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REMOVAL OF Cu(II) AND Ni(II) IONS FROM AQUEOUS SOLUTION USING CHITOSAN AND CHEMICAL MODIFIED CHITOSAN

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In this study, the removal of Cu(II) and Ni (II) ions from aqueous solution using chitosan and chemical modified chitosan in a batch adsorption system was studied. Our results led to the conclusion that chemical modification of chitosan decreased the adsorption capacity for Cu(II) and Ni(II) ions, but increased it's resistance in acidic medium.

Keywords: chitosan, adsorption, heavy metals, chemical modification, isotherm

1. Introduction

Waters polluted with heavy metals are a major source of concern due to their toxicity to many life forms. Wastewaters with heavy metal content result from many industrial processes such as mining, electroplating, metal cleaning, paper, fertilizer and alloy obtaining. Through the food chain these heavy metals can be accumulated by living organisms and they can cause serious threats to animals and man. The traditional methods used to eliminate the heavy metals from wastewaters are: precipitation, coagulation, oxidation and reduction, ion exchange, filtration and electro-chemical methods. These methods are inefficient for heavy metal contaminants at tracer levels, and some methods are expensive due to their maintenance and operation costs. Adsorption is one of the few promising alternatives for heavy metals removal and recovery from wastewaters, especially using low cost natural sorbents such as agricultural wastes, seafood processing wastes, clay materials, zeolites, activated carbon and biomass [1-4].

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Biosorption or sorption on natural materials is recognized as a more efficient and more economically method to remove heavy metals from wastewaters [18].

Chitosan is a cheap material which manly results from deacetylation of chitin, the second-most abundant biopolymer next to cellulose [5-7].

Its capacity to remove these pollutants is due to the presence of a large number of amine groups on the chitosan chain. The number of amine groups in chitosan is greater than the number of amino groups from chitin [8-12].

The features of the chemical structure of chitosan are responsible for its solubility in acidic medium, which significantly reduces the possibility of using of this material in treatment of wastewaters with heavy metal ions and acidic pH.

Glutaraldehyde is a very common cross-linking reagent long used for chemical modification of biomaterials. The glutar-aldehyde-crosslinking occurs through a Schiff's base reaction between aldehyde ends of the crosslinking agent and amine moieties of chitosan to form imine functions.

Both materials chitosan and the chemical modified chitosan were used in order to remove Cu(II) and Ni(II) from single and binary-metal synthetic solutions.

2. Materials and methods

Samples of chitosan flakes highly viscous purchased from Sigma Aldrich Chemie GmbH were used in this study. Practical grade chitosan from crab shells has a minimum of 85% percent deacetylation and a viscosity > 200cps (1% in 1% acetic acid); and the total impurities are ≤ 1%.

Glutaraldehyde was of analytical grade used without further purification. The solutions were prepared using deionized water.

Stock solutions of 6373 mg/L copper, and 1120 mg/L nickel were prepared by dissolving the corresponding salts ($CuCl_2$ and $NiCl_2.6H_2O$) (Merck a.r. grade) in distilled water. Aqueous solutions of Cu(II), Ni(II) and Cu(II) + Ni(II) used in this study were prepared by diluting the stock solutions.

Adsorption experiments were carried out through a batch method using a Heidolph RZR 2041 stirrer. The quantity of chitosan was 0.1 g, and the speed rotation was 150 rpm (rotation per minute). The solution volume used was 25 mL.

Metallic ion concentration in the initial solution, and in the solution after the adsorption on the chitosan and the chemical modified chitosan were determined by atomic adsorption spectrometry using a type AAS 1N Carl Zeiss Jena Atomic Adsorption Spectrophotometer.

Recently prepared highly viscous wet chitosan flakes were suspended in a 0.025 M glutaraldehyde solution to obtain a ratio of 1:1 with chitosan (mol GLA:mol NH_2). The chitosan flakes in the resulting glutaraldehyde solution were left standing for 24 h at room temperature with constant stirring. After 24 h the cross-linked chitosan flakes were intensively washed with distilled water, filtered and air-dried.

The physico-chemical characterization of modified chitosan was performed in other work [13]. In that study it was established that the possible structural formula of chemical modified chitosan can be:

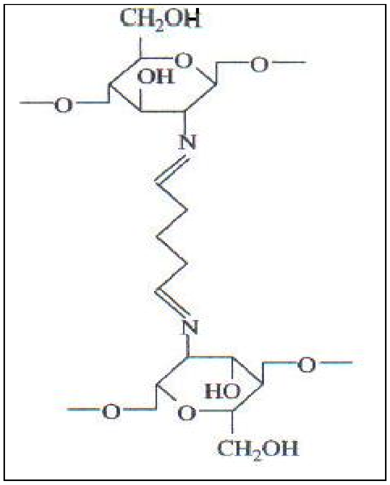

Fig. 1. Possible structure of the chemical modified chitosan with glutaraldehyde [13]

In the same study was shown that the high hydrophilicity of chitosan due to a primary amine group which makes chitosan easily soluble in acidic medium, was reduced by crosslinking. When the cross-linked chitosan was added to a solution which contains 5(v/v)% acetic solution, the cross-linked chitosan was observed to be insoluble. In a solution which contains 0.1M NaOH the chitosan and cross-linked chitosan were also insoluble [13].

3. Results and discussions

Kinetic studies of chitosan and cross-linked chitosan were performed as batch tests, with the sample removed from the shaker between 1 min and 1020 min. These tests were performed in order to establish the factors which influence heavy metal removal processes from wastewaters by chitosan and cross-linked chitosan.

The chitosan sample (0.1000±0.0001 g) was weighed into a glass vial with a screw top. A total of 25 mL of single and binary metal solution was added to each vial via a volumetric dropper, and the vials were capped. The initial concentration of Cu(II) and Ni(II) in solution was 740 mg/L for copper, and 620 mg/L for nickel in single and in binary metal solutions. Temperature was 22±2 °C. Each sample was then filtered and tested for metal ion concentration.

The same experiments were conducted y using 0.1000±0.0001 g of cross-linked chitosan, and 25 mL of single and binary solutions. All other conditions were maintained constantly. After the shaking of samples which contain cross-linked chitosan and binary metal solution at different time, the solutions were filtered and analyzed in order to determine the metal concentration in the final solutions.

The adsorption capacity of chitosan and cross-linked chitosan, Q, were calculated by means of equilibrium studies and then summarized using the equilibrium equations of Langmuir and Freundlich. Equation (1) establishes the mass balance of process at equilibrium condition:

$$Q=\frac{(C_i-C_f)\cdot V}{m} \tag{1}$$

where: Q = adsorbent capacity, mg/g; C_i = the initial metal ion concentration, mg/L; C_f = the metal ion concentration remained in solution at different times, mg/L; V = solution volume, L; m = adsorbent mass (g).

The quantity of heavy metal uptake by chitosan and cross-linked chitosan was calculated at different times, and experimental data is presented here in Fig. 2-5.

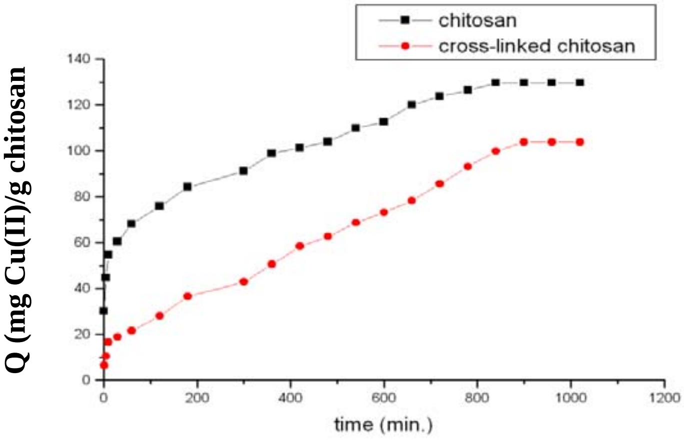

Fig.2. Adsorption isotherm of Cu(II) onto chitosan and cross-linked chitosan

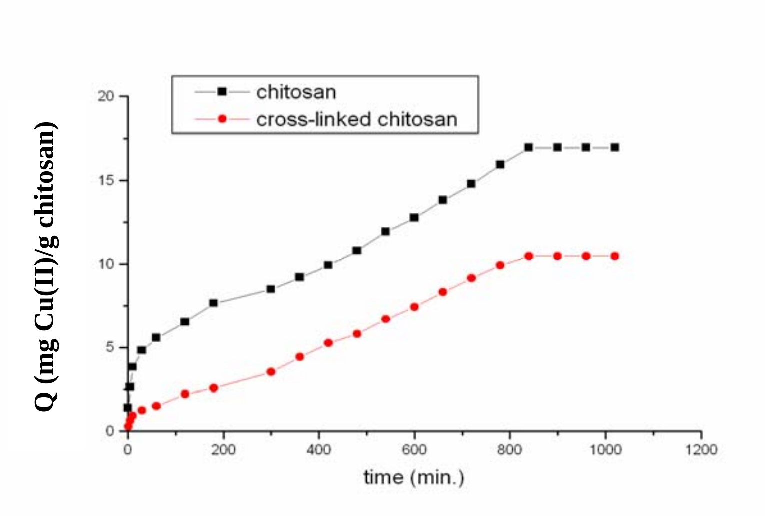

Fig.3. Adsorption isotherm of Ni(II) onto chitosan and cross-linked chitosan

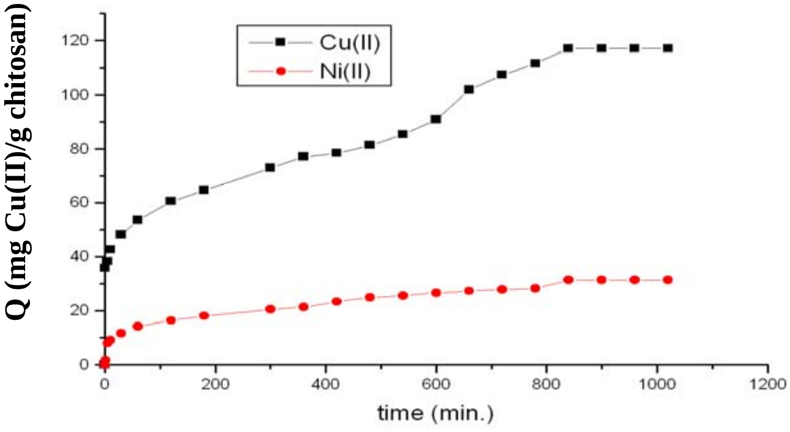

Fig. 4. Adsorption isotherm of Cu(II) and Ni(II) from binary solution onto chitosan

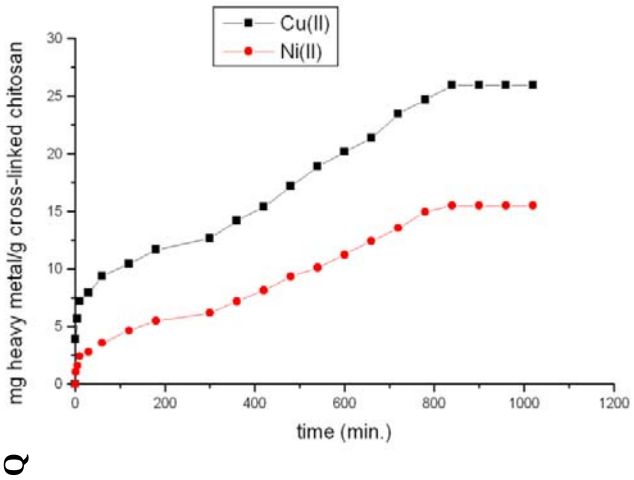

Fig. 5. Adsorption isotherm of Cu(II) and Ni(II) from binary solution onto cross-linked chitosan

From these figures it can be seen that the adsorption capacity of chitosan and cross-linked chitosan increases with time. The adsorption process is slow because the equilibrium was reached after 14 hours. The highest adsorption level of129.63 mg/g chitosan unmodified tested in this study was determined for Cu(II). The adsorption capacity of chitosan decreases by chemical modification of chitosan from 129.63 mg Cu(II)/g chitosan to 103.86 mg Cu(II)/g cross-linked chitosan. In case of nickel, the adsorption capacity decreases from 16.97 mg Ni(II)/g chitosan to 10.47 mg Ni(II)/g cross-linked chitosan.

In the case of the binary solution a slow decrease in the adsorption capacity of chitosan from 129.63 to 117.06 mg Cu(II)/g chitosan was observed, a with significant decreasing in the adsorption capacity of cross-linked chitosan from 103.86 to 28.18 mg Cu(II)/g cross-linked chitosan.

In the case of nickel absoption from the binary solution it was observed a slow increasing in the adsorption capacity from 16.97 to 25.95 mg Ni(II)/g chitosan and from 10.47 to 15.50 mg Ni(II)/g in the cross-linked chitosan.

These results are analogous with the results obtained from other studies [14-17].

4. Conclusions

Sorption equilibria of Cu(II) and Ni(II) from single - and binary solutions on chitosan and glutaraldehyde cross-linked chitosan were studied at 22±5ºC. The amount of metal sorption (Q) increased with time before equilibrium is reached. This result is important, as equilibrium time is one of the important parameters for an economical wastewater treatment system.

By cross-linking of chitosan with glutaraldehyde it was obtained an adsorbent with a much lower adsorption capacity than raw chitosan, but with a much higher stability in acidic solutions. This result is very important because many wastewaters resulting from different industries have one pH which is in an acid range.

From the experimental data, we can observe that the copper adsorption capacity of chitosan is much higher than the nickel adsorption chitosan's capacity. For this reason we can consider that chitosan has a bigger selectivity for Cu(II) than for Ni(II).

Acknowledgements

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