Adsorption Kinetics and Thermodynamic Studies of Zn(II) And Pb(II) ions by Biopolymeric Adsorbents obtained from Fish (*Lates niloticus*) Scale.

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Abstract:
The adsorption of Zn(II) and Pb(II) ions from aqueous solution has been investigated using chitosan and its derivatives from fish scale Lates niloticus as a function of contact time, initial metal ion concentration, pH and temperature. Batch adsorption experiments were carried out to obtain optimum conditions for the removal of the metal ions. The optimum conditions obtained were 60 minutes contact time, initial ion concentration of 75 mg/L, and pH 7. The kinetics of adsorption was studied for the contact time range of 30-70 minutes. The results obtained showed that the adsorption of the metal ions could be described by both first and second order kinetic models with correlation coefficient (R^2) values of 0.0003 and 1 for pseudo-first order and pseudo-second order for Zn^{2+} adsorption; 0.4987 and 0.08707 for pseudo-first order and pseudo-second order respectively for Pb^{2+} adsorption. The free energy change (ΔG^+) obtained at the optimal conditions is in the range of -4.567 to -28.919 for Zn^{2+} and 0.223 to 1.535 for Pb^{2+}. This result indicates that the adsorption process is spontaneous and thermodynamically favourable.

Keywords: *Adsorption, kinetics, thermodynamics, biopolymeric, adsorbent, Lates niloticus.*

I.   Introduction:
Bioaccumulation of heavy metals in food chains and their toxicity to biological systems due to increased concentration over time have led to tremendous pressure for their treatment and removal. Heavy metals can enter into water bodies through agricultural runoff, industrial effluents, household uses and from commercial applications.

There are different treatment processes that have been used to remove heavy metal ions from wastewater such as ion exchange, membrane filtration, precipitation and coagulation, electro dialysis, reverse osmosis and adsorption (Fenglain *et al*, 2011). Many of these processes are very expensive to operate, hence the need for adsorption of method which is used in many industries for the removal of water pollutants due to its low cost and applicability on a large scale.

Different adsorbents which are low-cost that have been used and tested to remove heavy metal ions are rice husk, wood sawdust, waste biomass, chitosan etc. In this research, chitosan and its derivatives which are derived from fish waste were used for the removal of heavy metals from aqueous and natural resources. Chitin and chitosan are bipolymers that have excellent properties in biodegradablility, biocompability, non-toxicity and absorption. Chitin and chitosan consist of 6.9% wt nitrogen in its structure which acts as a chelating agent (Hudson and Smith, 1998). Chelating agent is the term for organic compound with the ability to perform chelation. Meanwhile, chelation is described as the ability of the ion or molecule to bind with metal ion. The process involved the formation of two or more separate coordinate bond between a polydentate ligand with a central atom. This chelate effect described the enhanced affinity of the chelating ligand on metal ions. With possession of these ligands, chitin and chitosan are both excellent chelating agents.

Chitosan is a low cost adsorbent which is biodegradable and biocompatible polymer and is produced by deacetylation of chitin (Ashraf *et al*, 2007).

The purpose of using substitutes derived from fish waste is to replace the current reagents and resins produced from petroleum that are detrimental to the environment. Additionally, it is important to note that although ion exchange resins and activated carbon have been recognized as effective methods for treating wastewater, their low efficiency and high cost have limited their use in actual industrial scenarios (Park *et al.,* 2010).

II.   Materials and Methods

The fish scales used were obtained as waste from fish vendors at Lake Geriyo, Yola Adamawa State-Nigeria. All the chemicals used were of analytical grade with percentage purity of 99.9 %. Each chemicals purchased were accompanied by a certificate indicating the purity. Sodium hydroxide pellet and HNO_3 purchased from Burgoyne & Co., Mumbai India. $MnSO_4.H_2O$, $Zn(NO_3)_2.H_2O$, Glutaraldehyde, Acetic acid, Epichlorohydrin (ECH), HCl were purchased from Guangdong GuanghuaSci-Tech Co.,Ltd, China. Double distilled water was used throughout the experimental studies to prepare all solutions. Digital weighing balance (Weda, T18) from Ohaus Corporation, NJ USA; Magnetic stirrer (78HW-1 Constant), and Furnace (Nabertherm) both from Gallenkamp, England; Sonicator (BL30-720A) from Shanghai Bilon Instrument Co., Ltd and pH meter (BDH, 1-14).

Treatment of Sample
Dried fish scales (*lates niloticus*) were obtained as wastes from a local fish market at Yola, Adamawa State. These scales were soaked in doubled distilled water for 2 hours, and thoroughly washed with warm double distilled water. The fish scales were dried in an oven at 100^0C to constant weight. After pulverization to pass through 100μm sieve, they were stored in plastic containers at room temperature before use.

Isolation of Chitin from the Scale
The isolation of chitin from the fish scales were done using two basic steps; deproteinization and demineralization as reported by Kim and Park, (2001) and Mohanasrinivasan *et al.*, (2014).

Preparation of Swollen Chitosan Beads
To prepare highly swollen beads, 2 g of chitosan flakes were completely dissolved in 60 ml of 5% (v/v) acetic acid solution at room temperature with continuous stirring for 24 h(Wang and Fatinathan, 2008). In this case, 60 ml of acetic acid was dissolved in 1200 ml of distilled water to give 5% (v/v) acetic acid solution. Therefore, 40 g of chitosan flakes each of the ground scales were completely dissolved in 60 ml 5% (v/v) acetic acid solution at room temperature with continuous stirring. The viscous solutions were left overnight before adding them drop wise into 500 ml of 0.5 mol/L NaOH solution and stirred continuously. The chitosan beads were left in the solution for about half an hour to ensure that the acetic acids in the beads were neutralized. The beads were filtered, rinsed with distilled waters and air dried.
The chitosan beads were then ground and sieved to a constant particle size of less than 200 μm (> 200μm) before proceeding to modifications of the beads.

Preparation of Crosslinked Chitosan Beads with Glutaraldehyde (GLA)
 Cross linking with glutaraldehyde was done with (25% w/w) that is 25 ml of GLA dissolved in 100 ml of distilled water. 3 g of chitosan beads was used to dissolve in 50 ml of GLA solution. From the GLA solution prepared, 650 ml was used to cross – linked 38 g each of the chitosan beads respectively. The chitosan beads were heterogeneous cross – linked in (25% w/w) aqueous GLA solution without agitation at room temperature for 24 hrs. After 24 h, the cross- linked chitosan beads were filtered and washed with distilled water to remove unreacted glutaraldehyde. The solutions were cast into petri dish and dried overnight at room temperature to form the cross linked chitosan beads. The cross linked chitosan beads were dried further in an oven at 45^0C for 12 hrs to remove completely the residual solvent and kept in a closed container (Mohanasrinivasan *et al.*, 2014).

Preparation of Cross linked Chitosan Beads with Epichlorohydrin (ECH)
The adsorbents were synthesized by soaking 0.3g of chitosan beads in 50 ml of ECH solution (1% v/v), that is in every 1g of the chitosan beads, 150 ml of ECH solution was used. Therefore, 38 g of the chitosan beads were cross – linked in 5,700 ml of ECH solution respectively. The mixtures were stirred for 4 hrs at 40^0C and the spheres formed were rinsed with deionized water to remove the unreacted ECH residues. The spheres were then washed with distilled water until the pH becomes neutral.

Preparation of Stock Solutions
Stock solution of 25 mg/L of Pb was prepared by dissolving lead nitrate ($Pb(NO_3)_2$. To do this, 207.2g of lead (ii) nitrate was added to distilled water contained in 1000 ml volumetric flask. Stock solution of 25 mg/L of zinc is prepared by dissolving anhydrous zinc nitrate $(Zn (NO_3)_2.H_2O)$. To do this, 3.171g of zinc nitrate solution was added to distilled water contained in 1000 ml volumetric flask. Sodium hydroxide and hydrochloric acid were used to adjust the solution pH.

Adsorption Experiments
Batch mode adsorption experiments were conducted in 250 ml Erlenmeyer flasks to determine the best operating conditions, which will facilitate the adsorption of Pb, and Zn ions onto GR(CH), GR(GLA) and GR(ECH) respectively as adsorbents.

Equilibrium Contact Time
Experiments were carried out to determine the contact time needed by the system to reach equilibrium. The procedures are as follows: From the stock solutions, 0.1 g each of the adsorbents (chitosan and modified

chitosans) was added. Then the pH was adjusted to 6.0 using 1M HCl or 1M NaOH, then agitated in a rotary mixer at various times at room temperature.

After each time of agitation, the samples were filtered through 0.45 μm cellulose filter paper then the concentration of the metal remaining in the aqueous solution were determined using AAS. The metal uptake q (mg ion metal/g sorbent) was determined as follows:

$$q = (C_o - C_e). \ v/m$$

Where C_o and C_e are the initial and final metal ion concentrations (mg/l), respectively, v is the volume of solution (ml), and m is the adsorbent weight (g) in dry form. The graph of q vs time was plotted and the equilibrium time was determined and the amount of metal removed at this time.

Effect of Initial Metal Ion Concentration

At the equilibrium time of 1 h, pH 7, and temperature of 30° C, the batch experiment was repeated with various concentrations of metal ions (25 – 100 mg/L) and a fixed amount (0.1g) of chitosan and chitosan derivatives in order to calculate the amount of metal removed in terms of mg/g and percent (%). The percentage of metal ions removed is obtained from equation:

%Removal = {(Co – Ce) / Co} x 100

Where (% R) is the ratio of difference in metal concentration before and after adsorption.

Effect of pH

The effects of pH ranging from 3 to 11 were studied. 25 ml of stock solutions of the ions used (Pb^{2+}, and Zn^{2+}) were measured into different 250 ml conical flask and 0.1g adsorbents (chitosan and modified chitosan) were added and agitated at 150 rpm for 1 hr. The pH was adjusted to the required pH values using 1M HCl or 1M NaOH. The whatman filter paper was used to filter the mixture and the filtrate analysed to determine the concentrations of metal ions. The graph of q vs pH were plotted to determine the pH at which maximum amount of metal will be achieved.

Effect of Temperature

The experiment was carried out in an environmental incubator at various temperatures (30^0 C – 60^0 C) at a contact time. The amount of metal ion adsorbed was determined as described earlier, after attainment of equilibrium.

Adsorption Kinetics

Pseudo- First Order Model

The Pseudo- First Order Kinetic Model was used in this work to predict the metal adsorption kinetics. The metal adsorption kinetics following the Pseudo-first order model is given by Ho and McKay (1999a).

$$\frac{dq}{dt} = k_1 (q_e - q_t)$$

.... (1)

Where K_1 (min^{-1}) is the rate constant of the Pseudo-first order adsorption, q_t (mg/g) is the amount of adsorption at time t (min) and q_e (mg/g) is the amount of adsorption at equilibrium.

After definite integration by application of the conditions qt= 0, at t= 0, and qe = qt at t=t,

Equation (1) becomes

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t$$

.... (2)

By plotting log (qe-qt) versus t, the adsorption rate can be calculated

Pseudo- Second Order Model

The adsorption kinetic data can be analysed using Ho's Pseudo- second order kinetics (McKay and Ho, 1999b,c). This is denoted by

$$\frac{dq}{dt} = k_2 (q_e - q_t)^2$$

.... (3)

Integration of equation (3) and applications of the conditions $q_t = 0$ at t= 0, and $q_e = q_t$ at t = t gives

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{t}{q_e}$$

.... (4)

Where K_2 (g/mg min) is the rate constant, K_2 and q_e can be obtained from the intercept and slope.

Thermodynamic Parameters

In thermodynamic study, K is the equilibrium constant and it dependence with temperature can easily be used to predict the thermodynamic parameters including change in the free energy (G°), enthalpy (H°), and entropy (S°) associated to the adsorption process and were determined by applying the following equations (Ozcan *et.al*, 2005);

ΔG^o = -RTInK ……………………………………….. (1)

Where K = Langmuir constant

T = Absolute temperature (°K)

R = Universal gas constant (8.314Jmol^{-1}K^{-1})

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

The plot of In K as a function of 1/T yields a straight line from which H° and S° can be calculated from the slope and intercept, respectively.

III.   Results and Discussions

Effect of Contact Time on Zinc

From Figure 1 it is seen that the zinc ions removal was increased with an increase in contact time. The result shows that increasing the contact time increased the adsorption of zinc ions, and it remained constant after an equilibrium time of 60 minutes. All parameters (adsorbent dose, pH, initial concentration and temperature) were kept constant.

The result showed that zn(II) ions removal with GR/CH was increased from 97.84 to 99.20%; 97.88 to 99.44% with GR/GLA, and 96.96 to 97.72% with GR/ECH with the contact time variation from 30 to 60 minutes. The percentage removal however remained constant after 60 minutes which showed that equilibrium was reached at 60 minutes.
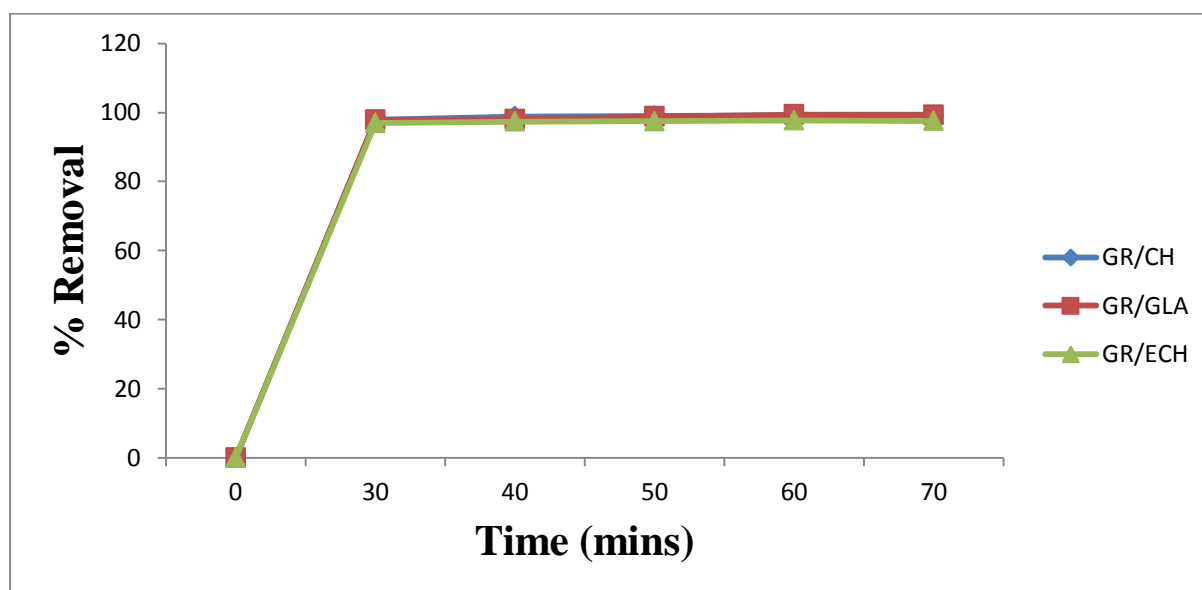

Figure 1: Effect of Contact Time on Zinc

Effect of Contact Time on Lead

Figure 2 showed that the metal ions removal increased with an increase in contact time before equilibrium time. The results also indicated that Pb(II) ions removal increased from 60.00 to 74.40% with GR/CH, 73.56 to 76.00% with GR/GLA and 80.00 to 98.00% with GR/ECH adsorbents respectively with contact time variation from 30 to 60 minutes.
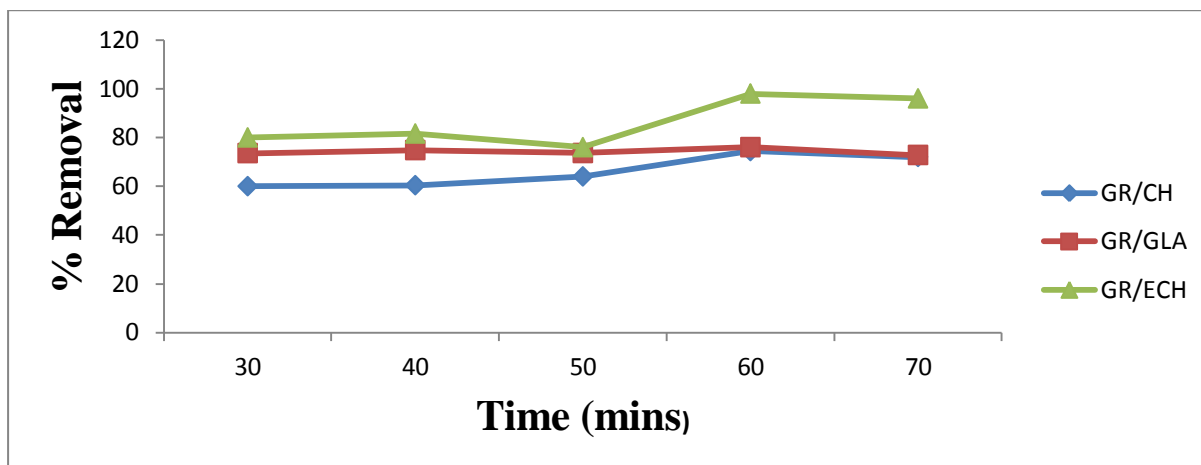
Figure 2: Effect of Contact Time on Lead

Effect of pH on Zinc Adsorption

From Figure 3, it can be deduced that pH influenced the removal efficiency of zinc ions in the aqueous solution. The result shows that the percentage removal of Zn(II) ions was increased with an increase in pH from 3 to 7, and decreased with a further pH increase to 11 at 30°C. The maximum percentage removal of Zn(II) ions was about 96.36% with GR/CH, 96.24% with GR/GLA, and 96.24% with GR/ECH at pH of 7 respectively. This therefore suggests that the optimal pH for the adsorption of Zn(II) ions is 7.

The dominant species of Zinc was Zn(II) which was mainly involved in the adsorption process when the pH was lower than 7. When the pH was greater than 7, zinc ions started to precipitate as $Zn(OH)_2$, this is in agreement with the work done by Karthikeyan *et.al* (2004).

The increase in metal removal as a result of the increased pH can be explained on the basis of the decrease in competition between protons and metal cations for same functional groups and by decrease in positive surface charge, which results in lower electrostatic repulsion between surface and metal ion. The decrease in adsorption of the metal ion at a pH higher that 7 is due to formation of soluble hydroxyl complexes (Ramya *et.al*, 2011). The adsorption of Zn(II) ions was found mainly to be influenced by pH of the solution.
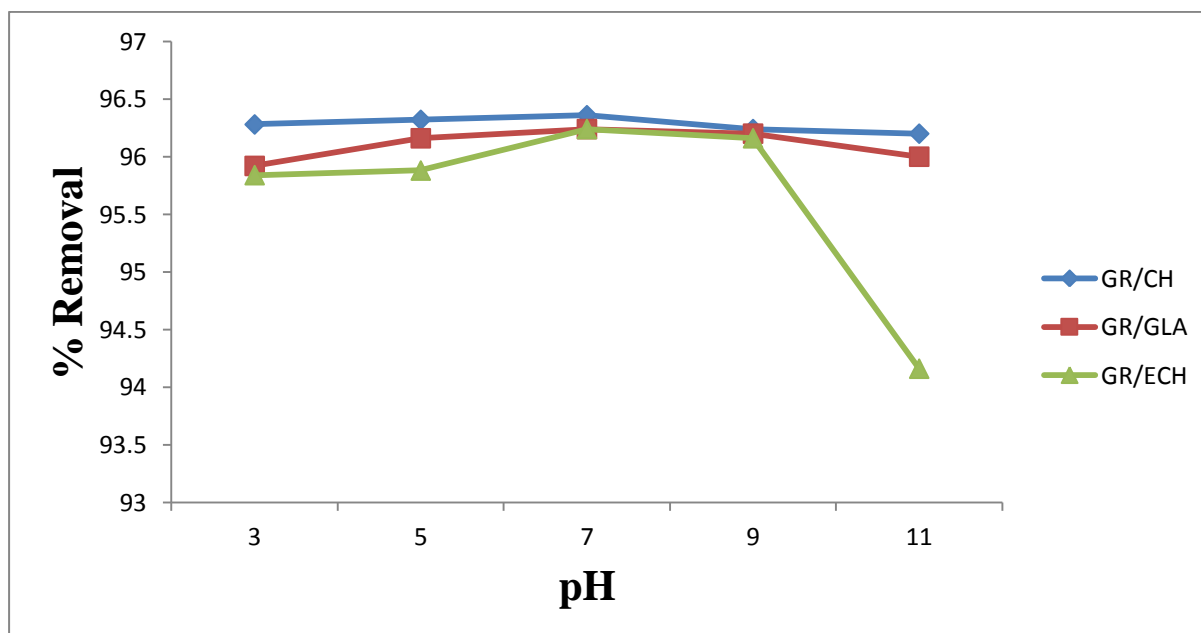

Figure 3: Effect of pH on Zinc Adsorption

Effect of pH on Lead Adsorption

Figure 4 showed that the pH influenced the removal efficiency of the Lead ions in the aqueous solution. The result shows that the percentage removal of Pb(II) ions was increased to maximum and then decreased with pH variation from 3 to 11 at a temperature of 30°C. The maximum percentage removal of Pb(II)

ions was about 85.60% with GR/CH, 96.00% with GR/GLA and 94.00% with GR/ECH at a pH of 7 respectively.

The dominant species of Lead was Pb(II) and was mainly involved in the adsorption process when the pH was lower than 7. When the pH became greater than 7, the Lead ions started to precipitate as $Pb(OH)_2$ also in agreement with Karthikeyan *et.al* (2004). Increases in metal removal with increased pH can be explained on the basis of decrease in competition between proton and metal cations for same functional groups and decrease in positive charge which results in a lower electrostatics repulsion between surface and metal ions. The decrease in adsorption at higher pH is due to the formation of soluble hydroxyl complexes (Ramya *et.al*, 2011).
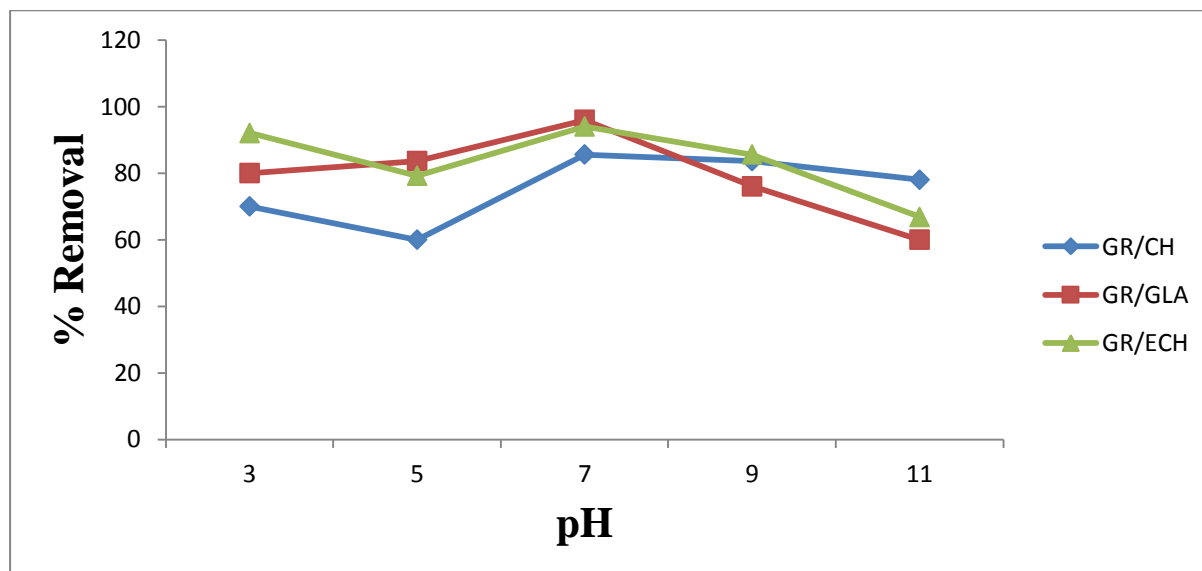
Figure 4: Effect of pH on Lead Adsorption

Effect of Zinc Initial Concentration on Adsorption

The effect of initial zinc concentration on adsorption is shown in Figure 5 at a range 25-100 mg/L, at a pH of 7, temperature of 30^oC, and contact time of 1 hour. The result shows that the amount of metal removed from the solution increased. However, the percentage removal decreased after the concentration of 75 mg/L.

At lower concentration of the metal ions, the number of metal ions available in the solution less as compared to the available sites on the adsorbent. But at higher concentrations, the available sites for the adsorption become fewer and the percentage removal of the metal ions depends on the initial concentration. Therefore, it was evident from the results that zinc adsorption was dependent on the initial metal concentration.
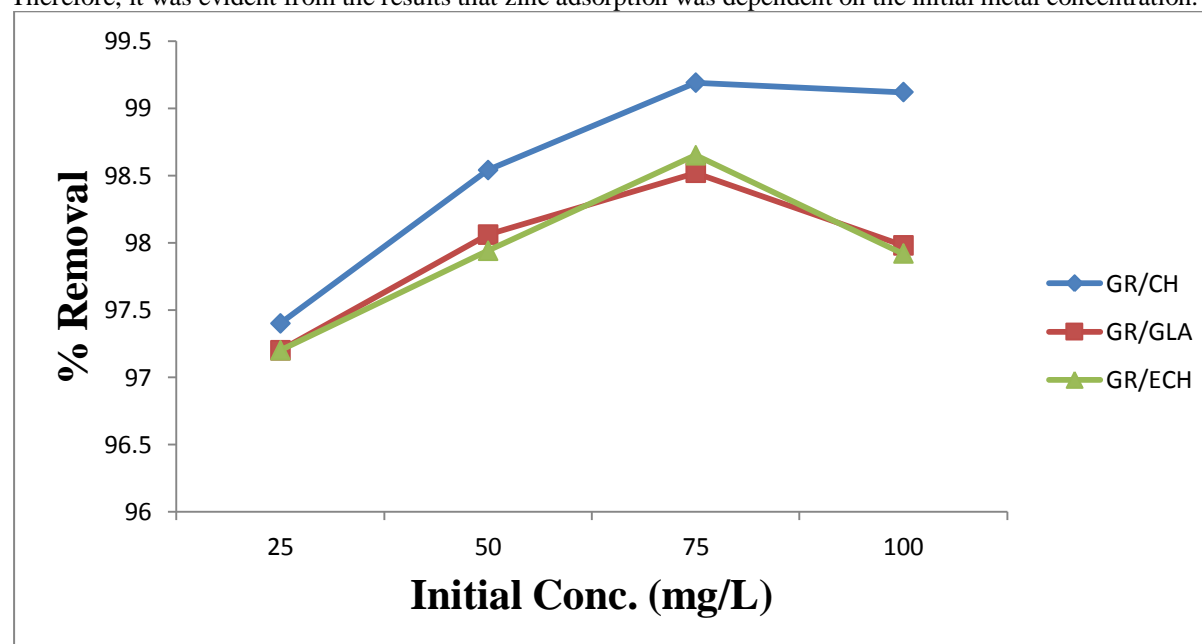

Figure 5: Effect of Zinc Initial Concentration on Adsorption

Effect of Lead Initial Concentration on Adsorption

The removal of Pb(II) ion by the adsorbents according to its initial concentration in solution is shown in Figure 6 at the range 25-100 mg/L at 30°C, pH 7 and the contact time of 1 hour. From the results shown above, it was observed that the amount of metal removed from solution increased with increase in the concentration of the solution. But the percentage of removal decreased after the concentration of 75 mg/L. This shows that the removal of this metal ion is highly concentration dependent. The poorer uptake at higher metal concentration was resulted due to the increased ratio of initial number of moles of Lead to the vacant sites available. For a given adsorbent dose, the total number of adsorbent sites available was fixed thus adsorbing almost the equal amount of adsorbate, which resulted in a decrease in the removal of adsorbate consequent to an increase in the initial Lead concentration.
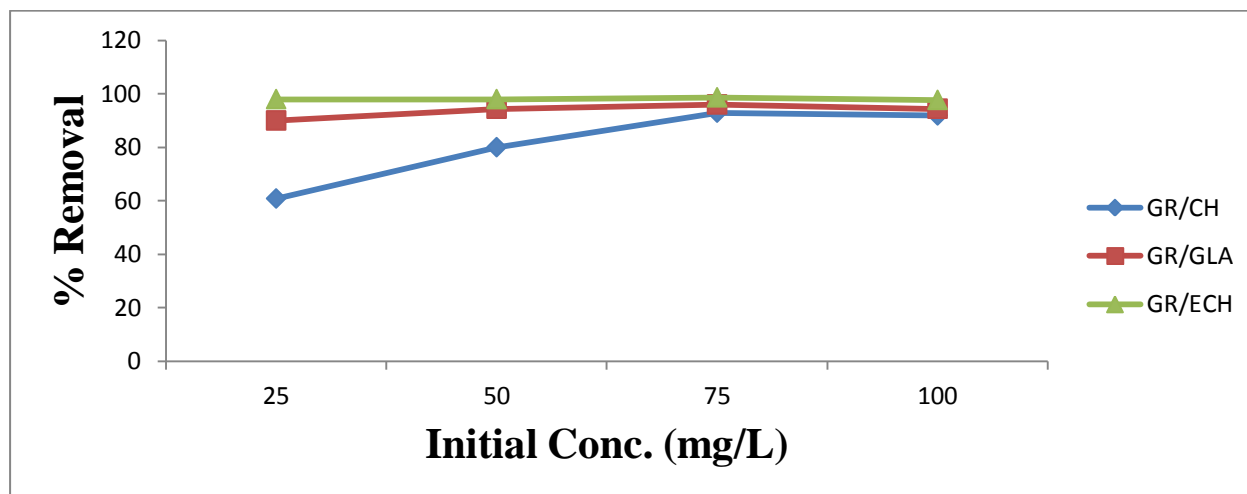

Figure 6: Effect of Lead Initial Concentration on Adsorption

Effect of Temperature on Zinc Adsorption

The effect of temperature on zinc adsorption process is shown in Figure 7. The data shows that the adsorption capacity decreases with increase in temperature, which shows that the process is exothermic. The effect of temperature on the removal of zinc ions using GR/CH, GR/GLA, and GR/ECH were studied within the range of 303-333K, keeping other parameters such as pH of the solution and adsorbent dosage constant. With increase in the temperature from 30-60°C, the percentage zinc removal were decreased from 96.20% to 94.00% using GR/CH, 98.08% to 94.40% for GR/GLA and 98.00% to 94.20% using GR/ECH respectively. From the figure 7, it is very clear the low temperatures are in favour of zinc ion removal. This can be explained further by the tendency of the zinc ions to escape from the solid phase to the bulk phase with an increase in temperature of the solution. The adsorption process for the removal of zinc ions from the aqueous solution is physical in nature. The adsorption process also brought about by electrostatic interaction which is related with low adsorption heat; therefore, it is exothermic in nature.
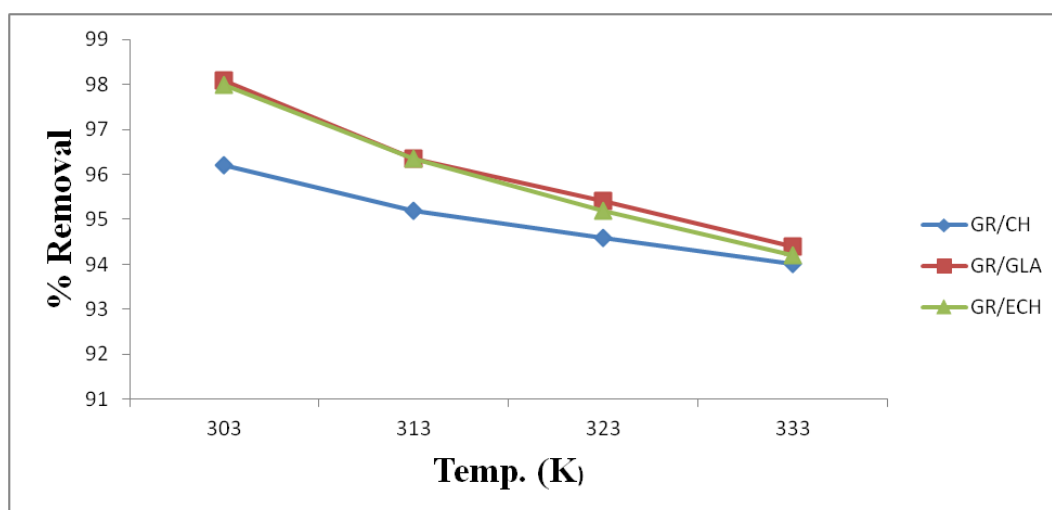

Figure 7: Effect of Temperature on Zinc Adsorption

Effect of Temperature on Lead Adsorption

The effect of temperature on the lead adsorption process is shown in Figure 8. The data shows that the adsorption capacity decreases with increase in temperature. The temperature effect on the removal of Pb ions using GR/CH, GR/GLA, and GR/ECH were studied within the temperature range of 303-333K, keeping other parameters such as pH of the solution and adsorbent dosage constant. With increase in temperature from 30-60°C, the percentage removal of Pb ions were decreased from 71.00% to 56.8% using GR/CH, 78.40% to 69.60% using GR/GLA and 77.92% to 66.00% using GR/ECH respectively. From the figure, it is very clear that the low temperatures are in favour of Pb ion removal. This can be deduced by the tendency of the lead ions to escape from the solid phase to the bulk phase with an increase in temperature of the solution. The adsorption process for the removal of lead ions from the aqueous solution is physical in nature. The adsorption process is also brought about by the electrostatic interaction which is related with low adsorption heat, therefore the process exothermic in nature.
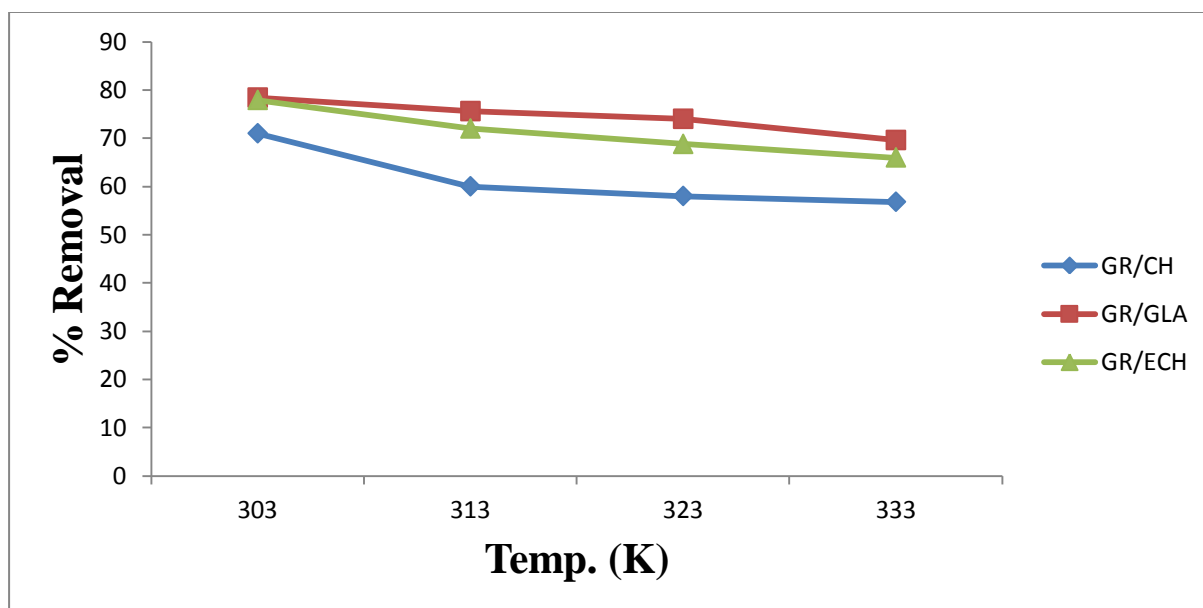

Figure 8: Effect of Temperature on Lead Adsorption

Adsorption Kinetics

The kinetics of adsorption was studied for a contact time ranging from 30 – 70 minutes. Data obtained from the effect of contact time on adsorption of the metal ions (Zn, and Pb,) were fitted into the kinetic models shown in Table 1 and Figures 9-12. The results obtained showed that the adsorption of the metal ions on GRCH, GRGLA and GRECH could be described by both first and second order kinetic models. From their correlation coefficient R^2, it was observed that the pseudo-second order gave a better fitting for all the metal ions (Zn, and Pb) used in this experiment with R^2 values of 1 and 0.8707 respectively as compared with the pseudo-first order which gave lower R^2 values of 0.0003 and 0.4987 respectively.

The high value of R^2 for pseudo-second order indicates that the pseudo-second order best describes the whole adsorption process which shows that chemisorption predominant on all absorbents as the rate determining step (Ajay, *et.al,* 2015). From the kinetic results of the metal ions (Zn, and Pb) onto GRCH, GRGLA and GRECH as shown by the pseudo-second order, the adsorption of zinc ions is more favourable than lead.

Table 1: Adsorption Kinetics of Zinc and Lead ions

Adsorbate		Absorbent	
Zinc	GRCH	GRGLA	GRECH
First Order			
K_1 (Lmin^{-1})	0.016	0.021	0.002
Q_e (mg/g)	0.093	0.226	0.037
R^2	0.017	0.039	0.000
Second Order			
K_2 (gmg^{-1}min^{-1})	0.281	0.165	0.492
Q_e (mg/g)	6.289	6.329	6.135
R^2	1.00	0.999	1.000
h (gmg^{-1}min^{-1})	11.12	6.623	18.518

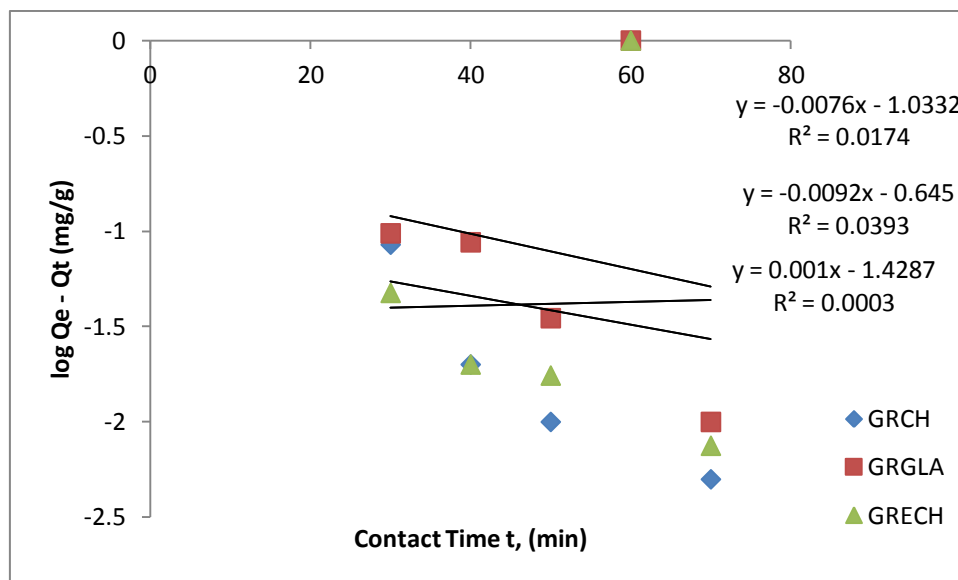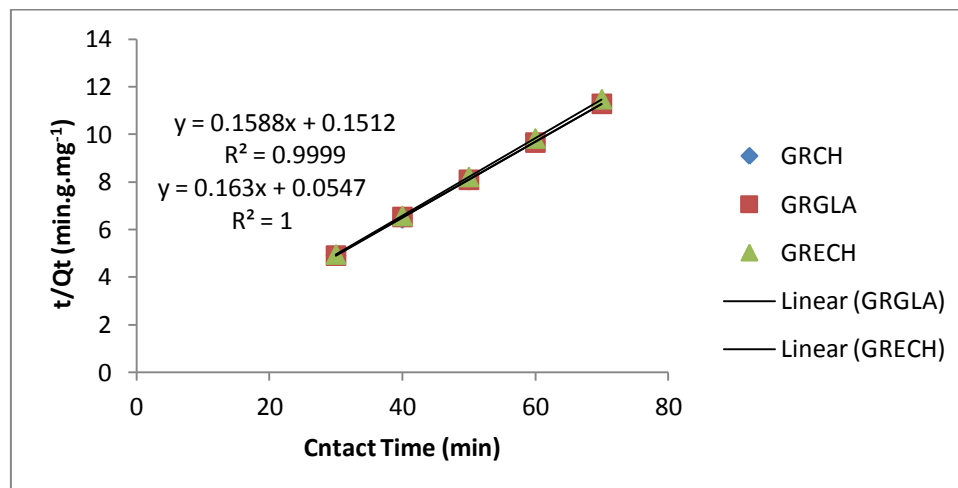| Lead			
First Order			
K_1 (Lmin^{-1})	0.035	-0.020	0.044
Qe (mg/g)	3.357	0.042	6.592
R^2	0.476	0.264	0.498
Second Order			
K_2 (gmg^{-1}min^{-1})	0.0095	-0.457	0.007
Qe (mg/g)	5.747	4.608	7.576
R^2	0.958	0.996	0.870
h (gmg^{-1}min^{-1})	0.313	-9.709	0.396

Figure 9: Pseudo-First Order Plot for Zn Adsorption

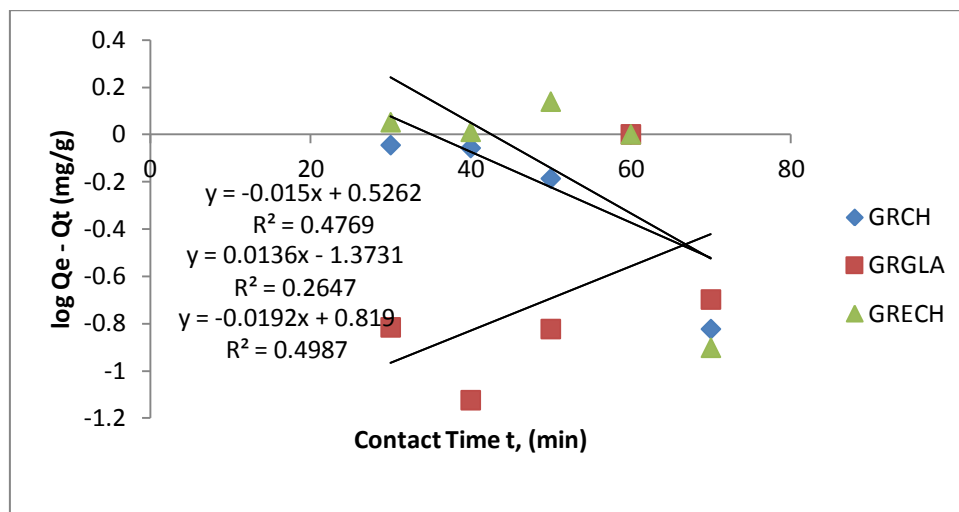**Figure 10: Pseudo-Second plot for Zn Adsorption**

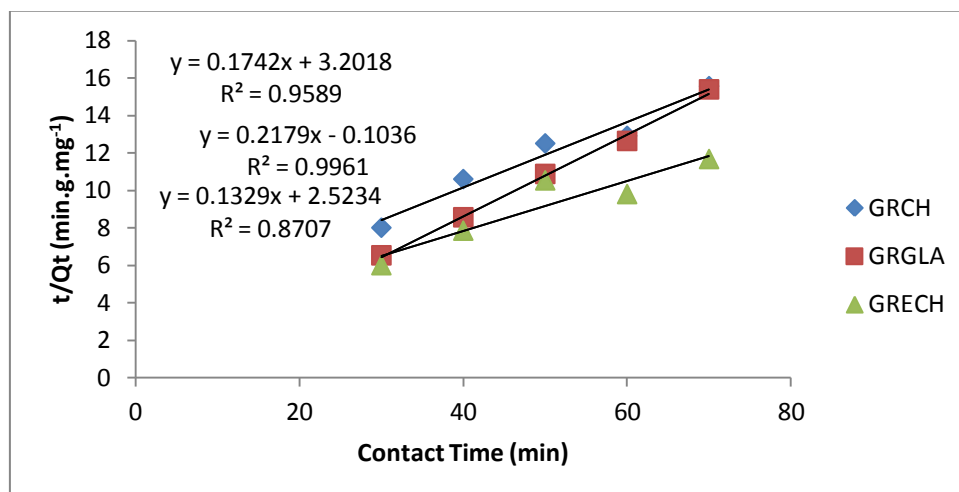**Figure 11: Pseudo-First Order Plot for Pb Adsorption**

Figure 12: Pseudo-Second plot for Pb Adsorption

Thermodynamics studies

The calculated values of thermodynamic parameters used to determine the spontaneity of adsorption are listed in Table 2 and Figures 13-14. The negative values of ΔG^+ suggest that the adsorption process is spontaneous and thermodynamically favourable. The ΔG^+ values also determines the rate of the adsorption, i.e. rate increases as ΔG^+ decreases and the reaction proceeds only when the energy requirement is fulfilled (Otuonye *et.al*, 2014). The ΔG^+ value in zinc adsorption for GRCH is the lowest showing that the rate of adsorption of zinc is highest in this system and might lead to strong binding. Also ΔG^+ in Lead adsorption for GRCH is the lowest showing that the rate of adsorption of Lead is highest in this system and might lead to strong binding than the others.

The ΔH^+ values equally indicate that the process is exothermic and low temperature is appropriate and makes it easy and feasible, as it does not consume energy. The magnitude and sign of ΔS^o gives an indication of whether the adsorption process is associative or dissociative mechanism (Nussey *et.al*, 2000). Therefore, the large negative values of ΔS^o obtained in this study suggest an associative mechanism.

Table 2: Thermodynamic values for the adsorption of Zinc and Lead on the various adsorbents

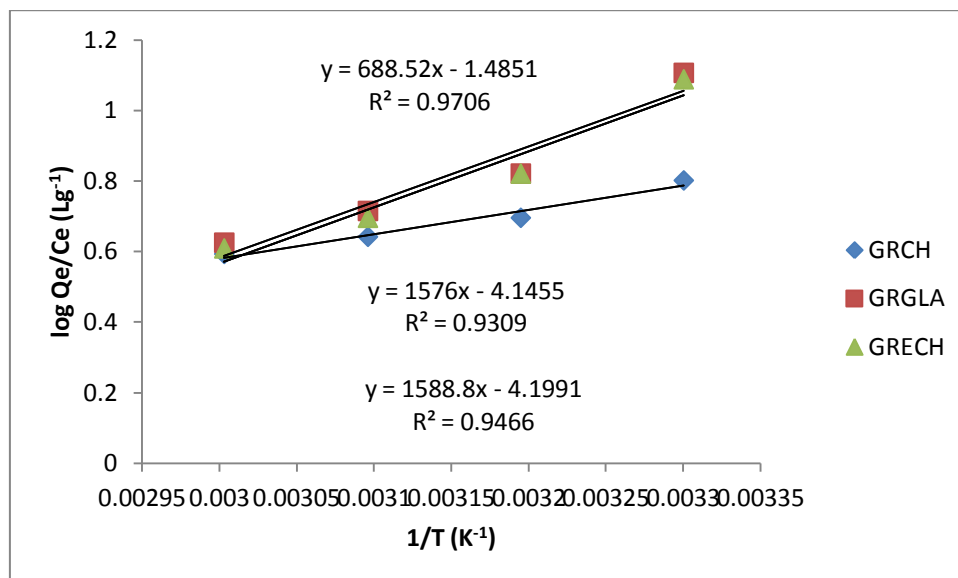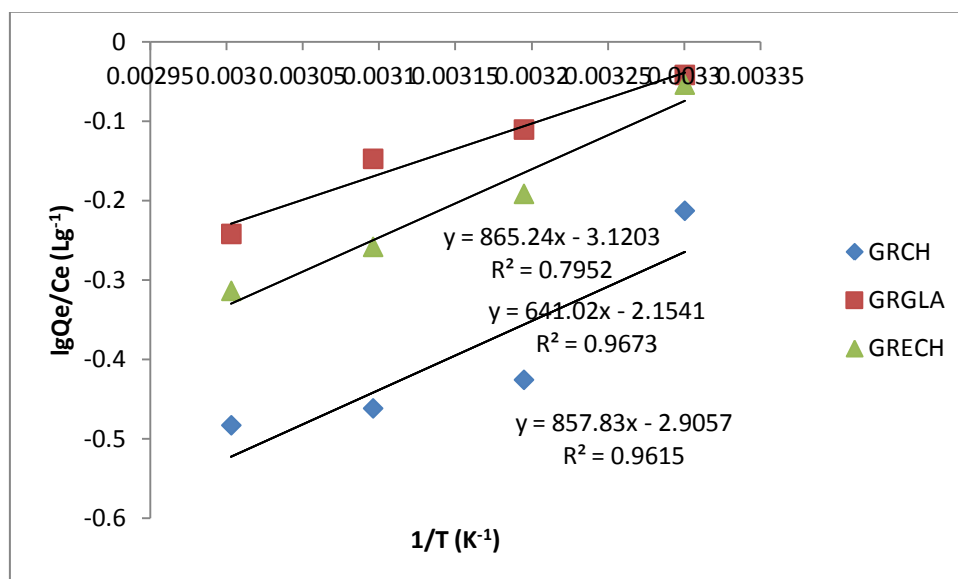| Adsorbate	Adsorbent	ΔH (KJ/mol.1000)	ΔS (KJ/MolK)	R^2	ΔG^+(KJ/mol.1000)
Zn	GRCH	-13.183	-.28.434	0.970	-4.567
	GRGLA	-30.176	-79.365	0.930	-28.919
	GRECH	-30.406	-80.399	0.946	-6.045
Pb	GRCH	-16.566	-59.739	0.795	1.535
	GRGLA	-12.273	-41.243	0.967	0.233
	GRECH	-16.424	-55.622	0.961	0.429

Figure 13: Thermodynamic studies for Zn adsorption

Figure 14: Thermodynamic studies for Pb adsorption

IV.   Conclusion

The adsorption of Zn(II) and Pb(II) ions from aqueous solution using chitosan and its derivatives from fish scale of *Lates niloticus* has been investigated. The kinetics of adsorption was studied for the contact time range of 30-70 minutes. The results obtained showed that the adsorption of the metal ions could be described by both first and second order kinetic models with correlation coefficient (R^2) values of 0.0003 and 1 for pseudo-first order and pseudo-second order respectively for Zn^{2+} adsorption; 0.4987 and 0.08707 for pseudo-first order and pseudo-second order respectively for Pb^{2+} adsorption. The free energy change (ΔG^+) obtained at the optimal conditions is in the range of -4.567 to -28.919 for Zn^{2+} and 0.223 to 1.535 for Pb^{2+}. This result indicates that the adsorption process is spontaneous and thermodynamically favourable. Also, the negative values of ΔG and ΔS imply a decrease in adsorption energy and an increase in the feasibility of the adsorption process at lower temperature.

References

[1].   Ajay, K.A., Mehendra, S.K., Chandrashekhar, P.P., and Ishwardas, L.M. (2015). Kinetics   study on adsorption of Ni^{2+} ions onto fly ash. Journal of Chemical Technology and   Metallurgy, 50, 5,601-605.
[2].   Ashraf, S., Asthiani, F. Z., Kaghazchi, T. (2007) Equilibrium studies of the sorption of Hg(II) ions onto chitosan. Chemical Engineering Journal, 133, 311-316.
[3].   Fenglian, F., Wang, Q. (2011). Removal of heavy metal ions from wastewater. Journal of Environmental Management, 92, 407-418.

[4]. Ho, Y.S., and G. Mckay. (1999a). A kinetic study of dye sorption by biosorbent waste product. Pith Resources Conservation Recycling, 25, 171–193.

[5]. Hudson, S.M., and Smith, C. (1998). Polysaccharide: Chitin and Chitosan: Chemistry and technology of their use as structural material. Biopolymers from renewal resource. New York: springer.

[6]. Karthikeyan, G., Anbalagan, K., and Muthulakshmi Andal, N. (2004) Adsorption dynamics and equilibrium studies of Zn (II) onto chitosan. Journal of chemical Science. 116, 119-127.

[7]. Kim, D.S and Park, B. Y. (2001). Effects on the removal of Pb^{+2} from aqueous solution by crab shell. Journal of Chemical Technology and Biotechnology. 76: 1179 – 1184.

[8]. Mckay, G. and Ho, Y.S.(1999b,c) Pseudo second-order model for sorption processes. Process Biochemistry, 34, 451–460.

[9]. Mohanasrinivasan, V., Mishra, M., Paliwal, J.S., Singh, S.K., Selvaranjan, E., Suganthi, V., and Subathra, C.D. (2014). Studies of heavy metal removal efficiency and antibacterial activity of chitosan prepared from shrimp shell waste. Biotechnology 4(2), 167-175.

[10]. Nussey, G., Vuren, J.V., and du Preez, H. (2000). Bioaccumulation of chromium, manganese, nickel and lead in the Moggel labeo umbratus (cuprinidae) form Witbank Dam, Mpumalanga, Water South Africa. 26(2): 269-284.

[11]. Otuonye, U.C., Barminas, J.T., Magomya, A.M., Kamba, E.A. and Andrew, C. (2014). Removal of Chromium (VI) as a heavy metal from aqueous solution using Chitin obtained from Bargi fish (Heterotis Miloticus) scale. Journal of Scientific Issues, Research and Essays Vol. 2 (3), pp. 128-131

[12]. Ozcan, A., Safa Ozcan, A., Tunali, S., Akar, T., and Kiran, I. (2005) Determination of the equilibrium, kinetic and thermodynamic parameters of adsorption of copper (II) ions onto seeds of Capsicum annuum. Journal of Hazardous Materials, 124, pp.200-208.

[13]. Park, D., Yun, Y., and Park, J. M. (2010) "The past the present and the future of bisorption". Biotechnology and Bioprocess Engineering, 15: 86 – 102, 2010.

[14]. Ramya, R., Sankar, P., Anbalagan, S., and Sudha, P.N. (2011) Adsorption fo Cu (II) and Ni (II) ions from metal solution using crosslinked chitosan-g-acrlonitrile copolymer.International journal of environmental science, 1 1323-1338.

[15]. Wang, W. N. and Fatinanthan, S. (2008) Adsorption of Cu (II) ions in aqueous solutions using chitosan beads, chitosan-GLA bead and chitosan-alginate beads. Chemical Engineering Journal, 143, 62-72.