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REMOVAL OF NICKEL AND LEAD IONS FROM AQUEOUS SOLUTIONS USING CHITOSAN ADSORBENT AND ITS DERIVATIVE FROM SYNODONTIS MEMBRANACEA (TILAPIA FISH) SCALE

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Abstract:

This research work utilizes the use of a biopolymeric adsorbent, chitosan and chitosan-GLA (cross linked chitosan) for the adsorption of these metal ions. The aim and objectives is to isolate and modify a biopolymeric adsorbent for the adsorption of nickel and lead ions. The steps involved are, deproteinization, demineralization, deacetylation and cross-linking of the adsorbent with glutaraldehyde. The adsorption capacities of these adsorbents were studied under the effect of time, adsorbent dosage, pH, initial concentration and temperature. Maximum adsorption for the effect of time was at 90 m, 0.4 g for the effect of adsorbent dosage, at pH 7, maximum adsorption was reached in studying the effect of pH and 100 mg/L for the initial concentration. Langmuir and freundlich isotherm were used to reveal which isotherm best fits the data obtained. The freundlich adsorption isotherm best fits the adsorption in this research work based on the correlation coefficient values (R^2) of 0.9484 and 0.8969 respectively for nickel (II) ions and 0.9959 and 0.9828 for lead (II) ions. Pseudo first order and second order adsorptions kinetics were also used to describe the adsorption kinetics, and the second order kinetics best fits the data obtained in this research work. The second order kinetics for the adsorption of nickel and lead; chitosan gave 0.9806 and 0.7519 respectively while chitosan-glutaraldehyde gave 0.9538 for nickel and 0.9464 for lead.

Keywords: Extraction, Glutaraldehyde, Biopolymeric, Adsorption Isotherm, Synodontis membranacea

Introduction

Environmental pollution by heavy metals has become a serious threat to living organisms in an ecosystem (Rovina *et.al.* 2015). Metal toxicity is of great environmental concern because of their bioaccumulation and non-biodegradability in nature (Gautam et et. al., 2014). Several inorganic metals like magnesium (Mg), nickel (Ni), chromium (Cr^{3+}), copper (Cu), calcium (Ca), manganese (Mn), and sodium (Na) as well as zinc (Zn) are vital elements needed in small quantity for metabolic and redox functions. Heavy metals such as aluminium (Al), lead (Pb), cadmium (Cd), gold (Au), mercury (Hg), and silver (Ag) do not have any biological role and are toxic to living organisms (Lakherwal, 2014).

The toxic nature of nickel (Ni) and lead (Pb) ions in the environment poses a major risk to the human health and the environment at large. Therefore, it is very essential to find suitable treatment method that is simple to operate and efficient in working. Agricultural wastes cause serious disposal complications and air pollution resulting from open field burning. Also, several industrial wastes cause environmental and health problems (Nile *et al.*, 2013). These low cost agricultural waste products are being utilized in solving these heavy metal water contamination problems.

The use of agricultural waste requires extensive research and development work towards maximizing the use of existing technologies for a sustainable and environmentally sound management. The efficient recycling of agricultural waste is adopted as they have no negative effect on the environment. There is need for the removal of nickel and lead from industrial effluents before disposal into water bodies because of their persistence in the ecosystem. This research work utilizes the use of a bio polymeric adsorbent, chitosan and chitosan-GLA (cross linked chitosan) for the adsorption of these metal ions.

Materials and Methods

Sample Collection/Preparation

The scales of synodontis membranecea were obtained from the local new market of Wukari, Taraba state Nigeria.

The fish scale used in this study were soaked in doubled distilled water for 2 h, and thoroughly washed with warm double distilled water. The scale was 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 scale were done using two basic steps - deproteinization and demineralization as reported by Kim and Park, (2001); 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 water and air dried. The chitosan beads were then ground and sieved to a constant particle size of less than 200µm before proceeding to modifications of the beads.

Preparation of Cross linked Chitosan Beads with Glutaraldehyde.

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. The chitosan beads were heterogeneously 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 chitosan beads were cast into petri dish and dried overnight at room temperature. It was dried further in an oven at 45^0C for 12 h to remove completely the residual solvent and kept in a closed container (Mohanasrinivasan *et al.,* 2014).

Characterization of Chitosan and cross-linked chitosan

The synthesized Chitosan and cross-linked chitosan were characterized before the adsorption process. Fourier transform infrared (FTIR) were used to determine the functional groups present.

Batch experiments

The adsorption capacities of the various adsorbents were studied under different experimental conditions such as, temperature, pH, adsorbent dosage, initial concentration and contact time. Each of the parameters investigated were stirred for 60 min at 210 rpm using an A-H4 Cyclic Vibrator, except for the effect of time which was varied, and at constant pH of 4.5 for Pb ions and 4.0 for Ni ions.

Results and Discussions

FT-IR Analysis of Adsorbents

The FTIR analysis was performed for all the adsorbents before and after modification. Infra-red spectroscopy is very important in identification of the possible functional groups which could play a great role in adsorption mechanism capacity. The FTIR analysis of adsorbents is shown in Table 1.

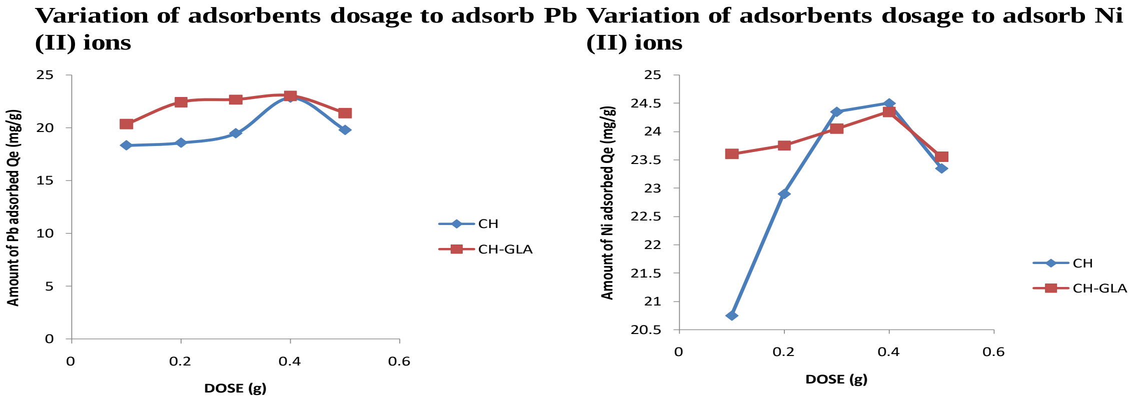
Table 1: FT-IR Analysis of Adsorbents

Group Freq (cm^{-1})	Functional groups	CH	CH-GLA	Assignment
4000-3000	Alcohol/Phenol	3442.00	3424.00	-OH stretch
3000- 2840	Alkane	2925.00	2917.00	C-H Stretch vibration
2000-1650	Alkanes	1999.00	1995.00	C-H bend
1680–1620	Amides	1634.00	1637.00	N-H Bend vibration
1450	Alkenes	1417.00	1418.00	C-H bend
1035-1050	Alcohol	1005.00	1042.00	O-H stretch

Table 1 contains the FTIR spectra for chitosan (CH) and chitosan cross-linked with glutaraldehyde (CH-GLA) respectively. The predominant peak for chitosan is clearly identified across all the spectra which indicates the adsorption band of the stretching vibration of –OH groups at 3442 cm^{-1} for CH and 3440 cm^{-1} for CH-GLA which are the main peaks around 3400 cm^{-1}. This reference vibration is comparable with the main vibration found from other chitosan spectra reported by other researchers (Ramya *et al*. 2012; Hastuti *et al*. 2016). The medium appearance at 2925 and 2925 cm^{-1} for CH and CH-GLA respectively are attributed to the stretching vibration of C-H groups. The common weak peak at 1999.00 cm^{-1}may be C-H bending. The peak at 1634.00 cm^{-1}may be attributed to N-H bending vibration in $–NH_2$. The C-H symmetry bending vibration in –CHOH was observed at 1417.00 cm^{-1}.

Adsorption Studies

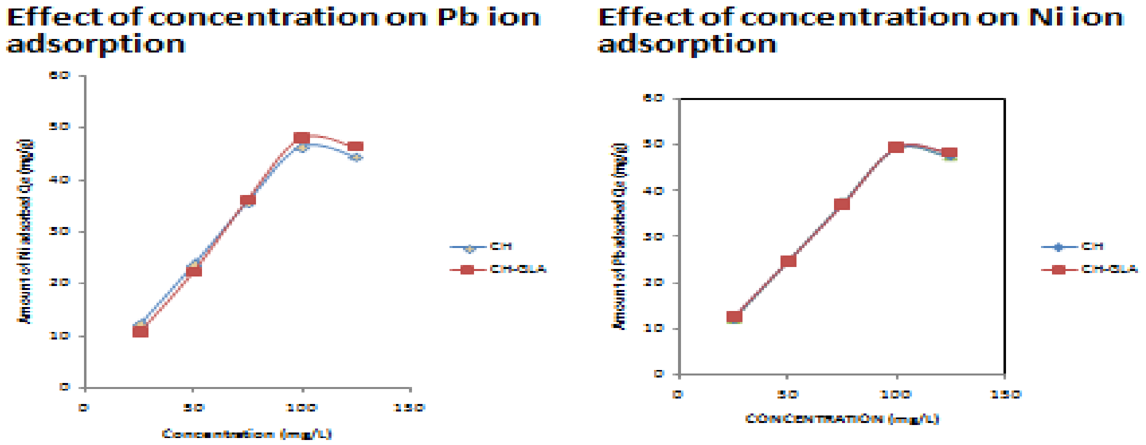
In adsorption procedures, equilibrium is reached when the concentration of the adsorbate in the bulk solution is in dynamic balance with that at the interface of the adsorbent.


Variation of adsorbents dosage to adsorb Pb (II) ions

Variation of adsorbents dosage to adsorb Ni (II) ions

Figure 1: Variation of adsorbent dosage to Pb and Ni ions

The adsorption capacity of chitosan and chitosan –GLA is greatly dependent on the adsorbent dosage to the metal ion. This parameter was studied at varying dose of 0.1 g, 0.2 g, 0.3 g, 0.4 g and 0.5 g while keeping all other parameters constant such as time 60 m, temperature at 27±℃ and concentration 50 mg/L. As the adsorbent dosage was increased for both adsorbents on the adsorbates, the amount of metal ion removed also increased as shown in the plot below. This effect is due to the availability of exchangeable sites for Ni^{2+} and Pb^{2+}. The maximum adsorption value of Pb (II) ions for chitosan is 79.12 % and 92.16 % for chitosan-GLA at 0.4 g. At 0.5 g there was a decrease in adsorption due to the fact that there was a reduction in the number of active site available for adsorption of the metal ions. The maximum percentage removal value of Ni (II) ions for chitosan was 98.0 % and 97.4 % for chitosan-GLA. From the results obtained the crosslinked chitosan (CH-GLA) has the highest percentage removal at 0.4 g. Increase in adsorbent dosage results to an increase in unsaturated sites thereby increasing adsorption capacity (Ngah and Fatinathan, 2010).


Effect of concentration on Pb ion adsorption

Effect of concentration on Ni ion adsorption

Figure 2: Effect of Concentration on Pb and Ni ions adsorption

As the initial concentrations of Nickel (II) and lead (II) ions were increased, adsorption also increases onto the surfaces of the adsorbent but at the highest concentration of 125 mg/L there was a reduction in the amount of metal ions adsorbed, this is because of the decrease in the number of active sites on the adsorbent, this implies that the maximum adsorption was attained at 100 mg/L. Pb ions are adsorbed more unto the chitosan and chitosan-GLA, this can be explained on the basis of their ionic radii (Ni =0.0012A˚ and Pb =1.21 A˚) and the hydration energy of Pb which is lower than that of Ni.

The pH was set at varying pH values, the adsorption of Ni^{2+} and $Pb^{2+}$was highly dependent on the pH of the individual metal ions, this is due to the fact that pH influences the solubility of the metal ions and also the ionization state of the functional groups existing on the adsorbents. It has been reported by Wan Ngah and Fatinathan in 2010 that the adsorption capacities were low for chitosan and chitosan-GLA at pH < 2 due to increase in the positively charge active sites (NH_3^+) at low pH for chitosan and chitosan-GLA (by resulting to a repulsion between the metal ions and the protonated –NH_2 (NH_3^+) bonding site). This implies that more H^+ results a reduction in adsorption capacity and also an increase electrostatic repulsion between the metal ion and the bonding site. As the pH moves towards the neutral region, adsorption increases due to the decrease in the protonation of the active sites. At pH 3-5 there is an increase in adsorption, at pH 7, there was maximum adsorption due to the balance in the concentrations of both hydrogen and hydroxyl ions. At pH above 7 there could be uncertainties due to the formation of metal hydroxides ($Pb(OH)_2$ and ($Ni(OH)_2$). The adsorption capacity of chitosan was higher while that of chitosan-GLA increases gradually for both metals. The maximum adsorption capacity of both metal ions for this study occurred at pH 7.

The effect of time was studied at 30 m, 50 m, 70 m and 90 m and 110 m while keeping all other parameters constant. The adsorption capacity of chitosan and chitosan-GLA increases as time increases; this is due to the fact that as time increases there is an increase in the chances of equilibrium attainment between the adsorbent and adsorbate. The highest percentage removal of chitosan for nickel is 90.54 % and 95.40 % for chitosan-GLA while the highest percentage removal of chitosan for lead is 73.95 % and 87.63 % for chitosan-GLA.

From the correlation coefficient (R^2) results obtained on the adsorption of Ni and Pb as described by both Langmuir and Freundlich, it is observed that the freundlich isotherm model gave the highest value of R^2. In the adsorption of nickel (II) ion on chitosan and chitosan-GLA for Langmuir isotherm model the R^2values obtained were 0.7619 and 0.6328 respectively, while for the adsorption of lead (II) ion the values were 0.9835 and 0.9148 respectively. In freundlich isotherm model the R^2values obtained for both chitosan and chitosan-GLA were 0.9484 and 0.8969 respectively for nickel (II) ions and 0.9959 and 0.9828 for lead (II) ions. This means that the Freundlich model best describes the experimental data than the Langmuir isotherm implying that there is a good fit of the experimental data that conforms to the heterogeneous adsorption mechanism (i.e. the active sites were heterogeneously distributed). It is also observed that the freundlich isotherm model fits more for the adsorption of lead by chitosan-GLA (CH-GLA) which was also observed by Ngah and Fatinathan, (2010) in a study of the bio-sorption of Pb(II) using chitosan and chitosan-GLA.

From the results obtained from the pseudo first order kinetic model and the second order kinetic model, the correlation coefficient values by the straight line plot of $1/Q_t$ against t of the second order kinetic model were much higher than for the pseudo first order model which is a plot of log Qe-Qt against t. This result indicates that the adsorption of Pb (II) and Ni (II) onto chitosan and chitosan-GLA is best fitted for the second order kinetic model. Based on the R^2 value in the pseudo first order model for the adsorption of nickel and lead, chitosan gave 0.0816 and 0.8438 respectively while chitosan-glutaraldehyde gave 0.0322 for nickel and 0.0562 for lead. In the second order kinetic model for the adsorption of nickel and lead, chitosan gave 0.9806 and 0.7519 respectively while chitosan-glutaraldehyde gave 0.9538 for nickel and 0.9464 for lead.

Conclusion

Chitosan and cross-linked chitosan adsorption was studied for the removal of nickel and lead ion. Metal adsorption capacity and efficiency of the cross-linked chitosan (CH-GLA) beads are higher compared to chitosan (CH). The optimum pH of adsorption of nickel (II) and lead(II) ions by chitosan and cross-linked chitosan is 7. The degree of adsorption varies with adsorbents dosage or mass, pH, contact time, initial concentration and temperature. Increase in the initial concentration of the metal led to a decrease in adsorption of Ni (II) and Pb (II) ions. As contact time increases there is a gradual increase in adsorption and adsorption equilibrium was attained at 1 h. The adsorption of Ni (II) and Pb (II) ions greatly increase as the adsorbent mass was increased. The efficiency of adsorption decreases as temperature increases due to an increase in the systems entropy. Isotherm modelling revealed that freundlich model best describes the adsorption of Pb (II) and Ni (II) ions onto the surface of the adsorbents and the kinetics of the adsorption process follows the pseudo second order kinetic model. Finally CH and CH-GLA shows great potential as an effective, low cost alternative material for metal removal from aqueous solution.

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