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Immobilized chitosan as a selective absorbent for the nickel removal in water sample

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Abstract: Method for preparation of chitosan immobilized on silica gel(CTS-silica) was described. The CTS-silica was used as absorbent for the absorption of nickel in water. The results showed that this absorbent had relatively high selectivity and strong affinity to nickel. The maximum absorption capacity for nickel can reach 667 mg/g of chitosan. Factors that affect the absorption capacity, such as pH, ion strength and the presence of calcium, EDTA and the mechanism of absorption were discussed in detail. The absorbent can be regenerated with acid and reused for several times. The recovery rate for nickel can reach 99.99%. This absorbent filled in a column can be used in nickel removal from wastewater and drinking water.

Keywords: immobilized chitosan; nickel; wastewater treatment

Introduction

Biological materials have shown potential for heavy metal binding, they have been used in metal remediation of industrial streams and for trace metal removal in drinking water(Susan, 1999). The main advantage of using biological material as an absorbent for water cleaning lies in that the biological adsorbent have less toxicity compare to the chemical synthetic polymer. But only biological material with sufficiently high metal-binding capacity and selectivity for heavy metal can be practically used in water cleaning process (Volesky, 1995; Kratochvil, 1998). Chitin is a natural polysaccharide, existing in shell of aquatic life or cell wall of fungi. Chitosan is the deacetylated chitin. Since it contains some functional groups, such as $-NH_2$ and $-OH$, it can be a suitable absorbent with potential selectivity material for heavy metals adsorption. Metal sequestration by bio-absorbent may involve complex mechanism, mainly ion exchange, chelation, surface precipitation and ion entrapment in inter-space of the structural polysaccharide network (Hughes, 1989). Not all of the binding site in bio-absorbent is specific for heavy metal(Masri, 1974), so, it can be assumed that the metal could not be absorbed by just one kind of binding site such as $-NH_2$, a mix absorption model must exist. All binding site can be divided into specific and non-specific binding site is assumed. The heavy metal binding on specific site could hardly be desorbed by alkali metal or alkali earth metal, whereas heavy metal binding on non-specific can be easily exchanged by metal especially with the same valence(Rees, 1982). So the selectivity or the binding capacity of the bio-absorbent for heavy metal is mainly determined by the number of specific binding site. In this paper, the selectivity and binding mode for nickel ion adsorbed by chitosan were discussed.

Pure chitosan have an obvious shortcoming in practical using as a water and wastewater treatment material. It is soluble in acid solution and lack of rigidity. Some methods for improving the stability of chitosan have been reported(Keisuke, 1986; Tzu-Yang, 1995). Cross-linking is one of these choices, but it is difficult to control the shape and size of pure cross-linking chitosan particles, which can render the column inoperable when gravity-feed is employed. To circumvent this problem, a technique for immobilizing chitosan on silica gel has been developed in this study. The conception of immobilizing biomass on several kinds of substrate has been used by some scientists(Darnall, 1986a; 1986b). The silica would be a good substrate for immobilization has been reasoned because it is relatively inert, noncompressible and available in a controlled size and porosities.

A new procedure for immobilizing chitosan on silica gel is described in this paper. Nickel is the model metal in this study for its toxicity and environmental concerning. The characteristic and mechanism of this new absorbent for nickel binding is discussed. Column study associated with absorption capacity, stability or potential recyclability of the immobilized-chitosan resin is reported.

1 Materials and methods

1.1 Instrumentation

A Perkin-Elmer model, 4000 atomic absorption spectrophotometer with air/C₂H₂ flame was used for Ni determination. The Ni hollow cathode lamp was operated at 4 mA and the 232 nm absorption line employed in conjunction with the monochromator entrance-slit of 1 nm.

1.2 Reagents

A Ni²⁺ stock solution was prepared from the analytical reagent grade sulfate salt (Shanghai Reagent Co). All buffer solution, HCl and NaOH solution was also prepared from analytical grade reagent water used in the experiment was distilled water.

1.3 Preparation of absorbent

Silica gel was added to chitosan solution of 1 mol/L acetic acid. Agitated for 2 h, the mixture was vacuum dried at 40 °C overnight. After that, the mixture was suspended in Dimethyl sulfoxide(DMSO) for 15 min, a portion of epoxy chloride propane was added and agitated for 24 h. The mixture above, after removing solvent, was added to 50 ml of 0.1 mol/L NaOH, and heated for 8 h at a constant temperature of 80 °C to produce immobilized cross-linking chitosan absorbent. This absorbent was separated from the solution and washed with distilled water to neutral pH and dry.

1.4 Absorption experiments

Batch sorption experiments were applied in inorganic base selection, cross-linker concentration determination tests, sorption kinetic study, sorption isotherm study, the effect of pH, ion strength and calcium ion on the absorption of nickel studies. Bath sorption experiments were conducted at room temperature(25 °C) in a rotary shaker using 250 ml glass bottles. Which contains mixture of 50 ml buffer solution and nickel solution and 0.25 g absorbent with nickel concentration varying for different purpose. The sorption time was 4 h, which was enough to reach sorption equilibrium according to the sorption kinetic studies. The absorbent was separated by filtration and the supernatant was analyzed for nickel concentration.

Absorption, desorption and regeneration of the absorbent for nickel ion spiked in water were carried out in a glass column. The glass column with 2.0 cm in diameter was filled up to a depth of 20 cm with absorbent. The solution was fed into the column through a peristaltic pump with flow rate of 2 ml/min, and the samples of effluent were collected periodically and analyzed for nickel.

Analysis of the nickel in solution was carried out using flame atomic absorption spectrophotometer. The absorption capacity in batch study and absorption rate in column study can be calculated by follow equation:

$$Q = \frac{(C_0 - C)V}{W \times a\%} \times 10^{-3} (\text{mg} \cdot \text{g}^{-1}); X\% = \frac{C_1 V_1}{C_0 V_0} \times 100\% .$$

Where, Q (absorption capacity) is the amount of adsorbed nickel on 1 g of chitosan(mg/g); C_0, C are the initial concentration and equilibrium concentration of nickel($\mu\text{g}/\text{ml}$); V is the volume of solution(ml); W is the weight of absorbent(g); $a\%$ is the content of chitosan in absorbent; $X\%$ is the absorption rate; V_0 is the total volume of nickel spiked solution fed onto the column(ml); V_1 is the volume of effluent(ml); C_1 is the nickel concentration in eluted solution.

1.5 Column experiment

Standard water sample was prepared from tape water spiked with nickel ion solution, the original tap water is free from nickel ion, final concentration of nickel in water sample is 1.0 $\mu\text{g}/\text{L}$. Wastewater sample containing nickel was collected from Hangzhou Electroplating Factory. The water sample was fed into the column filled with 4.0 g of CTS-silica by a peristaltic pump, the flow rate is constant in 1.0 ml/min. After the 1.0 L water sample passed though the column, the column was eluted with 0.1 mol/L HCl until no nickel ion was eluted, the eluted solution was received in a 10 ml volume flask and dilute to 10 ml with distilled water. The nickel concentration was determined by AAS. And the recover rate was calculated.

2 Results and discussion

2.1 Substrate and cross-linker concentration selection

Table 1 shows the absorption amount of nickel adsorbed by per gram of chitosan immobilized on four inorganic substrates: silica gel, active carbon, siliceous earth, and aluminum oxide. The results indicate that chitosan immobilized on silica gel is favorable with most absorption capacity. At mean time, the contrast tests were carried out and the result is shown in Table 2. Inorganic substrate themselves do not have a significant absorption capacity for nickel, especially for silica gel, concerning other quality, silica gel is selected as the substrate for immobilization of chitosan.

Table 1 Absorption capacity of different absorbents for nickel

Absorbents *	CTS-silica	CTS-active carbon	CTS-Al ₂ O ₃	CTS-siliceous earth
Adsoption capacity, mg/g	89.8	79.4	78.6	37.3

Notes: * : 0.8% (v/v) epoxy chloride propane, 5% CTS-silica

Table 2 Amount of nickel absorbed on different inorganic base

Inorganic base	Silica	Active carbon	Aluminum oxide	Siliceous earth
Adsorbed nickel, mg/g	0.158	0.527	0.669	0.799

The absorption capacity of CTS-silica depends on the concentration of epoxy chloro propane as a cross linker. Fig.1 shows the effect of the concentration of cross linker on the uptake of nickel. The results indicate a low concentration of cross linker favors the absorption of nickel and 1.6% of cross linker in absorbent reaches the maximum absorption capacity. It suggests that part of the absorption groups, - NH₂ and - OH, is cross-linked, hence, decreases the active absorption sites.

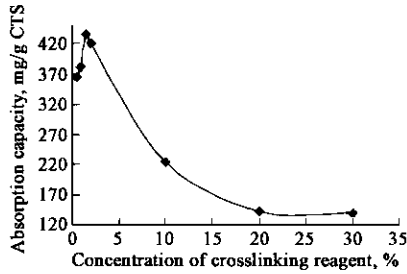


Fig.1 Effect of concentration of cross-linking reagent on absorption capacity

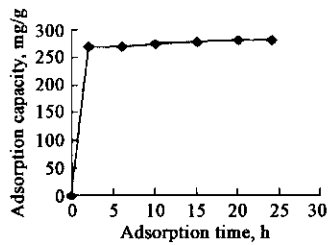


Fig.2 Adsorption dynamic curve

2.2 Adsorption kinetics and equilibrium study

The kinetics and the equilibrium of sorption are two important physico-chemical aspects for evaluation of the sorption process. The curve of absorption capacity Vs time at pH 5.5 with initial concentration of 100 μg/ml is shown in Fig.2. The rate of sorption was very rapid in the first 2 h, and decreased markedly afterwards. I. N. Jha *et al.* (Jha, 1989) has reported a similar initial rapid uptake of cadmium by chitosan particle. They have apotheosized that amino groups of chitosan act initially as cadmium coordination sites and the slower removal rate of metal after an initial rapid uptake can be due to the binding of cadmium by complexed metal ions. Based on the results shown in Fig 2, 4 h contact time ensures the attainment of equilibrium and was used for all further experiments.

Sorption isotherm of nickel using 5% CTS-silica cross-linked by 1.5% epoxy-chloropropane is similar to the Langmuir sorption isotherm. Data shown in Fig.3 were fitted to the linear form of the Langmuir equation:

$$\frac{[M]}{[AM]} = \frac{1}{b[AM]_{\max}} + \frac{[M]}{[AM]_{\max}}.$$

Where [M] and [AM] represent equilibrium concentration of nickel and the amount of absorbed nickel per unit weight of immobilized chitosan respectively; [AM]_{max} is the maximum amount of nickel sorbed per

unit weight of chitosan; and b is a measure of sorption capacity (L/mg). In this case, the linear form of langmuir equation can be expressed as:

$$\frac{[M]}{[AM]} = 0.0484 + 0.0015[M], \quad r^2 = 0.9451,$$

where $b = 0.0301$ L/mg and $[AM]_{\max} = 667$ mg/g which indicates that the absorbent has a considerable sorption capacity and can be a suitable absorbent for the removal of nickel from aqueous solution. On the other hand, the high quantity of absorbed metal show that the absorption cannot be just through coordination site based on stiochoimetry calculation. So, it is the obvious that mix absorption mechanism or different binding site must exist in chitosan resin.

2.3 Effect of pH

Fig.4 illustrates the effect of pH on nickel absorption. The results indicated that pH of the solution markedly affected the removal of nickel by CTS-silica absorbent. When the pH of solution was below 3, the removal of nickel was almost negligible. After that, the absorption capacity increased with an increase of pH, reached maximum point at pH 7, and decreased with the further increase of pH 7. This result differs from that of cadmium adsorbed by chitosan particle reported by I. N. Jha (Jha, 1989), in which only a slight increase in cadmium sorption amount with the increase of pH between 4 and 9. The discrepancy in results may be due to differences in metals and in absorbents.

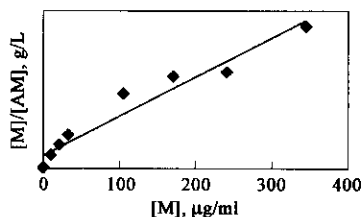


Fig.3 Absorption isotherm

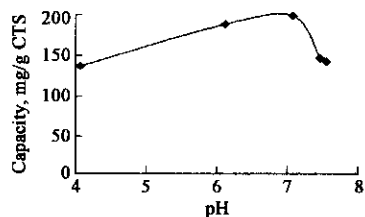


Fig.4 Effect of pH on absorption capacity

Nickel is presented essentially as hydrated Ni^{2+} in lower pH solution and as a monovalent cation, $Ni(OH)^+$, even as $Ni(OH)_2$ with the increase of pH. The distribution of these species is a function of pH. The decrease absorption capacity that observed above pH 7 could be due to the formation of more nickel hydroxyl complexes.

The amine nitrogen in chitosan has been suggested as the active or specific site for heavy metal ion coordination (Trezos, 1981). At lower pH, the metal ion coordinating with the amino group would have to compete with the H_3O^+ ions for active sites. The similar observations were reported by many scientists (Muzzarell, 1969; Trezos, 1983).

Based on observation above, the absorbent can efficiently remove nickel in wastewater with pH adjusted to near neutral pH and desorbs or regenerate at lower pH in preconcentration process.

2.4 Effect of ionic strength

Fig.5 shows the influence of ionic strength on absorption of nickel onto CTS-silica absorbent. The results indicate that there is no significant decrease in nickel uptake capacity. It cannot be explained by the ion-exchange mechanism, because absorption is sensitive to change of the ion strength if the electrostatic attraction as in the ion-exchange mechanism plays an important role. Trezos (Trezos, 1983) has proposed that uranium, thorium and other metal ions can be removed by chitin and chitosan mainly through coordination with amino groups. In this case the nickel binding through coordination force should be existed. Morris and Rees (Rees, 1982) proposed an "egg-box" model to explain the higher affinity of alginate polysaccharide for divalent metal resulting from array of affinity sites with cavities suitable for these metal. This mechanism may also exist in crosslinked chitosan.

2.5 Effect of calcium

Calcium, magnesium, potassium and sodium are common cations present in water, which may

interfere with nickel removal. Mozzarella and Tubertini (Mozzarella, 1969) have suggested that potassium, sodium, and magnesium are not detrimental for heavy metal removal by chitin. Fig.6 shows the effect of calcium on nickel absorption. The result indicated that the absorption quantity of nickel by CTS absorbent initially reduced with the increase of calcium ions, when the concentration of calcium ion reaches 100 $\mu\text{g/ml}$, the absorption capacity reduced insignificantly. It may suggest that nickel binding on non-specific site can be easily exchanged by calcium ion, but it does not seriously interference with the absorption of nickel on specific binding site. This result strongly confirms that at least two kinds of mechanism exist in nickel absorption process. It can be assumed that a portion of nickel ion, which can be easily desorbed, by calcium ion is caught in polysaccharide network, this mechanism is similar to the "egg-box" model proposed by Morris and Rees. This kind of binding site is not specific. The tightly binding nickel ion should coordinated with the amino group of chitosan, this portion of nickel can not be easily exchanged by calcium ion, because the affinity of amino group to calcium ion is much weaker than to nickel ion. So the amino group can be regarded as the specific binding site for heavy metal. As an adsorption material for heavy metal removal, the number of specific bind site determines the selectivity and enrichment efficiency of the absorbent.

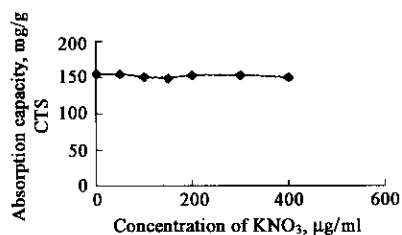
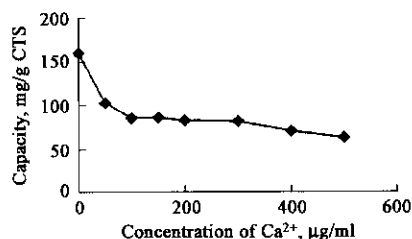


Fig.5 Effect of ion strength on absorption capacity

Fig.6 Effect of Ca²⁺ on absorption capacity

2.6 Column absorption, desorption and regeneration

Column absorption indicates that nickel adsorbed in column filled with CTS-silica absorbent, did not release with a considerable amount of distilled water, almost all of nickel desorbed from absorbent with 0.1 mol/L HCl. The observation suggests that protons effectively compete for the active sites (amino group) at low pH conditions and most of the absorbed nickel ions are binding with amino group since the process of surface complex is faster than the process of diffusion into network of polysaccharide. In column experiment, the absorption of metal ion requires a faster process. Nickel retaining on column can also be eluted by 0.1 mol/L EDTA solution. This can be explained by nickel coordinating with EDTA. The column can be recovered its absorption capacity by washing with 0.1 mol/L NaOH and distilled water.

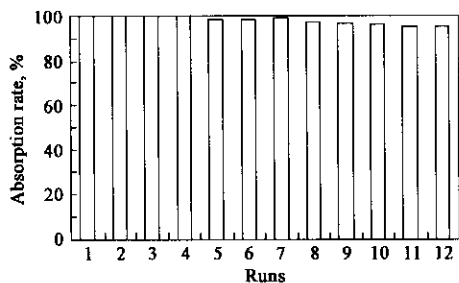


Fig.7 The absorption rates of nickel in a single column as a function of the number of adsorption-elution cycles

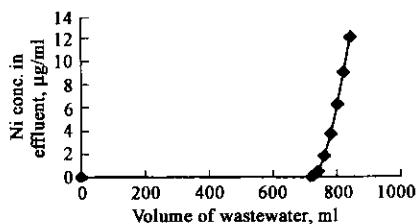


Fig.8 Breakthrough curve of wastewater in column experiment

The absorption column filled with regenerated CTS-silica absorbent can be reused. Fig.7 summarizes the results of regeneration and absorption rates of nickel adsorbed by CTS-silica absorbent. After twelve cycles, the absorption rate of nickel almost keeps 95% with 20 ml 100 $\mu\text{g/ml}$ nickel solution passing through the column every times. Nickel seems to desorb from CTS-silica absorbent efficiently with 0.1

mol/L HCl and the absorbent has a good regeneration capacity. I. N. Jha *et al.* (Jha, 1989) reported that using chitosan particle as the absorbent. After two cycles, the absorption rate of cadmium reduced to 81.3%. They suggested that the reduction in sorption resulted from the decrease in the weight of chitosan. The difference of the recovery between I. N. Jha's report and our results indicates the silica-based cross-linking chitosan can effectively prevent chitosan from dissolving in low pH solution.

2.7 Wastewater treatment

1 L of wastewater from electroplating industry that contains 25 mg/L nickels was fed into the column filled with 14.4 g of CTS-silica in which the percentage of immobilized chitosan account for 2.0% calculated by weight. In the initial 740 ml leakage, nickel was undetectable, and when 750 ml wastewater passthrough the column, the effluent concentration of nickel reach 1 $\mu\text{g/ml}$, after that nickel concentration in effluent increase sharply with the volume of wastewater passed. The breakthrough curve is shown in Fig. 8. According to this result, about 2.6 L wastewater with the nickel ion concentration of 25 mg/L could be treated by 1 g immobilized chitosan(Fig.8).

3 Conclusions

The present study on silica-based cross-linking chitosan(CTS-silica) as an absorbent indicates:

CTS-silica with easily shaping and high stable quality can be an efficient absorbent for the removal or collection of nickel from aqueous solutions.

At least two kinds of binding site exist in CTS-silica absorbent, one is the amino group, which is a specific site for heavy metal, and the absorption speed of this kind of binding site is fast. Another binding site is the polysaccharide network, which can catch divalent ion with a relative low speed and less selectivity.

The absorbent can be regenerated by acid treatment and reused. This kind of absorbent has a higher recovery rate and more durable than non-immobilized chitosan particle.

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