

Removal of Cd(II) And Mn(II) Ions from Aqueous Solution using Chitosan and Its Derivatives from Fish Scale 'Giwan Ruwa' (*Lates Niloticus*)

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Abstract: - In this research, the removal of Cd (II) and Mn (II) ions from aqueous solution using chitosan and its derivatives from fish scale *Lates niloticus* in a batch adsorption system was studied. Effects of parameters like adsorbent dose, pH, contact time, temperature and initial ion concentration were also studied. At lower pH values, the adsorption of the ions on chitosan and cross-linked chitosan beads is more because in the presence of H⁺, the amino groups of chitosan and cross-linked chitosan behaves as a quaternary ammonium ion to attract more of the ions from the reaction mixture. The uptake of the ions on chitosan (GRCH), chitosan-glutaraldehyde bead (GRGLA) and chitosan-epichlorohydrin bead (GRECH) was as follows; Cd(II) ions 99.12%, 96.80% and 96.20% respectively, while Mn(II) ions was 99.60%, 95.48% and 96.00% respectively.

Key Words: — Chitosan, Aqueous solution, Fish scale, *Lates niloticus*, Adsorption, Removal.

I. INTRODUCTION

In recent years, there has been an increasing ecological and global public health concern associated with environmental contamination by heavy metals. Also, human exposure has risen dramatically as a result of an exponential increase of the use of heavy metals in several industrial, agricultural, domestic and technological applications (Bradil, 2002). Reported sources of heavy metals in the environment include geogenic, industrial, agricultural, pharmaceutical, domestic effluents, and atmospheric sources (He, 2005).

Environmental pollution is very prominent in point source areas such as mining, foundries and smelters, and other metal-based industrial operations. The presence of heavy metals in water sources close to mining site has received more attention in recent years than in the past due to the increasing number of environmental regulations. Metals, such as Cu, Cd, Pb, Ni, Cr, Zn, Mn, Fe, Co, Hg, and As are considered heavy metals. These

metals are components of the Earth's crust that cannot be degraded or destroyed. As trace elements some of them are essential for the human's metabolism; however, at higher concentrations they can lead to poisoning. Among these metals, this study will focus on Cd, Cu and Mn. Although the essential roles of some of these heavy metals are difficult to define, some have been found to be particularly important in the body metabolism. For example Copper (Cu) is important for certain enzyme activities such as cytochrome oxidase and superoxide dismutase and Manganese (Mn) (Tseng *et al.*, 2003).

Nevertheless, at higher levels all heavy metals can lead to poisoning, representing a serious hazard to human health, fauna, and flora. For instance, the presence of heavy metals in ground water, soil, and air represents a risk for human health due to the characteristics of each metal. 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 method which is used in many industries for the removal of water pollutants due to its low cost and applicability on a large scale.

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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. 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 in Wukari, Taraba State- Nigeria. All the chemicals used were of analytical grade with percentage purity of 99.9 %.

All chemicals purchased were accompanied by a certificate indicating their purity. Sodium hydroxide pellet and HNO₃ purchased from Burgoyne & Co., Mumbai India. MnSO₄.H₂O, CdSO₄.8H₂O, Glutaraldehyde, Acetic acid, Epichlorohydrin (ECH), HCl were purchased from Guangdong GuanghuaSci-Tech Co.,Ltd, China. 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). Double distilled water was used throughout the experimental studies to prepare all solutions.

A. Treatment of Sample

Dried fish scales (*Lates niloticus*) were obtained as wastes from a local fish market at Wukari, Taraba State. These scales were soaked in doubled distilled water for a period of 2 hours, and thoroughly washed with warm double distilled water.

The fish scales were dried in an oven at 100⁰C to constant weight pulverized and passed through 100 μ m sieve; they were stored in plastic containers at room temperature before use.

B. 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).

C. Preparation of Swollen Chitosan Beads

Swollen chitosan beads were prepared according to the procedure reported by 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 μ m (> 200 μ m) before proceeding to modifications of the beads.

D. Preparation of Chitosan-Glutaraldehyde (GLA) Beads

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 hours. After 24 hours, 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 45⁰C for 12 hours to remove completely the residual solvent and kept in a closed container, (Mohanasrinivasan *et al.*, 2014).

E. Preparation of Chitosan-Epichlorohydrin (ECH) Beads

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 hours at 40°C 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.

F. Preparation of Stock Solutions

Stock solution of 25mg/L of manganese (II) ion is prepared by dissolving anhydrous manganese (II) sulphate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$). To do this, 3.076g of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ is added in distilled water contained in 1000 ml volumetric flask. Stock solution of 25 mg/L of Cd (II) is prepared by dissolving cadmium sulphate octahydrate ($\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$). To do this, 6.84g of ($\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$) is added in distilled water contained in 1000 ml volumetric flask. Sodium hydroxide and hydrochloric acid were used to adjust the solution pH.

G. 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 Cd and ions onto GR (CH), GR (GLA) and GR(ECH) respectively as adsorbents.

H. 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:

$$q = (C_o - C_e) \cdot V/m$$

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.

I. Effect of initial metal 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 (100 – 400 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:

$$\% \text{ Removal} = \{(C_o - C_e) / C_o\} \times 100$$

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

J. 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.

K. Effect of pH

The effects of pH ranging from 3 to 11 were studied. 25 ml of stock solutions of the ions used (Cd^{2+} and Mn^{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.

L. Effect of Temperature

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

III. RESULTS AND DISCUSSIONS

A. Equilibrium Contact Time

From the results shown in Figure 1, the removal of the metal ions (cadmium and manganese) increased with an increase in contact time before equilibration time was attained, with all other parameters (adsorbent dose, pH, initial concentration and temperature) kept constant. The equilibrium contact time attained at 60 minutes. Cd(II) ions with GR/CH increases from 98.08 to 99.12%, 96.20 to 96.80% with GR/GLA and 92.72 to 96.20% with GR/ECH respectively, while the percentage removal of Mn(II) ions with GR/CH increased from 98.80 to 99.60%, 93.88 to 95.48% with GR/GLA, and 91.00 to 96.00% with GR/ECH adsorbents respectively with contact time variation from 30 to 60 minutes.

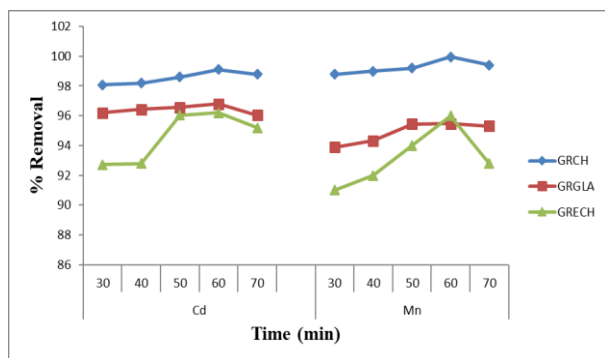


Fig.1. Plot of Equilibrium Contact Time for Cd and Mn ions

B. Effect of initial metal concentration

The effect of initial metal ion concentration on cadmium and manganese adsorption is shown in Figure 2 at a range 25-100 mg/L, at a pH of 7, temperature of 30°C, and contact time of 1 hour. The result shows a general trend in which 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; hence, the decrease in percentage removal of the metal ions observed. Therefore, it was evident from the results that cadmium and manganese adsorption was dependent on the initial metal concentration.

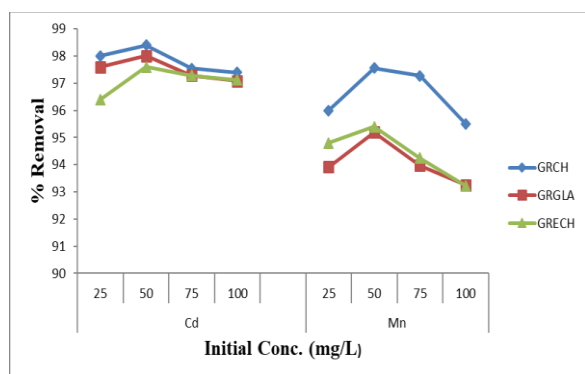


Fig.2. Effect of initial metal concentration on Cd and Mn ions adsorption

C. Effect of Adsorbent Dose

The adsorption capacity of cadmium and manganese ions was studied by varying the doses of the adsorbents (GR/CH, GR/GLA, GR/ECH) from 0.1 to 0.4 g keeping other parameters like time, initial concentration, pH, and temperature constant. The results as shown in Figure 3 indicates that, increasing

adsorbents dose increases the removal efficiency on the metal ions. This is because the higher dose of adsorbents in the solution brings about an increase in the availability of exchangeable sites for the ions.

This result shows that the percentage removal of Cu(II) ions is higher with the adsorbent GR/GLA, followed by GR/ECH and lastly GR/CH accordingly. i.e GR/GLA > GR/ECH > GR/CH. The maximum percentage removal of Cd(II) ions was recorded with adsorbent GR/CH with about 98.08% that of GR/GLA was 99.64% while that adsorbent GR/ECH was 98.20%. Mn(II) ions GR/CH was about 95.44%, GR/GLA was about 99.60% and the maximum percentage adsorption with GR/ECH was also about 99.60% respectively at adsorbent dosage of 0.4 g. This is a clear indication the rate of adsorption increases more with the modified forms of the adsorbents as compared with the unmodified form. This result also suggest that after addition of certain amount or dose of the various adsorbents, the equilibrium conditions was attained and therefore the amount of ions bound to the adsorbents and the amount of free ions in the solution remained constant despite more addition of the adsorbents.

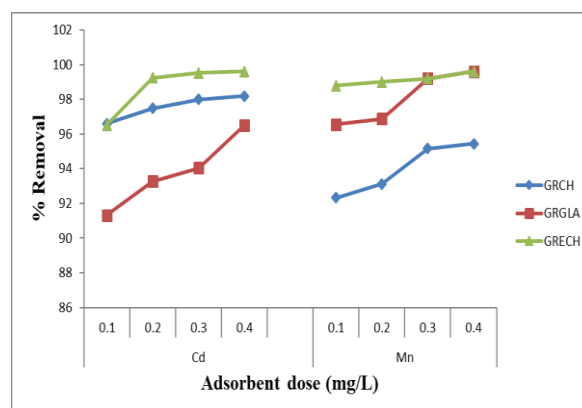


Fig.3. Effect of Adsorbent Dose Cd and Mn

D. Effect of pH

The result in Figure 4 shows that pH influenced the removal efficiency of the copper, cadmium and manganese ions in the aqueous solution. The maximum percentage removal of Cd(II) ions was about 96.12% with GR/CH, 96.04% with GR/GLA, and 96.24% with GR/ECH at pH 7 respectively. This behaviour can be explained by increasing of adsorption efficiency due to decrease of protons released in solution which is in competition with the metal ions to occupy the active sites. This is in agreement with the work done by Pavasant *et.al*, (2006), whereas at pH greater than 7, the adsorption efficiency was significantly decreased for each metal due to high concentration

of proton in the stock solution and this proton contend with metal ions in forming a bond with the active sites. The results are confirmed by Pavasant *et.al*, (2006). The maximum percentage removal of manganese was about 97.12% with GR/CH, 94.48% with GR/GLA and 95.32% with GR/ECH at pH of 7 respectively. The dominant specie of Manganese was free Mn(II) ion and was mainly involved in the adsorption process when the pH was lower than 7. At a pH higher than 7, Mn ions started to precipitate as Mn(OH)₂. This had been confirmed by Ramya *et.al*, (2011). Increases in metal removal with 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 a lower electrostatic repulsion between surface and metal ion. Decrease in adsorption at higher pH is due to formation of soluble hydroxyl complexes (Ramya *et.al*. 2011).

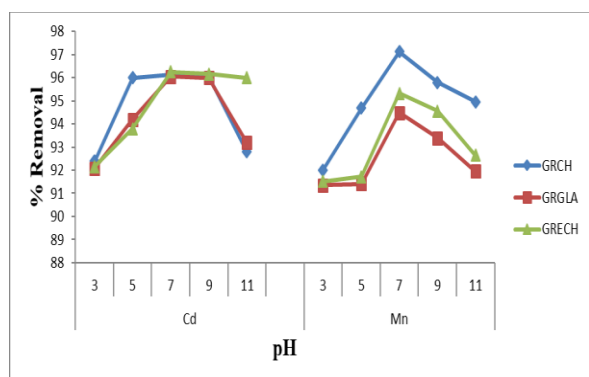


Fig.4. Effect of pH on cadmium and manganese ions adsorption

E. Effect of Temperature

The effect of temperature on copper, cadmium and manganese adsorption process is shown in Figure 5. 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 these 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. The percentage removal of Cd ions was decreased from 96.56% to 84.48% using GR/CH, 96.64% to 84.48% using GR/GLA and 96.60% to 84.64% with GR/ECH respectively. From Figure 5, it is very clear that the low temperatures are in favour of Cd ion removal. This can be deduced by the tendency of the Cd ions to escape from the solid phase to the bulk phase with an increase in temperature of the solution. The percentage removal of Mn ions was decreased from 98.80% to 76.16% using GR/CH, 92.56% to 72.16% using GR/GLA and 92.32% to 77.12% with GR/ECH respectively.

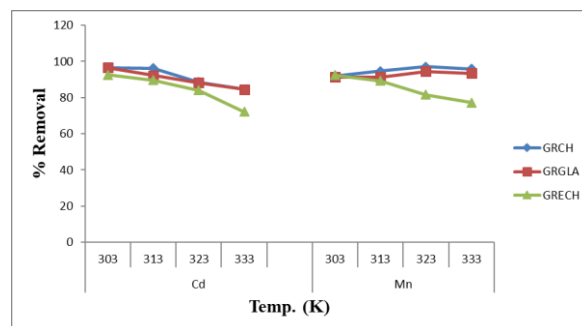


Fig.5. Effect of Temperature on cadmium and manganese adsorption

IV. CONCLUSION

Cadmium and manganese ions removal from aqueous solution using chitosan and its derivatives from fish scales of *Lates niloticus* in a batch adsorption system was studied. Parameters such as adsorbent dose, pH, contact time, temperature and initial ion concentration were varied and also studied. The removal of the metal ions (cadmium and manganese) increased with an increase in contact time before equilibration time was attained, the results also showed that at lower pH values, the adsorption of the ions on chitosan and cross-linked chitosan beads is more because in the presence of H⁺, the amino groups of chitosan and cross-linked chitosan behaves as a quaternary ammonium ion to attract more of the ions from the reaction mixture. The result shows a general trend in which the amount of metal removed from the solution increased with initial ion concentration. 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 is less as compared to the available sites on the adsorbent. But at higher concentrations, the available sites for the adsorption become fewer; hence, the decrease in percentage removal of the metal ions observed. The uptake of the ions on chitosan (GRCH), chitosan-glutaraldehyde bead (GRGLA) and chitosan-epichlorohydrin bead (GRECH) was as follows; Cd(II) ions 99.12%, 96.80% and 96.20% respectively, while Mn(II) ions was 99.60%, 95.48% and 96.00% respectively.

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