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Removal Of Pb(II) And Zn(II) Ions From Aqueous Solution Using Chitosan And Its Derivatives From Biopolymeric Material.

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ABSTRACT:
The adsorption of Pb(II) and Zn(II) ions onto chitosan and its derivatives from biopolymeric material has been investigated at different pH values, concentration range of 100-400 mg/L and at different time intervals. Chitosan was cross-linked with glutaraldehyde (GLA) and epichlorohydrin (ECH) in order to obtain sorbents that are insoluble in aqueous, acidic and basic medium in order to improve its swelling properties. Batch adsorption experiments were conducted to obtain the optimum conditions for the removal of the metal ions. The optimum conditions obtained were 60 minutes contact time, 400 mg adsorbent dose and pH 7. The uptake of Pb(II) ions on chitosan (GRCH), chitosan cross-linked glutaraldehyde (GRGLA) and chitosan cross-linked epichlorohydrin (GRECH) was 74.40%, 98.00% and 98.00% respectively; while, Zn(II) ions was 99.20%, 99.44% and 97.72% respectively.

Keywords: Chitosan, cross-linked chitosan, biopolymeric material, Pb(II) ions, Zn(II) ions.

I. INTRODUCTION

Pollution by heavy metals is a serious threat to aquatic ecosystems because some of these metals are potentially toxic, even at very low concentrations. Additionally, heavy metals are not biodegradable and tend to accumulate in living organisms, and they can cause severe problems to both human health and wildlife (Crini, 2005). Heavy metals have been excessively released into the environment due to rapid industrialization and have created a major global concern. Cadmium, chromium, nickel, lead, mercury and zinc are often detected in industrial waste waters, which originate from metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacturing, pesticides, pigment manufacture, printing and photographic industries etc (Kadirveluet al.,2001).

Natural processes and human activities have polluted and reduced the quality of water resources in Nigeria. Groundwater and superficial water have been contaminated in various ways; e.g. by mining wastes including cyanide and toxic heavy metals, by agricultural chemicals, by industrial and domestic sewage that is sometimes discharged without treatment into waterways and by natural trace elements (e.g. arsenic). In view of its high toxicity, environmental mobility, non-biodegradability and stability, its removal becomes an absolute necessity. Chronic exposure to these heavy metals poses a major threat to soil, water, and food safety because of their inherent toxicity to living organisms, especially humans (Fewtrelet al., 2004). Additionally, the absence of strict laws in developing countries plays an important role in the quality of the environment and people's health. Some companies in different industries emit thousands of pollutants into the environment without control, and hence more awareness and efficient processes need to be implemented in order to change or improve this situation.

Since it is important to eliminate or reduce the concentration of heavy metals in the aquatic ecosystems, various methods and technologies are commonly applied in the treatment of mining and refining industry effluents before they are discharged to receiving water. Traditional treatment techniques include chemical precipitation, membrane filtration, electrodialysis and ion exchange. Nevertheless, the application of such processes is sometimes restricted because of economic constraints and they may generate hazardous products or products which are difficult to treat (Kurniawanet al., 2006; Gavrilescu, 2004; Reddadet al., 2002).

In recent years, biomaterials have emerged as an option for developing economic and eco-friendly wastewater treatment process, therefore, applying biotechnology in controlling and removing metal pollution has been paid much attention, and gradually becomes hot topic in the field of metal pollution control because of its potential application. Chitin and its deacetylated form, chitosan, are two biopolymers that come from crustacean shells and have the ability to fix a great variety of heavy metals (Muzzarelli, 1977). The strong affinity of metal ions for these sorbents is explained by the relatively high proportion of nitrogen sites. These bio adsorbents in native form and chemically modified forms have been effectively used for separation of heavy metal ionsfrom industrial waste streams. The increasing need for new and low-cost adsorbents, ever growing problems of waste disposal, the high cost of synthetic resins and high ability and selectivity of chitosan for metal sorption, make it one of the most suitable materials for wastewater treatment (Babel et al., 2003). Three major points should be considered when choosing the metals for adsorption: the metal toxicity, recovery interests, and how representative is the metal in terms of its behaviour.

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_3purchased 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 (latesniloticus) were obtained as wastes from a local fish market at Yola, Adamawa State. These scales were soaked in doubled distilled water for 2 hrs, 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) andMohanasrinivasanet al., (2014), and summarized below;

In the first deproteinization step, 5g portions each of the ground scales were weighed into conical flasks and a 100ml of 5% NaOH was added. The mixtures were boiled and stirred at 100^0C for 2 hrs in a water bath. The deproteinized scales were collected on a coarse sintered glass funnel and washed with distilled water at pH 7.0 followed by drying to a constant weight at 100^0 C for 2 h.

The second method involved demineralization by extracting 1g of the deproteinized scale with 20ml of 5% hydrochloric acid at room temperature with continuous mixing for 18 hrs to dissolve calcium carbonate in the sample. The crude chitin was collected on a coarse sintered glass funnel and washed with double distilled H_2O at pH 7.0 and then dried in the oven to a constant weight at 100^0C.

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 200µm (> 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 (Mohanasrinivasanet 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, 38g 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 ofPb, 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 0.45μm 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^o 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:

$$\%Removal = \{(Co – Ce) / Co\} \times 100$$

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

Effect of Adsorbent Dose

Different dosages of the adsorbents (0.1 – 0.4g) were added in different conical flasks containing 25ml of aqueous solution, corked and agitated in a shaker for 1h at a speed of 150 rpm at various times at room temperature. The content of each flask were filtered and analysed after each time of agitation.

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 250ml 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 or1M 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 wasdetermined as described earlier, after attainment of equilibrium.

III. RESULTS AND DISCUSSIONS

Effect of Adsorbent Dose on Lead

Adsorption capacity of lead(II) ions was carried out by varying the doses of absorbents from 100mg to 400mg keeping other parameters (pH, contact time, initial concentration, and temperature) constant. Figure 1 shows that the removal capacity of the absorbents on lead was improved by increasing adsorbent doses. This is achieved because the higher amount of absorbents in the solution provides greater availability of exchangeable sites for the ions. Figure 1 also shows that the number further increased in adsorption after a certain amount of adsorbent(GR/CH, GR/GLA, GR/ECH) was added i.e 400mg. The maximum percentage (%) removal of Pb(II) ions with adsorbent GR/CH was about 77.92%, with GR/GLA, the maximum percentage (%) removal was 98.00% and that of GR/ECH was 92.00% at the dosage of 400mg respectively.

This results shows that the percentage removal of Pb(II) ions is higher with absorbent GR/GLA followed by GR/ECH and lastly GR/CH accordingly. It was observed that after 400mg of the absorbent, there is no significant change in the percentage removal of the Pb(II) ions and this may be due to the overlapping of active sites at high absorbent dosage which reduces the effective surface area because of the conglomeration of the particles exchange. Therefore, 400mg is considered as the optimum absorbent dosage which is used for further studies.

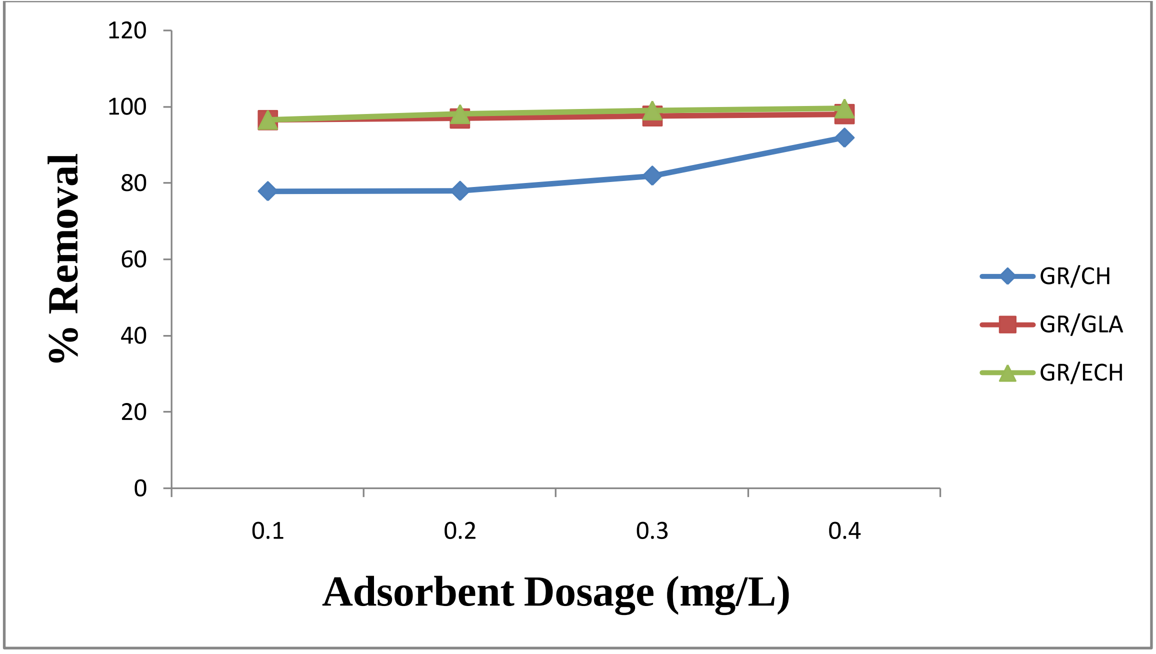

Figure 1:Effect of Adsorbent Dose on Lead

Effect of Absorbent Dosage on Zinc

Figure 2 shows that the adsorption proficiency of Zn(II) ion was studied by varying the doses of the absorbents (GR/CH, GR/GLA, GR/ECH) from 100 to 400mg keeping other parameters like time, initial concentration, pH, and Temperature constant. The figure shows that, increasing adsorbents dose increases the removal efficiency on zinc. This is because the higher dose of absorbents in the solution brings about the higher availability of exchangeable sites for the ions. From the figure also, there is a clear indication that the number of zinc ions adsorbed increases after a certain amount of the absorbents (GR/CH, GR/GLA, and GR/ECH) was added (400mg). The maximum percentage (%) removal of zn(II) ion with the absorbent GR/CH was about 98.40%, that of GR/GLA was 98.99% and the maximum percentage removal of zinc(II) with GR/ECH was about 99.80% at the dosage of 400 mg respectively.This results shows that the percentage removal of zn(II) ion is higher with the absorbent GR/GLA, followed by GR/ECH and lastly GR/CH accordingly. That is GR/GLA > GR/ECH > GR/CH. The result also suggest that after the addition of a certain dose of the various absorbents, the equilibrium conditions was reached and therefore, the amount of ions bound to the absorbent and the amount of free ions in the solution remain constant even with more addition of the absorbents.

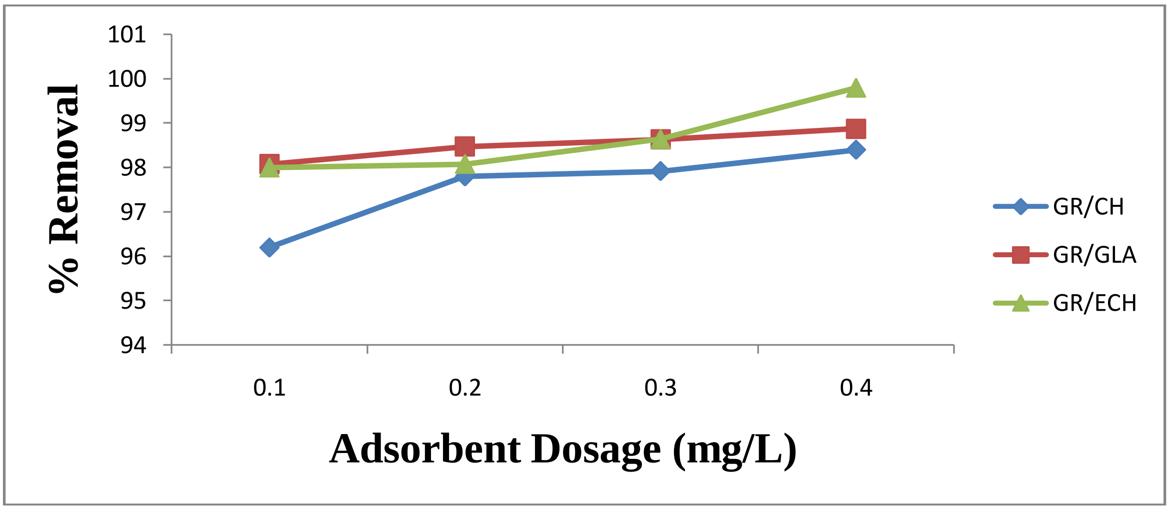

Figure 2: Effect of Adsorbent Dose on Zinc

Effect of Contact Time on Lead

Figure 3 showed that the metal ions removal increased with an increase in contact time before equilibrium time. Keeping all parameters(adsorbent dose, pH, initial concentration and temperature) constant. 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. The percentage removal however remained constant after 60 minutes which showed that equilibrium was reached at 60 minutes. Based on these results, the contact time of 60 minutes was set for all adsorption experiments for the removal of all metal ions under study. The equilibrium contact time is an important parameter for an economical waste water treatment system. The contact time is a vital parameter for the removal of Pb(II) ions pollutants from water.

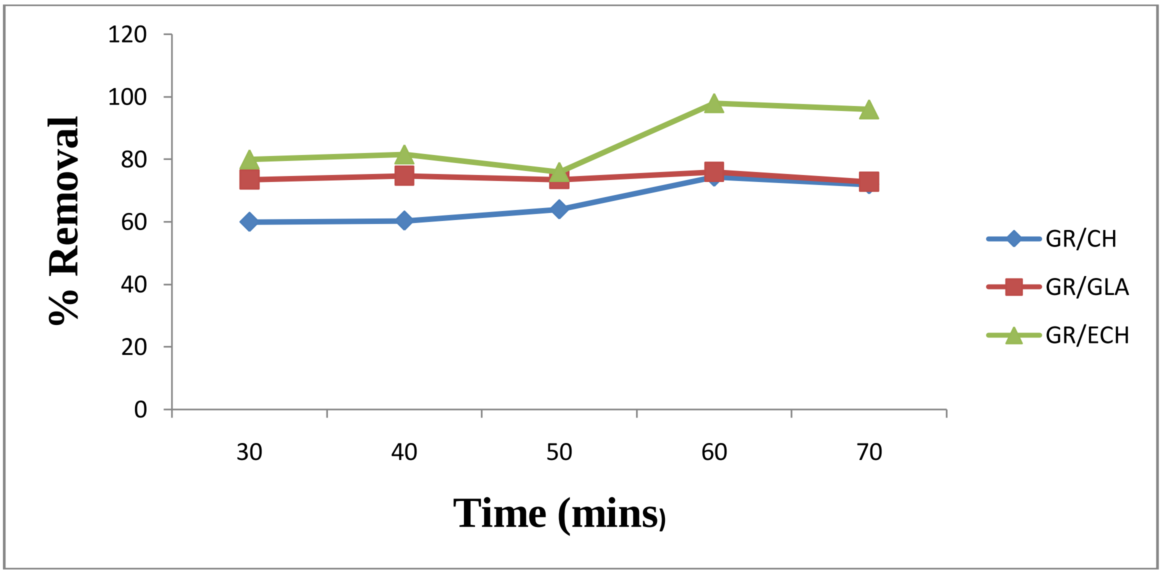

Figure 3: Effect of Contact Time on Lead

Effect of Contact Time on Zinc

From Figure 4 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 above 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.

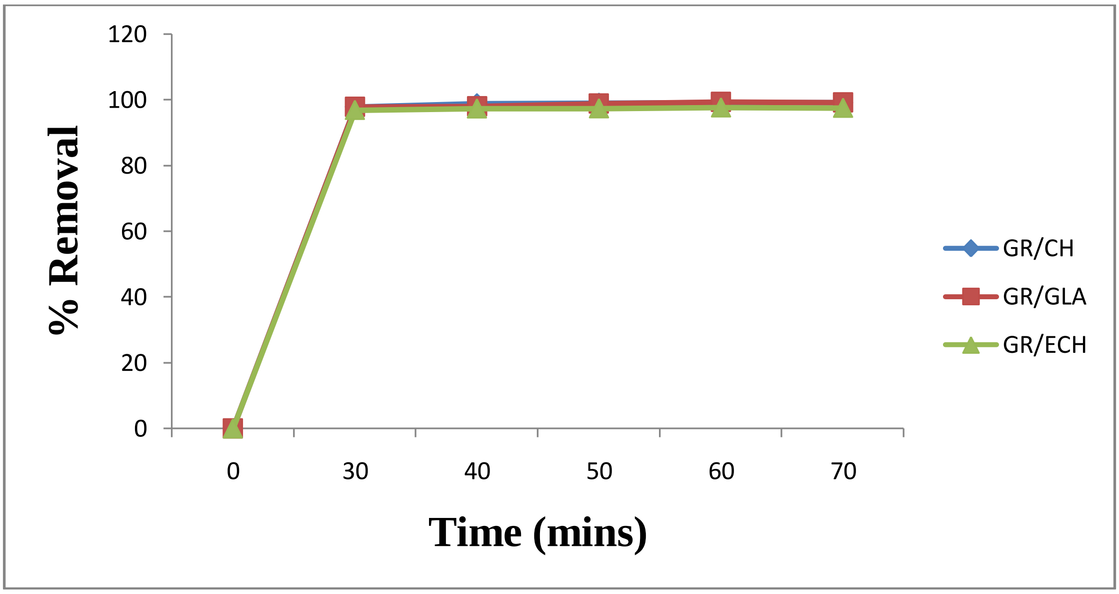

Figure 4:Effect of Contact Time on Zinc

Effect of pH on Lead Adsorption

Figure 5 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 Karthikeyanet.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 (Ramyaet.al, 2011).

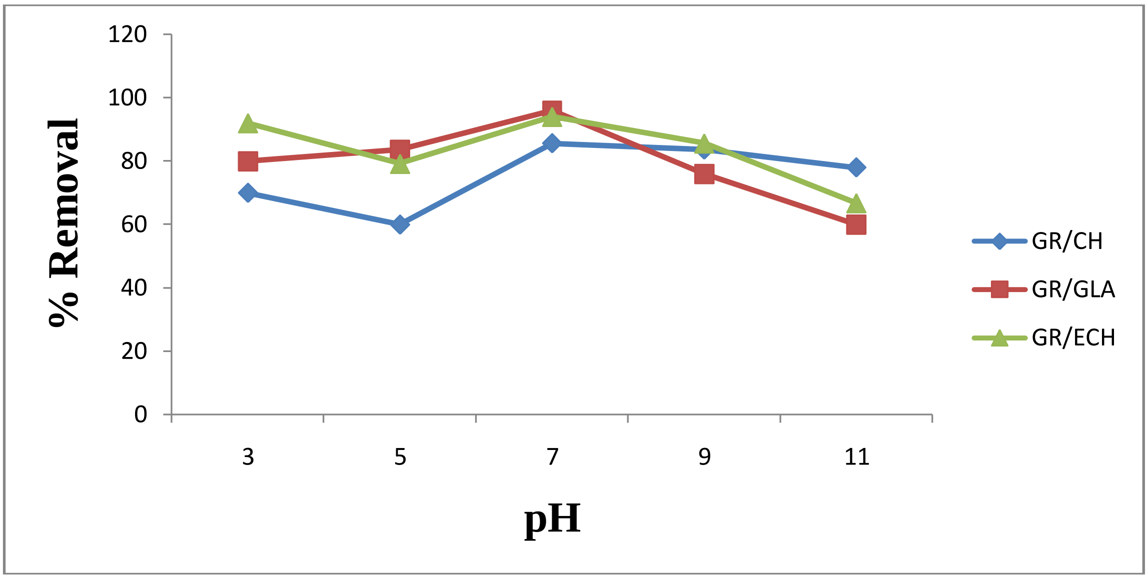

Figure 5: Effect of pH on Lead Adsorption

Effect of pH on Zinc Adsorption

From Figure 6, 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 Karthikeyanet.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 (Ramyaet.al, 2011). The adsorption of Zn(II) ions was found mainly to be influenced by pH of the solution.

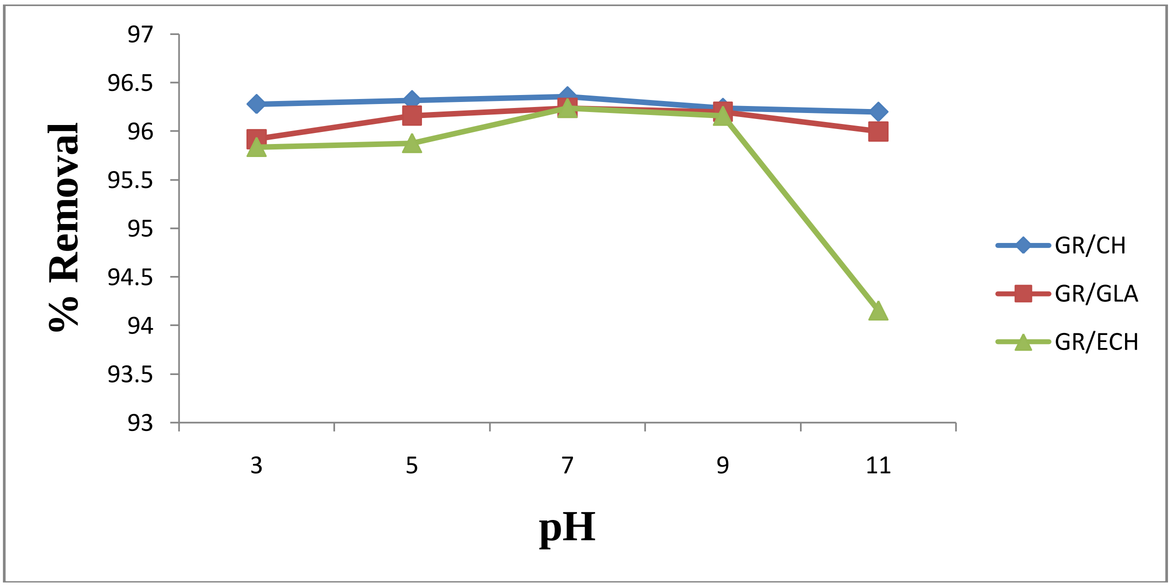

Figure 6: Effect of pH on Zinc Adsorption

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 7 at the range 25-100mg/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 75mg/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.

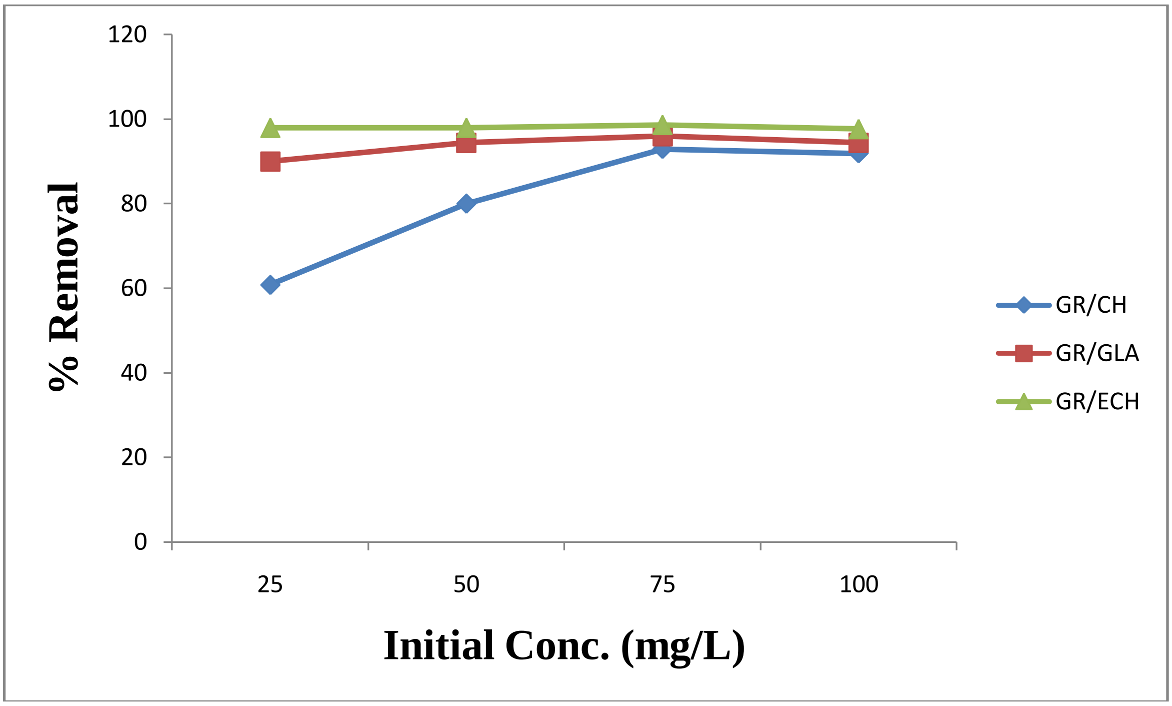

Figure 7: Effect of Lead Initial Concentration on Adsorption

Effect of Zinc Initial Concentration on Adsorption

The effect of initial zinc concentration on adsorption is shown in Figure 8 at a range 25-100mg/L, at a pH of 7, temperature of 30°C, 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 75mg/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.

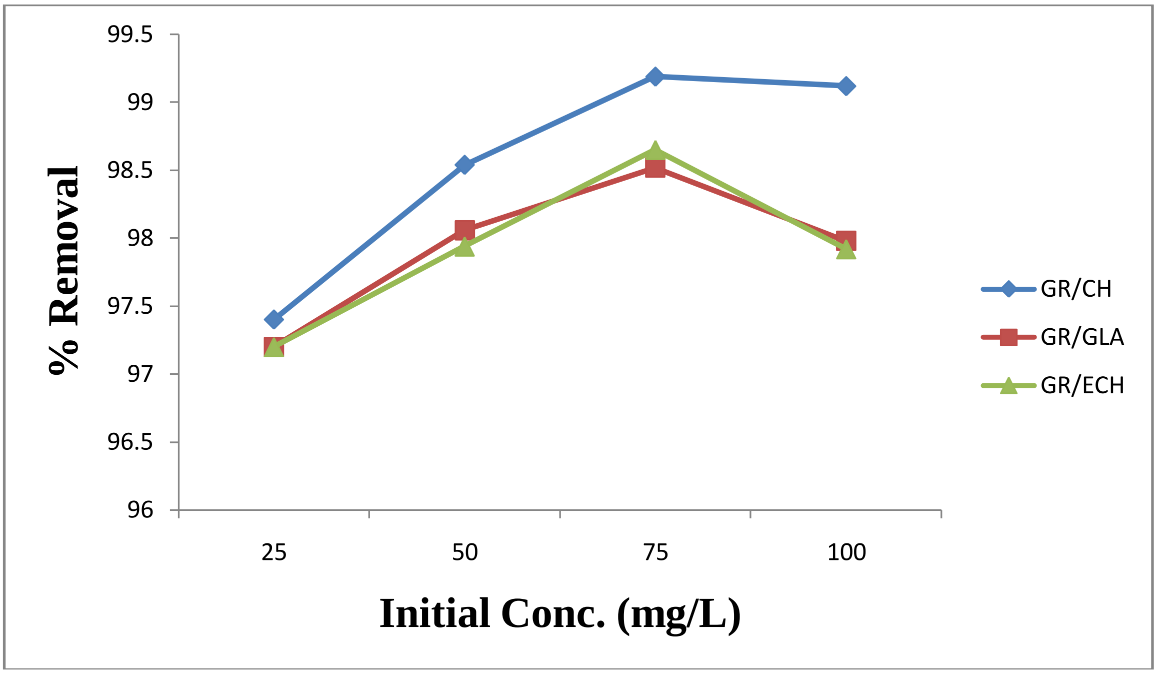

Figure 8: Effect of Zinc Initial Concentration on Adsorption

Effect of Temperature on Lead Adsorption

The effect of temperature on the lead adsorption process is shown in Figure 9. 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^{o}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.

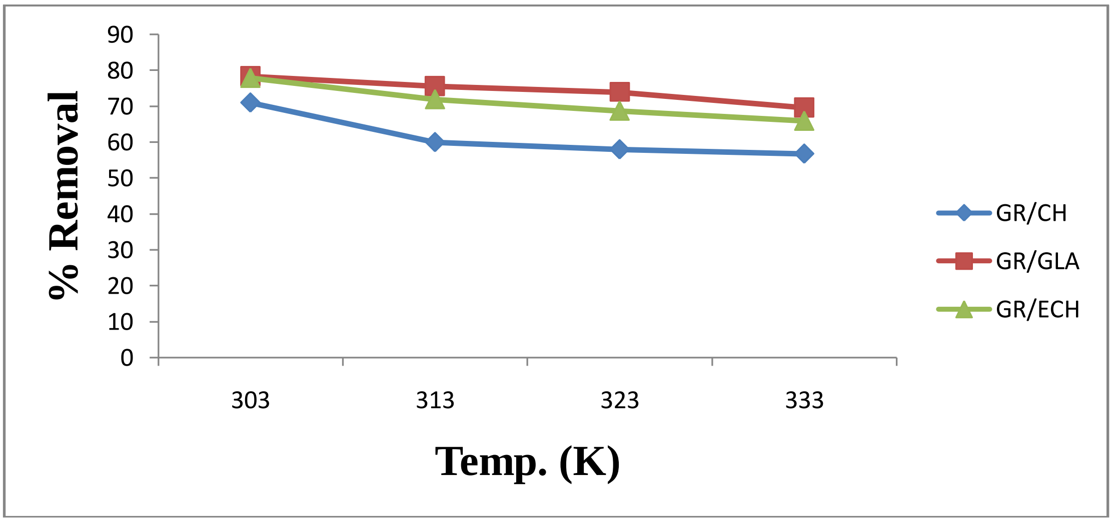

Figure 9: Effect of Temperature on Lead Adsorption

Effect of Temperature on Zinc Adsorption

The effect of temperature on zinc adsorption process is shown in Figure 10. 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 10, 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.

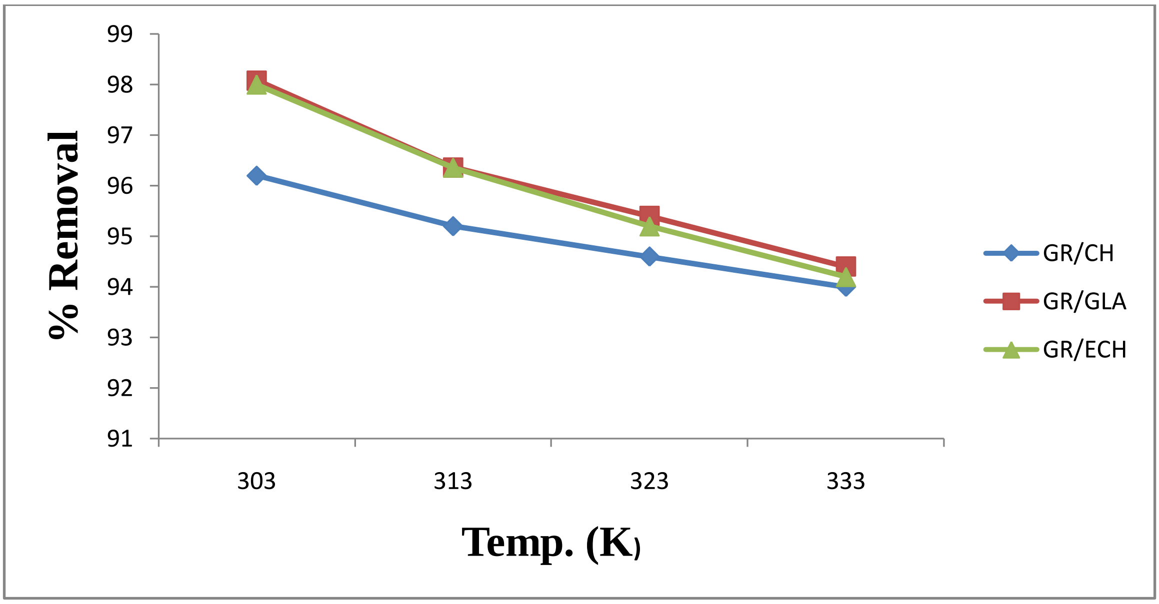

Figure 10: Effect of Temperature on Zinc Adsorption

IV. CONCLUSION

The adsorbents, GRCH, GRGLA, and GRECH from fish scales exhibited good physicochemical attributes as adsorbents. From this research, it was observed that the adsorptions of heavy metals Pb(II) and Zn(II) ions are affected by adsorbent dose, contact time, pH, initial ion concentration and temperature. The optimum conditions obtained were 60 minutes contact time, 400 mg adsorbent dose and pH 7. The uptake of Pb(II) ions on chitosan (GRCH), chitosan cross-linked glutaraldehyde (GRGLA) and chitosan cross-linked epichlorohydrin (GRECH) was 74.40%, 98.00% and 98.00% respectively; while, Zn(II) ions was 99.20%, 99.44% and 97.72% respectively.

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