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ADSORPTION STUDIES FOR Cr(VI) ONTO MAGNETIC PARTICLES COVERED WITH CHITOSAN

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ABSTRACT

The magnetic carrier, called magnetic biosorbent, was prepared using magnetite nanoparticles and a biopolymer from the chitin of exoskeletons of marine invertebrates, the chitosan. Experiments of adsorption in batch systems were carried out to investigate the removal of Cr(VI) ions from pH 3 solution using this magnetic biosorbent. Radioisotope Cr-51 was used as the radioactive tracer to mark the Cr in solution, so the concentrations of Cr(VI) ions were determined by gamma spectrometry with a NaI(Tl) detector. Dosage of magnetic biosorbent was studied in the adsorption of chromium ions from dilute metal ion solutions. The removal efficiency obtained was 97% at a dosage of 50 g L^{-1}. Freundlich and Langmuir isotherm models were used to evaluate the data of equilibrium isotherm in the range of Cr(VI) concentration from 50 mg L^{-1} to 1200 mg L^{-1}. The Langmuir model was found to best represent the equilibrium isotherm. Recovery of the Cr(VI) ions from loaded magnetic biosorbent was possible by desorption process using a NaOH solution of pH 10. The results demonstrated that the magnetic biosorbent is effective for the removal of hexavalent Cr ion from solutions by sorption process and the recovery by desorption process is possible. The suspended particles of the magnetic biosorbent exhibited a strong magnetization in the presence of a magnetic field, and being easily attracted and removed from aqueous solutions using a magnet, so indicating the application viability in magnetic separation process.

1. INTRODUCTION

Presence of heavy metals on concentrations of pollutants in the ecosystems is one of the most common environmental contamination problems. Industrial and mining waste waters are the major sources of pollution by heavy metals. Waste water containing Cr is of considerable concern regarding the potentially hazardous to human health. Of its two oxidation states, Cr(III) and Cr(VI), the hexavalent form is highly toxic and considered to be serious environmental pollutant because of its carcinogenic property [1]. Generally, Cr(VI) is produced from anthropogenic sources and therefore their waste water must be treated prior to discharge into natural water bodies.

Nowadays, an integrated process which couples magnetic separation together with adsorption is been considered as an alternative technology in industrial waste water treatments [2,3,4]. This technology uses magnetic carriers that combine separation by sorption and magnetic recovery into a simple and compact process. Also called of magnetic adsorbent provides a simple way to remove contaminants from solutions under a wide range of chemical conditions. The effectiveness of the process has been demonstrated at bench scale for uranium, americium, and plutonium at Argonne National Laboratory [5].

Magnetic adsorbents are composed of a magnetic core coated with a material containing functional groups. Due to magnetic core, these adsorbents respond to magnetic field, being easily attracted by a magnet but do not become magnetized. The functional groups have the capability to bind either by chemical or physical adsorption or both to molecules and metal ions of pollutants, removing from effluents. Then, after adsorption of pollutants by magnetic adsorbent, a rapid and efficient removal of pollutants loaded-magnetic adsorbent from waste water is achieved by application of an external magnetic field. With removal of the magnetic field, the magnetic adsorbents do not form magnetically induced aggregation, and may be resuspended in another aqueous system. The pollutants loading can be removed from adsorbent by using a desorbent solution. The magnetic carriers are then regenerated and can be reused.

The objective of the present work was to present some results concerning the adsorption of Cr(VI) from aqueous solutions using a magnetic adsorbent prepared with nanoparticles of magnetite and chitosan. In the work, this magnetic adsorbent was called magnetic biosorbent because it is derived from a natural biopolymer.

The chitosan is derived from the deacetylation of chitin. Chitin is a biopolymer widely distributed in nature, especially in marine invertebrates and insects. However, chitosan is only manufactured from crustaceans, as crab, krill and crayfish, primarily because a large amount these materials is available as a byproduct of food processing. Chitosan is a biodegradable cationic polymer, and has been reported to have high potential for adsorption of metal ions [6]. The Cr(VI) ions, as $Cr_2O_7^{2-}$ species, can bind to amine groups of the chitosan by adsorption, and can be removed from effluent. Due to the presence of magnetite, the loaded magnetic biosorbent containing the Cr ions can be recovered from effluent by application of an external magnetic field.

2. EXPERIMENTAL

2.1. Magnetic Biosorbent

Magnetite particles were prepared in our laboratory according to the reference 3. One gram of magnetite powder was added into 5 mL of chitosan 10 g L^{-1} in acetic acid solution. The mixture was homogenized under magnetic stirring. Afterwards, to form the coating layer of chitosan on the surface of magnetite particles, droplets of NaOH solution were mixed and stirred. The product was filtered, washed extensively with distilled water until nearly neutral pH, and dried at room temperature. Magnetic biosorbent was obtained and exhibited superparamagnetic behavior [3], was stored, and used in the adsorption experiments. All reagents were purchased from Merck.

2.2. Adsorption of Chromium Ions

The Cr(VI) solutions were prepared by dissolving a known amount of potassium dichromate in distilled water. The chromium concentration was varied from 10 to 1200 mg L^{-1}. Radioisotope Cr-51 was added into the each solution, as the radioactive tracer, to mark the chromium in solution so the dichromate concentrations were determined by counting gamma of ^{51}Cr conducted with a NaI (Tl) scintillation counter.

The adsorption experiments were carried out in tubes of 10 mL. Fifty milligrams of magnetic biosorbent were contacted with 1.0 mL of Cr solution containing ^{51}Cr tracer under shaking for 40 min at room temperature. The time of 40 min required to reach equilibrium was determined in another work as described previously [7]. Afterwards, a permanent magnet was placed at the bottom of the tube, and magnetic separation was carried out. The ^{51}Cr counting of the supernatant was made. Because of its high sensitivity, the radioactive tracer method has been applied successfully in this work, and it has provided analysis of a large number of samples in a relatively short time period.

The removal percentage (% removal) was monitored by analyzing the equilibrium metal concentrations after shaking the magnetic adsorbent particles and the metal solution. The % removal was calculated from Eq. (1). All results represent measurements with an estimated standard deviation of about 3%.

$$\%\ \text{removal} = (C_i - C_f)/\ C_i * 100 \quad . \qquad (1)$$

where C_i and C_f are the initial and final Cr concentrations (mg L^{-1}) in the aqueous phase, before and after the contact of the aqueous phase with the biosorbent phase, respectively.

2.3. Desorption of Cr from Magnetic Biosorbent

After the Cr adsorption process, for the subsequent assay of desorption, the Cr loaded-magnetic biosorbent was rinsed with a small amount of water to remove the Cr ion contained in the intra-particle liquid. It was resuspended in 1.0 mL of distilled water by removal of the magnet, and was separated from water by magnetic separation. One milliliter of NaOH solution, pH 10, was then added into the magnetic biosorbent for the desorption. The solution was shaken for 40 min, and the Cr concentration of the supernatant was determined by gamma counting. The desorption process was repeated twice more. The Cr from the supernatant of the 3 separations were combined and used for the determination of the recovered amount. Amount of Cr desorbed was defined by the following Eq. 2:

$$\%\ \text{desorbed} = Cr_{des} * V_{des}/Cr_{ads} * 100 \quad . \qquad (2)$$

where Cr_{ads} is the Cr mass (mg) adsorbed in the magnetic biosorbent, Cr_{des} is the Cr concentration (mg L^{-1}) in the desorbent phase at equilibrium, and V_{des} is the volume (L) of desorbent.

3. RESULTS AND DISCUSSION

3.1. Influence of Biosorbent Dosage

The influence of the biosorbent dosage on the removal efficiency of Cr(VI) was studied with a Cr solution 13 mg L^{-1}, at pH 3. The results are shown in Fig. 1. As it is seen from these data, in the studied range, chromium ion uptake increased rapidly with the increasing biosorbent dosage up to a dose of 10 g L^{-1}. This behavior is attributed to the increase of functional groups concentration of surface with the increase the dose. But after this dose, chromium adsorption increased slightly. The efficiency of removal increases gradually, from 80 to 90%, in the biosorbent dosage above 15 g L^{-1} to 50 g L^{-1}. The high dosages affected the adsorption capacity of magnetic biosorbent. This behavior was related to the specific surface area of adsorbent. High dosage increases the concentration of adsorbent, however, reduces the specific surface area of the total amount of adsorbent.

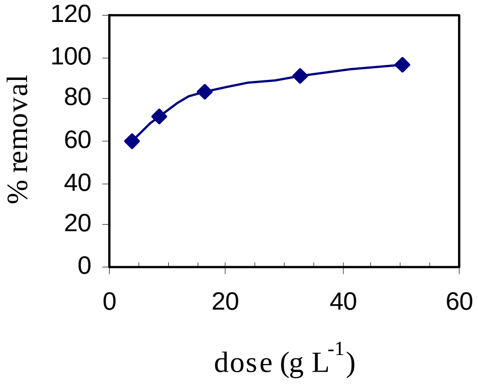

Figure 1. Influence of the magnetic biosorbent dose on Cr removal.

3.2. Adsoption Isotherm

For determining the sorption capacity of the magnetic biosorbent for Cr(VI), it is necessary to obtain the equilibrium adsorption data at various Cr concentration values. For this purpose 50-1200 mg L^{-1} of Cr(VI) solutions, pH 3, were contacted with 4 g L^{-1} of magnetic biosorbent. These data were evaluated by Langmuir and Freundlich adsorption isotherms equations, two isotherm models usually used to interpret the efficiency of metal biosorption [8]. Langmuir isotherm assumes monolayer adsorption, and is presented by the Eq. 3 and 4.

$$\text{Langmuir model in nonlinear form } q_{eq} = Q_{max} * K_L * C_{eq}/(1+K_L * C_{eq}) \qquad (3)$$

$$\text{Langmuir model in linear form } C_{eq}/q_{eq} = 1/(Q_{max} * K_L) + 1/\,Q_{max} * C_{eq} \qquad (4)$$

Where q_{eq} is the amount adsorbed (mg g^{-1}), C_{eq} is the equilibrium concentration of solute in the solution (mg L^{-1}), Q_{max} is the maximum adsorption capacity (mg g^{-1}), and K_L is the constant related to the free energy of adsorption.

The Freundlich model is presented by the Eq. 5 and 6.

$$\text{Freundlich model in nonlinear form } q_{eq} = K_F * C_{eq}^{\ 1/n} \tag{5}$$

$$\text{Freundlich model in linear form } \log q_{eq} = \log K_F + 1/n * \log C_{eq} \tag{6}$$

where C_{eq} is the equilibrium concentration (mg L^{-1}), q_{eq} is the amount adsorbed (mg g^{-1}), K_F is a parameter of relative adsorption capacity of the adsorbent related to the temperature and *n* is a characteristic constant for the adsorption system.

The linearized Langmuir and Freundlich isotherms obtained for Cr(VI) are, respectively, shown in Fig. 2 and 3, and their corresponding parameter values are presented in Table 1. The values of the correlation coefficient r^2 demonstrate that experimental data may be perfectly fit by both models. The correlation coefficient for Freundlich was 0.981. This shows that adsorption of Cr ions onto biosorbent approximates to a Freundlich model. In contract, the correlation coefficient for the Langmuir model was 0.997. This indicates the adsorption system was best described by this model.

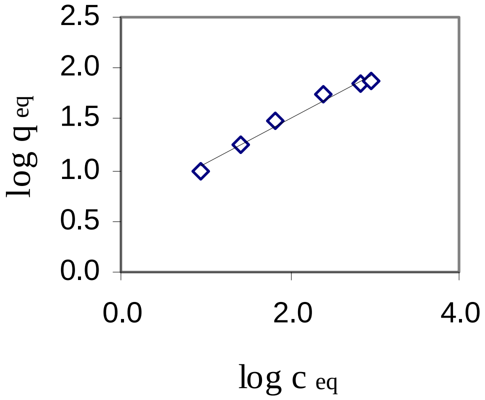

Figure 2. Linearized Freundlich isotherm.

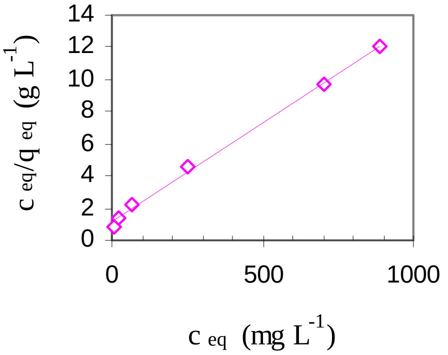

Figure 3. Linearized Langmuir isotherm.

Table 1. Parameter values of the Langmuir and Freundlich isotherms for the Cr(VI) ions by magnetic biosorbent.

Isotherm model	Q_{max} (mg g^{-1})	K_L (L mg^{-1})	1/n	K_F	r^2
Langmuir	81	0.011	-----	-----	0.997
Freundlich	-----	------	0.436	4.307	0.981

Fig. 4 compares the predicted data by the Langmuir and Freundlich models for system with the experimental data. It is clear from this figure that the Freundlich model fitted the experimental data reasonably well, and the Langmuir fitted best, being very close to experimental isotherm data corroborating with the value of r^2 of the Langmuir higher than of the Freundlich models. The figure shows that the adsorption capacity increases with an increase in equilibrium concentration and ultimately attains a saturated value, and the maximum Cr adsorption capacity of the biosorbent was obtained to be 81 mg Cr per g of dry biosorbent.

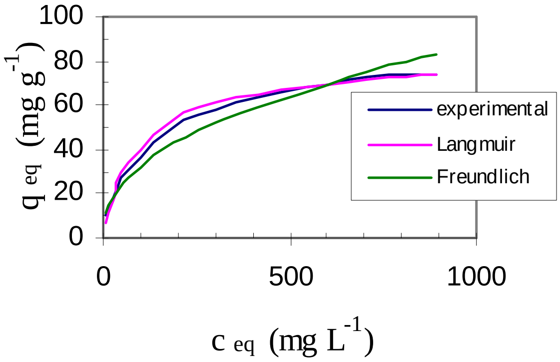

Figure 4. Comparison between experimental data of the Adsorption Isotherm of Cr(VI) by magnetic biosorbent and different isotherm models.

3.3 Desorption of Cr(VI) from Magnetic Biosorbent

For the development of an effluent treatment complete system using adsorbent is important to also evaluate the desorption efficiency of the metal-loaded adsorbent. The desorption of Cr ion from magnetic biosorbent was investigated with NaOH solution as the desorbent.

For desorption experiments, different dosages of Cr-loaded magnetic biosorbent were used. The recovered amount by desorption is the Cr(VI) accumulated in the 3 desorption assays as previously described. The relationship between desorption and dose is shown in Fig. 5, and as it can be seen, an interesting result was obtained. It depicts a lower percent desorbed in the low dose range. Percent desorption increased rapidly with the increase in dose up to 10 g L^{-1}. At higher dose range from 15 g L^{-1} to 50 g L^{-1}, the desorption increased at a slower rate reaching an equilibrium in about 93%. This curve shows a behavior similar to the removal of Cr with the increase of dose. From this result, NaOH solution was found to be effective for desorption of Cr ion from magnetic biosorbent when the dosage is higher than 50 g L^{-1}.

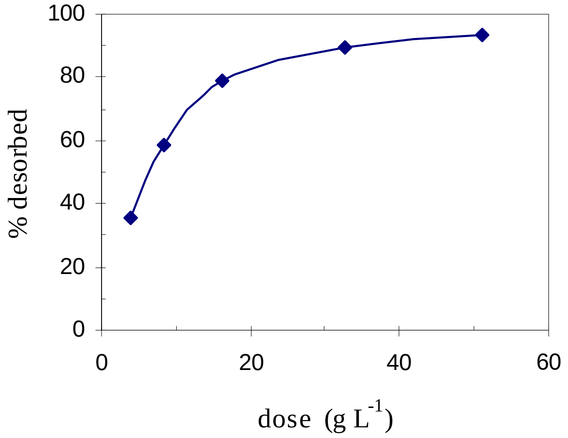

Figure 5. Desorption behavior of Cr(VI) from the magnetic biosorbent using NaOH solution, pH 10.

4. CONCLUSIONS

Magnetic biosorbent composed of nanoparticles of magnetite covered with chitosan was prepared and investigated for Cr removal as an economically feasible alternative adsorbent of metal contaminants from industrial effluents. It possesses functional groups to which ions can bind by adsorption process and it is environmentally safe. The use of magnetic biosorbent based on the magnetite nanoparticles conjugated with chitosan to treat industrial effluents is to deal with a sustainable technology.

From diluted solution of about 13 mg L^{-1}, pH 3, it was possible to remove 90% of Cr(VI) on 50 g L^{-1} of magnetic biosorbent. The desorption of Cr ion from loaded magnetic biosorbent was easily carried out with NaOH solution , pH 10, as the desorbent. With three batch assays, about 93% of Cr was recovered from the magnetic biosorbent. Freundlich and Langmuir isotherms show very good fit with the experimental adsorption equilibrium data for Cr. The

Langmuir isotherm model appears to fit the isotherm data better than Freundlich model, and the maximum chromium adsorption capacity of the magnetic biosorbent was obtained to be 81 mg Cr per g of dry biosorbent. The results demonstrated that the magnetic biosorbent is effective for the removal of hexavalent Cr ion by sorption process. The suspended particles of the magnetic biosorbent exhibited a strong magnetization in the presence of a magnetic field, being easily attracted and removed from aqueous solutions using a magnet, so indicating the possibility of application in magnetic separation process. Furthermore, the magnetic biosorbent is environmentally safe and inexpensive. For industrial application, further studies including influence of others metals and column test would be necessary.

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