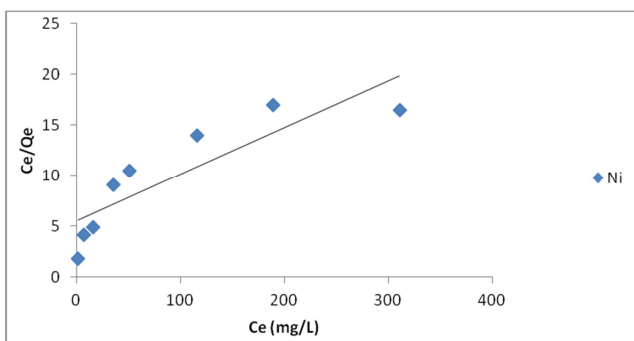


Figure 11. Plot of Langmuir Isotherm for Ni^{2+} Ion.

4.3. The Freundlich Isotherm

The Freundlich isotherm model applies to adsorption on heterogeneous surfaces with the interaction between adsorbed molecules, and the application of the Freundlich equation also suggests that sorption energy exponentially decreases on completion of the sorption centers of an adsorbent [69, 23]. The Freundlich isotherm equation is used for the description of multilayer adsorption with the interaction between adsorbed molecules. The model predicts that the adsorbate concentration in the solution will be increasing. The non-linear form of Freundlich equation may be written as:

$$\log q_e = \log K_F + 1/n_F \log C_e \quad (3)$$

Where C_e is the equilibrium concentration (mg/L), q_e is the amount of metal adsorbed at equilibrium (mg/g), K_F and n_F are Freundlich constants; n_F gives an indication of the favorability and K_F the capacity of adsorbent. Figure 12 shows the plots of $\log q_e$ against $\log C_e$ for Pb^{2+} and Ni^{2+} ions. Then value indicates the degree of nonlinearity between solution concentration and adsorption as follows: if $n = 1$, then adsorption is linear; if $n < 1$, then adsorption is a chemical process; if $n > 1$, then adsorption is a physical process [71]. The calculated Freundlich constants as presented in Table 1 showed that the values of n_F for both metal ions were greater than 1 indicating a favorable adsorption process (chemical process). The high correlation coefficient, R^2 values proved that the data complied with Freundlich isotherm. The results then indicated heterogeneous system, better adsorption mechanism and formation of relatively stronger bond between the adsorbent and adsorbate. Patil *et al.*, 2006 [72] submitted similar report using PAC and Babbul back for Ni^{2+} removal.

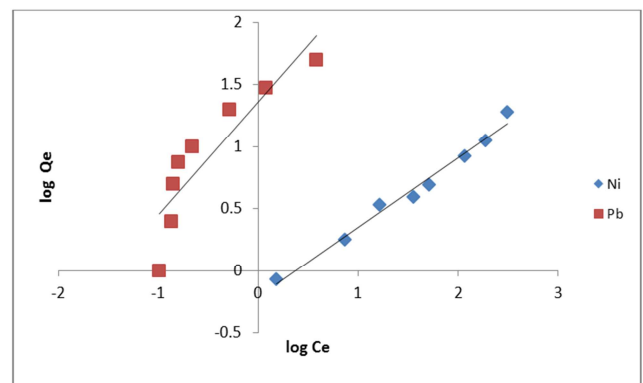


Figure 12. Plot of Freundlich Isotherm Model of Pb^{2+} and Ni^{2+} ions.

4.4. The Temkin Isotherm

The Temkin isotherm model [73] suggests an equal distribution of binding energies over a number of exchange sites on the surface. The Temkin isotherm in its linear form is given by the equation;

$$q_e = B_T \log K_T + B_T \log C_e \quad (4)$$

The magnitude of the Temkin parameters B_T is related to

the heat of adsorption and K_T is equilibrium binding constant. Figure 13 shows the Temkin curves for metal ions adsorption, examination of the data showed that the Temkin isotherm provided a very good fit for both Pb^{2+} and Ni^{2+} ions with high correlation coefficient, R^2 values of 0.736 and 0.991 for Ni^{2+} and Pb^{2+} ions respectively.

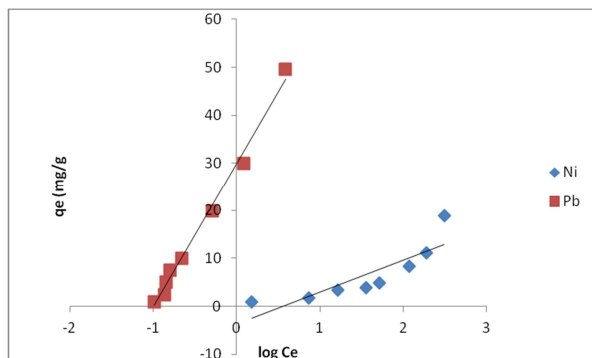


Figure 13. Lots of Temkin Isotherm of Pb^{2+} and Ni^{2+} ions.

Table 1. Sorption Isotherm Parameters for Pb^{2+} and Ni^{2+} ions.

Isotherm model	Parameters	Lead (Pb^{2+})	Nickel (Ni^{2+})
Freundlich	K_F	22.845	0.612
	N_F	1.102	1.784
	R^2	0.7973	0.984
Langmuir	K_L	0.204	0.008
	q_m	121.951	21.834
	R^2	0.125	0.752
Temkin	K_T	9.883	0.281
	B_T	30.048	6.675
	R^2	0.991	0.736

The isotherm parameters as presented in Table 1 show the comparison of correlation coefficient for Langmuir, Freundlich and Temkin models. Freundlich and Temkin models were more obeyed than Langmuir model which suggested that the adsorption system was heterogeneous.

5. Conclusion and Recommendation

In conclusion this study has revealed that removal of Pb^{2+} and Ni^{2+} ions from aqueous solutions was established using chitosan powder prepared from snail (*Helix pomatia*) shells and maximum adsorption was obtained at pH 5 for Pb^{2+} ion and pH 7 for Ni^{2+} ion with 82.1% and 68.28%, at a maximum adsorption temperature of 335K for Pb^{2+} ion and 355K for Ni^{2+} ion with 87% and 80% metal removal respectively. The study clearly shows that effect of initial metal ion concentration and adsorbent dose on metal adsorption has shown that adsorption increase both the metals with increase in amount of chitosan derived from snail shell with Pb^{2+} and Ni^{2+} ions having a maximum adsorption dose of 0.50g and 0.75g with a 99.93% and 70.58% metal removal at contact time showing that the removal efficiency increased with increase in contact time until equilibrium was reached at 180 mins for Pb^{2+} ion and Ni^{2+} ion with 99.83% and 70.37%, respectively. The data from batch studies for the adsorption of Pb^{2+} and Ni^{2+} ions showed that pseudo-second order

kinetic model was suitable compared to pseudo-first order and the isotherm studies showed that Freundlich and Temkin models were obeyed unlike Langmuir model going by their correlation coefficient, R^2 values.

It is therefore recommend that from the results obtained in this study and field observation during sampling, the following recommendation is been offered;

- The adsorption thermodynamic parameters may be an area of further research in this study.
- Adsorbents used should be regenerated using a suitable regenerating agent and the adsorbents used again.
- The use of alternate methods such as columns or beds is highly recommended.

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