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ADSORPTION OF TOXIC METAL IONS ONTO CHITOSAN AS BIOSORBENT

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ABSTRACT

Chitosan, a biopolymer produced from crustacean shells, has applications in various areas, particularly in drinking water and wastewater treatment due to its ability to remove metallic ions from solutions. The adsorption capacity of chitosan depends on a number of parameters deacetylation degree, molecular weight, particle size and crystallinity. The purpose of this work was to study the adsorption of Copper and cadmium on chitosan produced from shrimp shells at a laboratory level. The experimental work involved the determination of the adsorption isotherms for each metal ion in a batch system. The resulting isotherms were fitted using the Langmuir model and the parameters of the equation were determined. Kinetic studies of adsorption for different metallic ions at different concentrations and with different particle sizes were performed in batch and column systems. The results showed that the adsorption capacity depends strongly on pH and on the species of metallic ions in the solution. The optimum pH value for the metallic cation adsorption was between 4 and 6, whereas for arsenic adsorption it was about 3. When the pH is not controlled, the adsorption capacity is independent of the initial pH with the solution reaching a final pH of about 7. It was also found that the Langmuir equation described very well the experimental adsorption data for each metallic ion. The adsorption capacity for the metals on chitosan is more in Copper than Cadmium.

INTRODUCTION

Toxic metals can be distinguished from other pollutants, since they are not biodegradable and can be accumulated in nature. The complete removal of toxic heavy metal ions that are incompatible with biological systems requires expensive treatment in order to produce water that is again useful for domestic use. It is essential to extend methods for removal of metal ions to decrease the pollution load on the environment. Classical techniques of heavy metal removal from solutions include the following processes: solvent extraction, precipitation and co-precipitation, electrochemical reduction, chemical- and biosorption, pre-concentration.[1-2]

In recent years, the adsorption process has also received much attention and has become one of the more popular methods for the removal of heavy metal ions from wastewater, because of its competitive and effective process. Numerous adsorbents have been reported for the removal of toxic metal ions, such as chitin, chitosan, starch, cellulose , guaran , and cyclodextrin , which are not only eco-friendly and cost-effective but are also effective in remediation of common effluents present in wastewater. Other polysaccharide-based materials and alumino-silicates are used as adsorbents in wastewater treatment .Adsorption using commercial activated carbon.[3-4]

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.[5] The strong affinity of metal ions for these sorbents is explained by the relatively high proportion of nitrogen sites. The use of these biopolymers can be a low cost alternative for the removal of contaminants from industrial effluents and from the natural water supply. The metal sorption capacity of chitosan varies with crystalline, affinity for water, deacetylation degree and amino group content. Kinetic studies have demonstrated that the rate of metallic ion sorption onto chitosan differs depending on the raw material (shrimp, crab or lobster shells), preparation method, chemical modification, and chitosan particle shape. Wu evaluated the sorption capacities and rates for Cu(II) onto flakes and bead forms of chitosan prepared from fishery wastes.[6] Structure of chitosan is given below.

It is widely known that chitosan can build complexes with certain metal ions. Amino sites are the main reactive groups for metals ions, although hydroxyl groups (especially in the C3 position) may contribute to sorption (Guibal, 2004). Adsorption, ion exchange, and chelation have been discussed as the mechanisms responsible for complex formation. The type of interaction depends on the composition of the solution, the pH of the solution, and the speciation of metal ions (Vold *et al.*, 2003). The affinity of chitosan for cations adsorbed on film presents selectivity in the following order: $Cu^{+2}>>Hg^{+2}>Zn^{+2}>Cd^{+2}>Ni^{+2}>Co^{+2}\sim Ca^{+2}$, and $Eu^{+3}>Nd^{+3}>Cr^{+3}\sim Pr+3$ (Rinaudo, 2006).The objective of the present work has been to study the removal of and Arsenic   from aqueous solution using chitosan.[7] Equilibrium and kinetic experiments at different metallic ion concentrations and with different particle sizes have been performed. The objective of the present work has been to study the removal of Hg and As from aqueous solution using chitosan. Equilibrium and kinetic experiments at different metallic ion concentrations and with different particle sizes have been performed. The experimental data have been tested with the Langmuir equation, and simplified kinetic models have been applied to determine the rate-controlling mechanisms for the adsorption process.[8]

MATERIAL AND METHODS

Chitosan (from Sigma Aldrich Mol wt. 22742 Da and degree of deacetylation of 0.75 pH Buffer tablet (pH 1 to 6) ,All reagents were analytical grade and were used without further purification.

Production of Chitin and Chitosan on a Laboratory Scale

Raw material was provided by CAMANICA S.A., a shrimp-processing company. The chitin extraction process was based on chemical deproteinization, demineralization, and Depigmentation of the shrimp shells on a laboratory scale. Chitosan was obtained by the deacetylation of chitin. 0.3 kg of shrimp shells were placed in 1.5 L of a 10% sodium hydroxide solution. The mixture was stirred for 1 hour at room temperature. Later, the solid was separated from the liquid and washed with soft water (without Ca^{2+} and Mg^{2+} ions). The solid was placed in 12 L of 1.8N hydrochloric acid for 12 hours at room temperature to remove minerals such as calcium and magnesium carbonate. Subsequently, the liquid was removed and the solid was washed with soft water. 12 L of 0.38% sodium hypochlorite was poured into the vessel containing the solid and the suspension was agitated until the pigmentation of the solid disappeared (about 15 minutes). The white solid (chitin) was washed and dried in an oven at 50 ºC for 12 hours. At the end, 735 g of chitin were produced. The deacetylation of chitin was performed as follows. 150 g of chitin was mixed with 1.125 L of 50 % sodium hydroxide and the suspension was kept in an oven at 110 ºC for one hour. The mixture was washed with soft water several times to remove residual sodium hydroxide, until pH 8 was achieved. The material was dried in an oven at 50 ºC.[9]

Chemical and Reagents

These stock solutions were obtained from a standard (1000 mg L^{-1}) of Cd (II), and Cu (II)from is Cadmium chloride and Copper chloride. Deionised water was used to prepare all the solutions. The pH of the metallic ion solutions was adjusted by adding drops of 1.25 N hydrochloric acid or 0.5 – 3.0 % sodium hydroxide. The pH was measured by a 410A Orion pH meter. and solutions of various concentrations were obtained by diluting the stock solution with distilled water. Copper and cadmium concentrations were determined by AAS. All the chemicals used were of analytical grade reagent and all experiments were carried out in 500 ml glass bottles at the laboratory ambient temperature of 25^{o}C.

Batch sorption Experiment

All the sorption experiments were performed at 25°C with 150 rpm on an orbital shaker and 30 minute shaking time. For that 100 mg of the sorbent was taken in a 250 ml flask containing 100 ml of Copper and cadmium metal solution. Batch adsorption experiments were conducted to examine the sorption kinetics and equilibrium. In the sorption kinetic experiments, 1 ppm of Copper and cadmium solutions at different initial solution pH were used. The sorption isotherm experiments were conducted over 24 h .The pH of 100 ml metal solution was adjusted to 5 and mix with 100 mg of sorbent. Mixture was allowed to equilibrate by shaking for 30 min. Same procedure was repeated by adjusting pH to 6,4,3,2 and 1 using buffer tablet. After sorption, the sorbent was separated from the solution by membrane filtration and rinsed with distilled water The metal concentration in the filtrate was analyzed using a flame atomic absorption spectrophotometer AAnalyst200 (Perkin Elmer, USA) . All the sorption experiments were conducted in duplicate, and the mean values were reported. 1 ppm (100 microgram per 100 ml) metal was loaded for batch study of metal sorption and then decreasing metal concentration from aqueous phase was calculated in percentages.[10-11]

RESULT AND CONCLUSION

Sorption Kinetics Study

Graph shows the sorption kinetics of Cd (II), and Cu (II) metal ions using the sorbent composite at different solution pHs. The sorption of both the metals was time dependent. The sorption kinetics of copper was rapid in the first 60 min, before becoming more gradual until equilibrium was reached. At pH4 and pH5, the equilibrium for copper sorption was attained within 120 and180 min, respectively. In cadmium sorption, the sorption kinetics was similar. As the sorbent surface is bare in the initial stage, the sorption kinetics is fast and normally governed by the diffusion process from the bulk solution to the surface. In the later stage, the sorption is likely an attachment-controlled process due to less available adsorption sites.[12-13]

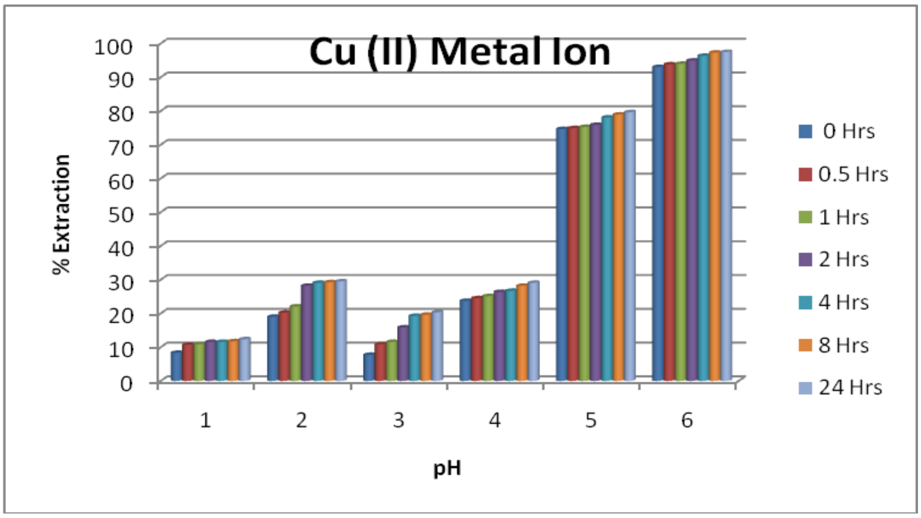

Fig.2: % Extraction of Copper Metal ion at different pH

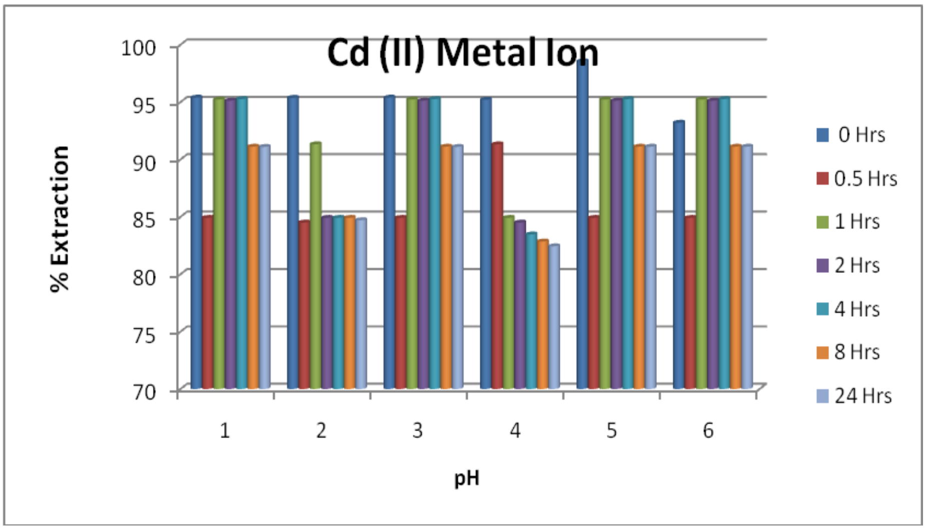

Fig.3: % Extraction of Cadmium Metal ion at different pH

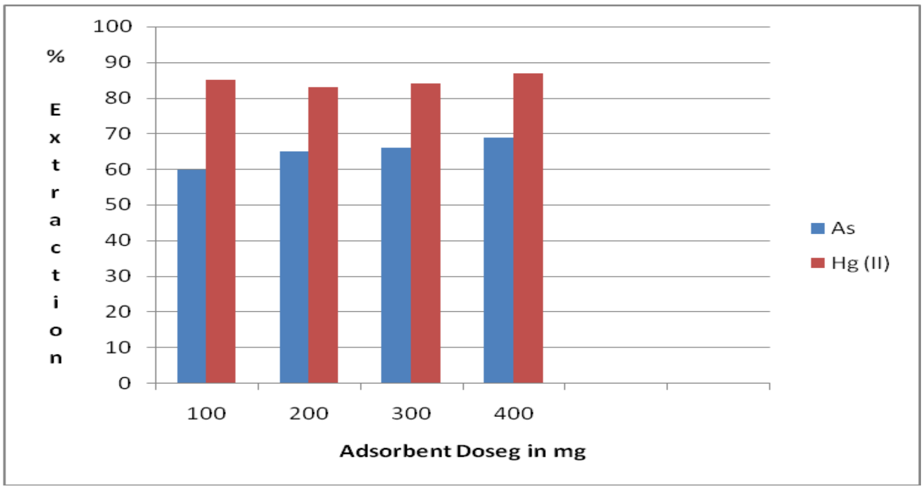

Fig 4: Effect of adsorbent dose on the removal of Metal ion

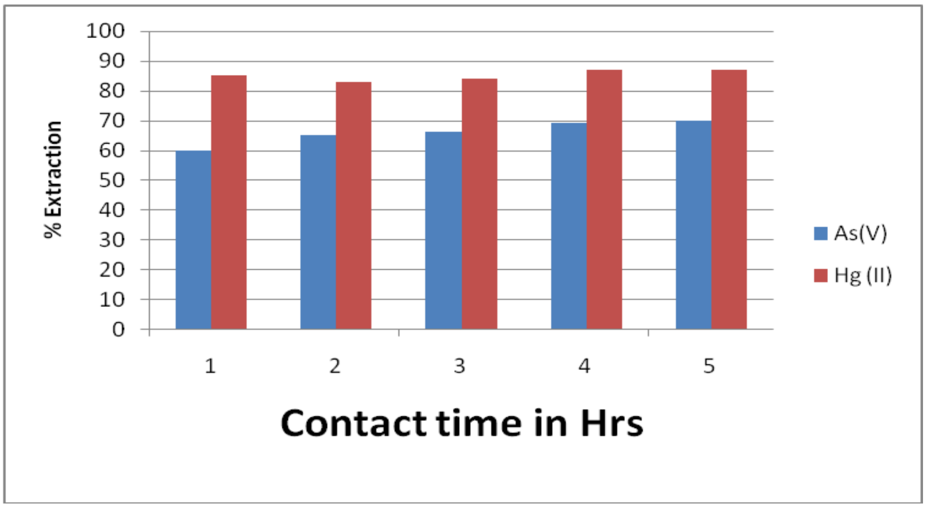

Fig.5: Effect of contact time on the removal of Metal Ion

Effect of pH on Metal Sorption

pH is an important parameter that affects metal ion sorption; it not only influences the properties of sorbent surface but also affects metal speciation in solution. In our experiments, the initial solution pHs at 5.0 and 6.0 for copper metal (Fig 1) gives 80-90% of metal extraction. But for cadmium in get adsorbed higher at pH 4 (Fig 2). The sorption capacity increased with an increase in initial pH upto pH-6. The final solution pH after 24 h of sorption (shown in Figure1) The results of the kinetics of copper sorption on the sorbent at pH 5 without pH adjustment during the sorption.[14]

Effect of Adsorbent Dose

The dependence of metal adsorption was studied by varying the amount of adsorbent from 100 to 400 mg, while keeping other parameters (pH, and contact time) constant. From Figure 5.6 it can be easily be inferred that with fixed metal concentration, the percent removal of metal ions increases with increase in adsorbent dose. This initial increase in percent removal of heavy metal ions with increase in adsorbent dose was due to the greater availability of exchangeable sites for the metal ions.[15]

CONCLUSION

Natural bio polymer "Chitosan" based sorbent provides green route of metal extraction The study showed that the solution pH strongly affects the adsorption capacity of chitosan. It was observed that the greatest adsorption of Cu(II) occurs at high pH, whereas the greatest adsorption of Cd(II) takes place at low pH. The Langmuir isotherm fits the experimental data well for the ions studied. The adsorption capacity of the metals on chitosan follows the sequence Cu>>Cd. Although it was found that arsenic is effectively removed by chitosan. The large differences between adsorption capacities reported in literature suggest that there are important structural differences related to the raw material and the production of chitosan .The present study showed that the adsorbent particle size strongly affects the copper adsorption capacity. The kinetics for the adsorption of Copper and cadmium onto chitosan are best described by a pseudo-second-order equation, except for copper adsorption at high initial concentrations and large particles size, where intraparticle diffusion is the rate-controlling mechanism.

The chitosan is material gives information about pore size, good chemical and thermal stability which revels applicability towards Metal extraction. This low-cost adsorbents are effective for the removal of metal ions from aqueous solutions shows order of % extraction i.e. Cu>>Cd. The batch method was employed parameters such as pH, contact time and metal concentration were studied at an ambient temperature 25^{o}C. The optimum pH corresponding to the maximum adsorption of Copper and cadmium was pH 5-6.Copper and cadmium ions were adsorbed onto the adsorbents very rapidly within the first 120 min.

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