

Heavy Metal Ions Adsorption on Chitosan-Magnetite Microspheres

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Abstract – Composite chitosan-magnetite microparticles (Fe-Cc) were evaluated as a new adsorbent for cobalt and nickel ion separation from aqueous solutions. Sorption batch experiments were conducted for optimizing the pH, initial target ion concentration and adsorbent amount. The experimental data were fitted using Langmuir, Freundlich, and respectively Dubinin-Radushkevich isotherm models. The Langmuir model is the best fit. The material has a maximum adsorption capacity of 588.24 mg/g for cobalt ions and respectively 833.34 mg/g for nickel ions, superior to other magnetic chitosan adsorbents reported in the literature. Desorption and regeneration study revealed that the particles might be used up to three times without significant loss in adsorption capacity. Copyright © 2012 Praise Worthy Prize S.r.l. - All rights reserved.

Keywords: Chitosan-Magnetite Microspheres, Cobalt, Nickel, Adsorption, Regeneration

I. Introduction

Heavy metal ions such as cobalt and nickel are highly toxic for aquatic ecosystems even at low concentrations due to their non-biodegradability and to the tendency to produce severe illnesses upon accumulation in living organisms. Their removal from used industrial water before drainage is an important environmental concern. Current separation techniques include: biological treatments, membrane processes, chemical and electrochemical techniques and adsorption procedures [1]. Due to its high efficiency, adsorption is considered the most economic method in water decontamination treatment. Various types of materials have been used for cobalt and nickel sorption, such as zeolite [2], palygorskite [3], fruit peels [4], carbon nanotubes [5], [6], algal species [7], clinoptilolite [8], chelating resins [9] etc.

Recently, the application of biopolymers in solving environmental problems has received considerable attention. Natural polymers, especially polysaccharides that are readily available, inexpensive and biodegradable, possess numerous reactive groups able to participate in metal ion adsorption [10]. Typical examples of polymers used for this purpose are chitosan and alginate [11], [12], [13]. However, some disadvantages related to their poor chemical resistance and weak mechanical properties still limit large-scale industrial applications with efficient sorbent regeneration. An innovative technology that gains attention in resolving these issues is the use of particulate magnetic materials incorporated in natural polymeric matrices. This approach leads to good performance due to high specific surface area and to the possibility to remove the used adsorbent from the contaminated waste streams by an external magnetic field in order to regenerate it for subsequent reuse [14], [15].

Many articles that cover a various types of composite magnetic particles were reported in the literature. Ngomsik et al. [16] investigate the uptake of cobalt ions by magnetic alginate beads, Zhou et al. [17] reported thiourea- modified magnetic chitosan microspheres for the adsorption of nickel and recently, Monier et al. [18] and Chen et al. [19] studied the adsorption of cobalt and nickel ions from aqueous solutions onto modified magnetic chitosan chelating resin, and xanthate-modified magnetic chitosan, respectively.

Our group previously reported a method for obtaining chitosan-magnetite composite microspheres (Fe-Cc) using and in-situ procedure [20]. In this study we evaluate this material as a new adsorbent for cobalt and nickel ion separation from aqueous solutions.

II. Materials and Methods

Analytical grade chemicals were used throughout this study. Magnetic iron oxide/chitosan composite particles were synthesized in our laboratory and used as a new adsorbent material. Stock solutions containing Co^{2+} or Ni^{2+} ions were prepared by dissolving $\text{CoCl}_2 \times 6 \text{H}_2\text{O}$ or $\text{NiCl}_2 \times 6\text{H}_2\text{O}$ (Sigma Aldrich) in ultrapure water.

II.1. Preparation of Chitosan- Magnetite Composite Particles

Chitosan- magnetite microspheres were prepared by an in- situ procedure, as previously reported [19]. The magnetic material was produced by oxidation of ferrous ions incorporated in a chitosan-Fe(II) complex, using nitrate ions as a mild oxidizing agent, under alkaline conditions. The chitosan matrix was then crosslinked by addition of an aqueous glutaraldehyde solution under mechanical stirring. The cleaning procedure involved multiple aqueous washes and an acid-base treatment

followed by dialysis. The particles used in this study (batch denoted Fe-Cc) had an average diameter of 40 μm and a saturation magnetization of 24 emu/g (estimated magnetic material content of about 47% by weight).

II.2. Sorption Experiments

The adsorption of Co^{2+} and Ni^{2+} on chitosan-magnetite particles was investigated by using a batch method. In order to optimize the metal ion separation conditions, the effect of the most important process variables, namely: initial solution pH and target ion concentration and also the adsorbent dosage was studied. The experiments were carried out by mixing 10 ml of aqueous sorbent dispersion (containing 0.025- 0.15 g solid material) with 10 mL aliquot of metal ion solution, with initial concentration in the range of 0.92 to 4.64 mg/mL. The mixture was agitated for 24 h at 200 rpm in a temperature controlled orbital shaker (298.15 K) to reach adsorption equilibrium. The system was adjusted to the desired initial pH (in the range of 2.5-7.0) by adding small volumes of 0.1M HCl or NaOH solution. Following the adsorption procedure, the Fe-Cc material was separated by centrifugation and the residual concentration of the metal ions left in the supernatant phase was determined spectrophotometrically at 510 nm for the cobalt complex and respectively at 720 nm, for the nickel complex. UV- Vis spectroscopy was performed on a Perkin- Elmer Lambda 650 UV-VIS Spectrometer. The sorption process is described by the ion distribution coefficient, K_d (mL/g), calculated using Eq. (1):

$$K_d = \frac{(C_i - C_e)}{C_e} \times \frac{V}{m} \quad (1)$$

where C_i and C_e are the initial and respectively the equilibrium concentrations of the metal ion solution (mg/mL), V is the volume of aqueous phase (mL), m is the mass of solid sorbent (g).

The amount of adsorbed metal ion at equilibrium, q_e (mg/g) was calculated from the mass balance using equation Eq. (2):

$$q_e = \frac{(C_i - C_e)V}{m} \quad (2)$$

where all the symbols are the same as shown above.

II.3. Desorption and Regeneration Studies

To investigate the desorption ability of Co^{2+} or Ni^{2+} from Fe-Cc microspheres, desorption experiments were carried out as follows: after reaching the adsorption equilibrium using initial pH 5.5, sorbent mass of 0.1g and metal ion initial concentration of 3.4 mg/mL, the adsorbent was separated from the suspension and washed with ultrapure water to remove the un-adsorbed cobalt or nickel ions. The resulting magnetic composite bearing

complexed Co^{2+} or Ni^{2+} ions was left in contact with 0.1M EDTA solution for a period of 24 h.

The final concentration of metal ions released into the solution was determined by UV-Vis spectroscopy. The percentage of ions recovered by desorption from Fe-Cc material was calculated using the initially adsorbed metal ion amount and the final concentration found in the desorption medium, according to Eq. (3):

$$\text{Recovery (\%)} = \frac{(\text{metal}_{ads} - \text{metal}_{des})}{\text{metal}_{ads}} \times 100 \quad (3)$$

where metal_{ads} is the amount of adsorbed metal ions (mg/g), and metal_{des} is the amount of desorbed metal ion (mg/g)

III. Results and Discussions

III.1. Cobalt and Nickel Adsorption

Effect of pH

The values of distribution coefficient K_d as a function of pH, calculated with Eq. (1), for Co^{2+} and Ni^{2+} , were plotted in Fig. 1. The pH of the aqueous solution is an important parameter that influences both the availability of metal ions in solution and the number of binding sites on the adsorbent [21]. The pH values selected in the experiments were chosen to be lower than the precipitation limit for each metal ion (i.e. pH 6.0 for Co^{2+} and respectively 7.0 for Ni^{2+}). The effect of the initial pH upon the adsorption capacity of Fe-Cc composite was investigated in the pH range 2.5- 7.0 in a series of experiments in which the initial target ion concentration and the adsorbent amount were kept constant at 3.4 mg/mL and 0.1g, respectively.

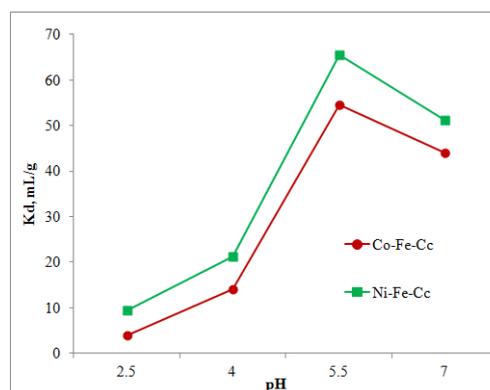


Fig. 1. Distribution coefficient for Co^{2+} and Ni^{2+} ion adsorption as function of pH

At low pH the protons compete with the metal ions for the binding sites located on amino groups belonging to chitosan. Sorbent protonation also causes an electrostatic repulsion effect. At higher pH, as the proton concentration decreases, more binding sites are available and the metal uptake is higher. The maximum adsorption occurred at pH=5.5 for both ions. The particles show higher affinity for Ni^{2+} than for Co^{2+} when the initial

concentration is the same. The result is in agreement with other published studies performed on chitosan composites [18].

Effect of sorbent mass

In the next series of experiments the amount of adsorbent was varied from 0.025 to 0.15 g while keeping the pH and the initial metal concentration constant at 5.5 and respectively at 3.4 mg/mL. The results presented in Fig. 2 show that the distribution coefficient increases when the sorbent amount is higher, up to 0.1g, due to a higher availability of active sites for the target ions. Beyond this value, the distribution coefficient decreases slightly for both ions due to the high solid content of the mixture (i.e. larger “m” in Eq.(1)).

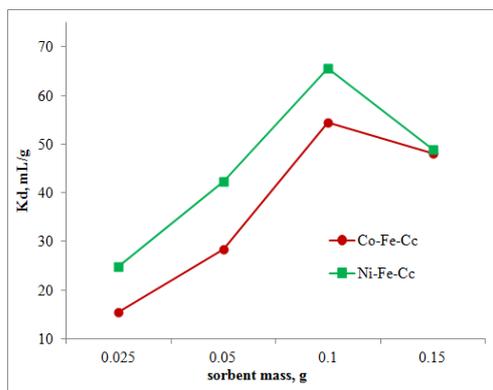


Fig. 2. Effect of sorbent mass on the distribution coefficient for Co^{2+} and Ni^{2+} ion adsorption on Fe-Cc material

Effect of initial metal ion concentration

The initial target ion concentration was varied in the range of 0.92- 4.64 mg/mL while keeping the pH and the sorbent mass constant at 5.5 and 0.1 g, respectively.

The distribution coefficient decreased with increasing initial concentration of both ions, as shown in Figure 3, until complete coverage of the binding sites of the sorbent has been reached. The data are further discussed in the “Adsorption isotherms” section.

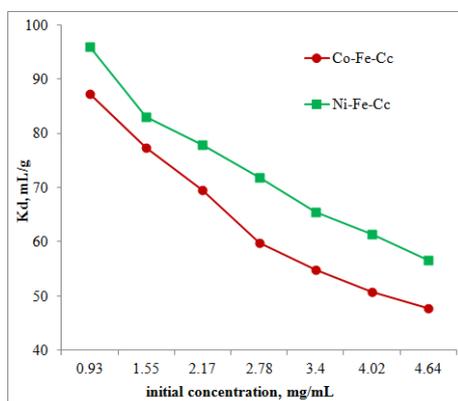


Fig. 3. Effect of initial ion concentration on the distribution coefficient for Co^{2+} and Ni^{2+} ion adsorption on Fe-Cc material

III.2. Adsorption Isotherms

The adsorption isotherms are used to characterize the interaction of Co^{2+} and Ni^{2+} ions with the adsorbent, by expressing the relation between the amount of metal ion uptake and metal ion concentration in solution at equilibrium. The experimental data collected at 281.15K and a sorbent mass of 0.1 g were fitted on the general models used in wastewater treatment applications: Langmuir, Freundlich, and respectively Dubinin-Radushkevich isotherm.

The simple Langmuir model is based on the assumption that the solid surface has a limited adsorption capacity that is energetically and sterically independent of the adsorbent quantity, valid for monolayer sorption [22]. The linearized expression of the Langmuir isotherm is shown in Eq. (4):

$$\frac{C_e}{q_e} = \frac{1}{K_L \times q_m} + \frac{C_e}{q_m} \quad (4)$$

where C_e is the solute equilibrium concentration in the liquid phase (mg/mL), q_e is the amount of solute adsorbed per mass of adsorbent (mg/g), q_m characterizes the saturated adsorption capacity (mg/g) and K_L is related to the affinity of the sorbate for the adsorbent (mL/g). This model reaches a plateau, a type “L” isotherm for both ions.

The Freundlich model for metal sorption is based on the relation between the adsorbed quantity and the solute concentration remained in the liquid phase [23], expressed in linearized form in equation (5):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

where K_F and $1/n$ are the Freundlich constants; K_F represents the relative sorption capacity, and $1/n$ characterizes the nature and the intensity of the sorption process and the distribution of active sites.

The linearized Dubinin- Radushkevich (D-R) equation [24] may be written as:

$$\ln q_e = \ln X_m - K_{DR} \mathcal{E}^2$$

where K_{DR} is a constant related to the adsorption energy (mol^2/kJ^2), X_m is a constant that indicates the sorption degree characterizing the sorbent (mg/g) and \mathcal{E} is the Polanyi potential shown in Eq. (6):

$$\mathcal{E}^2 = RT \ln (1 + 1/n) \quad (6)$$

where T is the absolute temperature (K) and R is the ideal gas constant ($R = 8.314 \text{ J/molK}$).

The free energy of adsorption E_S is calculated with the equation (7):

$$E_S = (-2K_{DR})^{-1/2} \quad (7)$$

The results revealed that the data for the adsorption of Co^{2+} and Ni^{2+} on the composite particles fitted better the Langmuir model (the correlation coefficient $R^2 > 0.99$) than the other two models. The Freundlich and D-R isotherms were applied in order to characterize the general adsorption mechanism. The calculated Langmuir, Freundlich and Dubinin-Radushkevich parameters that resulted from the data fitting are summarized in Table I. The maximum adsorption capacity of the Fe-Cc material was 588.24 mg/g for cobalt ions and respectively 833.34 mg/g for nickel ions, as obtained from the Langmuir plots. The new material showed higher adsorption capacity than other sorbents containing magnetite and chitosan that were previously described in the literature [12], [18], [23].

Bayramoglu et al. [25] expressed an equilibrium parameter, R_L (Eq. (8)), obtained from the Langmuir isotherm that is used for predicting whether an adsorption system is favorable or not:

$$R_L = \frac{1}{1 + K_L C_i} \quad (8)$$

The value of R_L indicates the shape of isotherm to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). In this study, of cobalt and nickel sorption onto the Fe-Cc microspheres, the R_L values, listed in Table I, are in the range of 0-1 (when using an initial ion concentration of 3.4 mg/mL). These results confirmed the favorable nature of the composite for the adsorption of heavy metal ions from aqueous solutions. The suitability of Langmuir model shows that the sorption mechanism is monolayered and that the material has a constant adsorption capacity.

The values of the n ($n > 1$) parameter in the Freundlich model vary with the degree of heterogeneity, indicating that Co^{2+} and Ni^{2+} ions are favorably adsorbed on the Fe-Cc material. The n values in this study were in the range 10-13, corresponding to a high adsorption intensity.

The Freundlich and D-R constants obtained for cobalt and nickel are similar in value (K_F is 56.89 for cobalt and respectively 59.5 for nickel; X_m is 57.16 for cobalt and respectively 59.5 for nickel), results that are in agreement with our previous study of thorium and uranyl ions sorption onto the same material [26].

TABLE I
CONSTANTS OBTAINED FROM THE LANGMUIR, FREUNDLICH AND DUBININ-RADUSHKEVICH SORPTION ISOTHERMS

Metal ion		Co^{2+}	Ni^{2+}
Langmuir constants	R^2	0.9952	0.9958
	q_m , (mg/g)	588.24	833.34
	K_L (mL/mg)	0.175	0.127
	R_L	0.63	0.7
Freundlich constants	R^2	0.9207	0.9236
	K_F	56.89	59.5
	n	12.85	11.82
Dubinin-Radushkevich constants	R^2	0.9165	0.9236
	X_m (mg/g)	57.16	59.5
	K_{DR}	0.178	0.195

The mean adsorption energy E_S calculated from the D-R isotherm is helpful in predicting the nature of the adsorption process: physical (when E_S values are in the range of 1-8 kJ/mol) or chemical (when E_S values are higher than 8 kJ/mol) [27].

The calculated data indicate a physical sorption mechanism for both ions. Moreover, the magnitude of E_S (kJ/mol) in the D-R models is characterizing the adsorption type.

The positive values obtained for this system (1.67 kJ/mol and 1.6 kJ/mol, respectively) indicate that adsorption is endothermic in nature.

III.3. Regeneration and Reuse Studies

The regeneration ability of the material during adsorption/desorption cycles is an important factor in designing large-scale applications. A 0.1 M EDTA solution was used as an elution agent for the desorption of cobalt and nickel ions from the used Fe-Cc sorbent. More than 90% desorption efficiency was achieved within 24 h as shown in Table II.

The material was tested in three cycles of sorption/desorption and it demonstrated reproducible performance.

TABLE II
DESORPTION RESULTS ON MAGNETIC CHITOSAN COMPOSITE PARTICLES LOADED WITH METAL IONS

Radioactive ion	Desorption in 0.1 M EDTA solution, %
Co^{2+}	94.24
Ni^{2+}	95.84

IV. Conclusion

In this study, the performance of composite chitosan-magnetite microparticles for the removal of Co^{2+} and Ni^{2+} ions in aqueous solution has been evaluated. It has been demonstrated that these metal ions can be effectively removed by using relatively small amounts of particles due to their large surface area and presence of functional groups.

The parameters for the adsorption procedure were optimized: initial solution pH (5.5) and target ion concentration (3.4 mg/mL) and sorbent mass (0.1g). The experimental data were fitted using isotherm models, Langmuir, Freundlich and Dubinin-Radushkevich. The data showed that the Fe-Cc material adsorption capacity was 588.24 mg/g for cobalt and 833.34 mg/g for nickel ions. The material has higher affinity for the nickel ions. Regeneration study demonstrated that Fe-Cc particles might be reused up to three times without significant loss in adsorption capacity.

Acknowledgements

This work was supported by CNCSIS - UEFISCDI, project number PNII-IDEI code 314/2008 (contract 660/2009).

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