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CHITOSAN-COATED MAGNETITE NANOPARTICLES AS ADSORBENT FOR THE REMOVAL OF MOLYBDENUM IONS

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ABSTRACT

Metal ions in wastewater, even at low concentrations, affect a large number of organisms due to their high degree of toxicity. Research has developed some alternative methods for metal removal from the wastewater, as adsorption using a biosorbent of combined chitosan with magnetic particles. Chitosan is a natural biopolymer, which has a highly reactive active sites in its structure, composed of amino and hydroxyl groups with affinity to bind to metal ions. In this study, magnetic nanoparticles of coated magnetite with chitosan as an adsorbent of molybdenum(VI) ions in aqueous medium was investigated. The adsorption experiments were performed varying the time contact from 5 to 150 min, the pH from 0.5 to 11 and the molybdenum concentrations in nitric solutions. All molybdenum analyses were carried out by gamma spectroscopy using a HpGe detector and ^{99}Mo as radioactive tracer. Results showed that the chitosan-coated magnetite particles are good adsorbent for Mo ions from aqueous medium in the range of pH from 0.5 to 9 with a removal higher than 99%. Among the studied isotherm models, the Freundlich model fitted best the equilibrium adsorption isotherm of Mo(VI) ions.

1. INTRODUCTION

In recent years, discussions related to the environmental issues have been intensified in order to reduce caused impacts on the biosphere by industrial wastes. In this sense, the removal of metal ions from the wastewater has attracted special attention because, even at low concentrations, metals affect a large number of organisms due to their high degree of toxicity.

Due to the rapid industrial development, large amounts of high levels of heavy metals, including molybdenum, are discharged to the environment without an adequate treatment [1]. The released high concentrations in soils, sediments, sludges and waters, either through natural sources or by the environmental pollution, result in a disastrous impact on the environment, causing damage in the short term to humans and to animals. Also, the metals can stay too long in nature due to its low degradability, entering the food chain through plant uptake, direct soil ingestion by animals or by water [2, 3].

Molybdenum is used in metallurgical applications. The adding of molybdenum in the metallic alloys increases the strength and heat resistance and reduces the potential for corrosion of the alloy. Leguminous plant fertilizers contain in their composition approximately 2 to 6 ppm of molybdenum [4]. Molybdenum can be found in oxidation states II, III, IV, V and VI where the molybdenum (V) and molybdenum (VI) are predominants [5].

In animals and humans, the poisoning by molybdenum can lead to a series of adverse effects such as severe gastrointestinal irritation, diarrhea, coma in ruminants, death from heart failure, deformed bones, and disturbances in the metabolism of fats and proteins [3].

It is an essential micronutrient that occurs in trace levels in almost all living organisms, with relativity low toxicity, and is acts in several enzyme activities as well as in the nitrogen cycle.

Thus, there is a need for routine monitoring and control of exposure levels of toxic metals in biological and environmental samples, and the development of appropriate techniques for removing of metals [6].

Moreover, from an economic standpoint, molybdenum is a precious metal used in many technological applications, and his recovery from wastewater is becoming more attractive than the disposal as waste [7].

The classical treatment of wastewater containing metals involves chemical and physical processes of precipitation followed by sedimentation and filtration, ion exchange and electrochemistry. However, these traditional techniques are inadequate for the decontamination of large volumes of wastewater containing metals in low concentrations due to low operational efficiency and high costs. Alternative methods are being studied, such as electrodialysis, reverse osmosis, ultrafiltration and adsorption by biosorbent, for example chitosan. The adsorption process has some advantages over other methodologies: the low generation of secundary waste, the easy recovery of metals and reuse of the adsorbent [8]. Research in all world has developed some alternative methods for metal removal by adsorption using a biosorbent of combined chitosan with magnetic nanoparticles.

Chitosan is a natural biopolymer, which has extremely reactive active sites in its structure, composed of amino and hydroxyl groups with affinity to bind to metal ions [9]. In this study, magnetic nanoparticles of coated magnetite with chitosan as an adsorbent of molybdenum(VI) ions in aqueous medium was investigated.

2. EXPERIMENTAL

2.1. Reagents

Chitosan flakes and nitric acid (HNO_3) both purchased from Sigma-Aldrich; ferric chloride hexahydrate, ($FeCl_3.6H_2O$), ferrous chloride tetrahydrate ($FeCl_2.4H_2O$), sodium hydroxide (NaOH) and, acetone, all purchased from Merck; sodium molybdate dihydrate ($Na_2MoO_4.2H_2O$) from Fluka; acetic acid from Baker.

Molybdenum(VI) stock solution was prepared by dissolving $Na_2MoO_4 .2H_2O$ in distilled water. Various Mo solutions of different pH and different concentrations were prepared by the dilution from the Mo stock solution. An aliquot of Mo-99 tracer was added into each Mo solution. ^{99}Mo radioactive tracer provided by the Center of Radiopharmacy – CR/IPEN/CNEN.

2.2. Equipament

The activity measurements of the ^{99}Mo were obtained using a Hyperpure Germanium detector (HPGe), Canberra (model 747), at the Center of Radiopharmacy – CR/IPEN/CNEN.

2.3. Preparation of the Particles of Magnetite-Chitosan as Magnetic Adsorbent

The $FeCl_3.6H_2O$ and $FeCl_2.4\ H_2O$ were separately dissolved in distilled water, and then mixed in a beaker. Into that beaker, a solution of 5 mol.L^{-1} NaOH was added causing the simultaneous precipitation of Fe^{2+} and Fe^{3+} ions forming the magnetic particles of magnetite.

Chitosan flakes were dissolved in 2% acetic acid resulting in the solution of chitosan. The coating of magnetite particles was obtained by the addition the solution of magnetic particles on the solution of chitosan. The polymer was solidified by adding 5 mol.L^{-1} NaOH into the solution. All these steps were performed under constant stirring. The magnetic particles/chitosan were washed, first with distilled water to remove the dispersed material in the medium, and then with acetone to accelerate the drying process and obtaining of magnetic particles coated in dehydrated form (PMQd).

2.4. Adsorption Test

The solution of radioactivity labeled molybdenum (rMo) was placed in contact with the adsorbent (PMQd), previously weighed in glass vial, and under constant stirring. The proportion rMo/PMQd in each flask was 1000 µL/50 mg. The tests were performed according to the Table 1.

Table 1. Variables used in the study of Mo adsorption on the PMQd.

pH of the Mo(VI) solution	contact time (min)	Mo(VI) (mg.mL^{-1})
0.5; 1; 3; 5; 8; 9;10 e 11	5; 10, 20; 40; 60; 90;120; 150	10; 50; 100; 200; 300; 400; 500; 600; 1000; 2000; 3000

After completing the contact time (rMo/PMQd), the material was subjected to magnetic separation by placing the vial on a magnet. The rMo/PMQd was retained in the bottom of the vial due to the action of the magnetic field. Then, an aliquot of 500 µL of supernatant was transferred into another flask. The supernatant aliquot and 500 µL of initial solution were subjected to the activity measurements. The vials containing the samples were placed in the lower part of an acrylic shelf positioned in the center of the detector. The counted energy was at 740 kev. The counting time for each sample was 180 min.These measurements were related to the Mo concentrations. All tests of each variable were carried out in duplicate.

2.5. Adsorption Behaviour

The adsorption behaviour was investigated by the values of adsorbed percentage (eq.1), and the equilibrium adsorption isotherm was evaluated by the models of Langmuir and Freundlich (eq. 2 and 3).

$$\textbf{adsorbed (\%)} = \frac{C_0 - C}{C_0} * 100 \quad \text{(1)}$$

C_o ($mg.L^{-1}$) e **C ($mg.g^{-1}$)** = Mo concentrations in the aqueous phase before and after contact with the adsorbent

$$C_{eq}/q_{eq} = \frac{1}{Q*K_L} + \frac{C_{eq}}{Q} \text{ (linear)} \quad \text{(2)}$$

C_{eq} = Mo concentration in the supernatant **($mg.L^{-1}$)**
q_{eq} = adsorbed quantity **($mg.g^{-1}$)**
Q_{max} = constant related to maximum adsorption capacity **($mg.g^{-1}$)**
K_L = Langmuir constant related to adsorption energy **($L.mg^{-1}$)**

$$\text{Log } q_{eq} = \text{Log } K_F + 1/n \log C_{eq} \quad \text{(linear)} \quad \text{(3)}$$

K_F = Freundlich constant **[($mg.g^{-1}$) * ($L.mg^{-1}$)]**
1/n = related to the intensity of adsorption

3. RESULTS AND DISCUSSION

3.1. Influence of pH

As can be seen in Fig. 1 the Mo adsorption is higher than 99% in range of pH from 0.5 to 9. In pH >9, the adsorbed quantity decreased fast to close zero at pH 11.

This result shows that chitosan has a high rate of Mo ions adsorption from the nitric medium to pH equal 9 of the basic medium. It is important to observe that an acid medium very concentrated of H^+ ions can dissolve the chitosan coating as well as the magnetite particles.

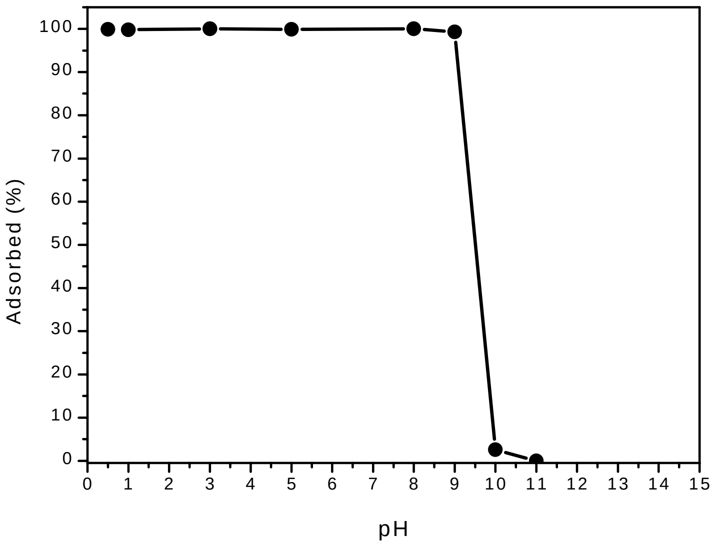

Figure 1. Adsorption behaviour of Mo(VI) ions on the chitosan-coated magnetic particles in the range from pH 0.5 to 11.

3.2. Equilibration Time

It is observed in Fig.2 that the removal of Mo ions increased rapidly with the increasing of the contact time until 90 min. After 90 min, the adsorbed quantity of Mo became constant, which suggests that the equilibrium time was reached.

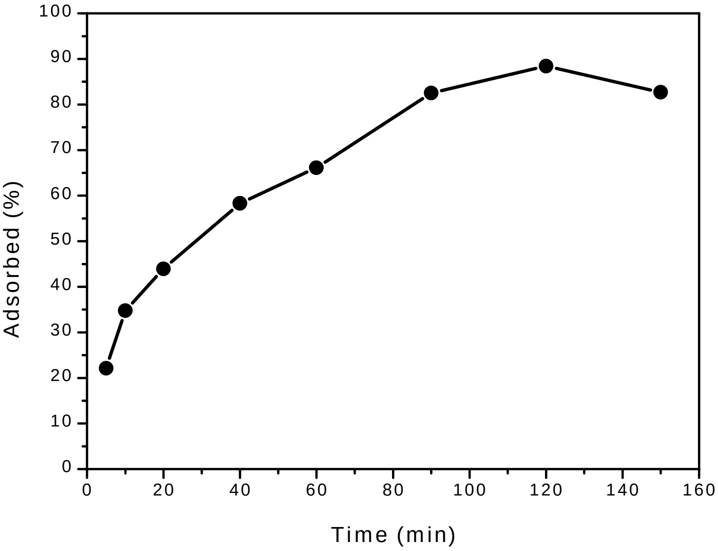

Figure 2. Removal of Mo(VI) ions as a function of contact time, pH=5.

3.3. Adsorption Isotherm

The 3.3. adsorption isotherm of Mo (VI) ions on the PMQd was obtained in the range from 10 mg.L^{-1} to 3000 mg.L^{-1} at pH 1, where the mass of adsorbent was 50 mg, and the contact time was 120 min. The equilibrium adsorption isotherm was obtained by plotting the quantity of Mo (VI) adsorbed (Q_{eq}) on the PMQd against the equilibrium concentration (C_{eq}) in the solution, as shown in Fig. 3. This result showed that the adsorption increased rapidly with the increasing of the Mo concentration in the solution, and the saturation of the chitosan coating did not occurred in the investigated concentration range.

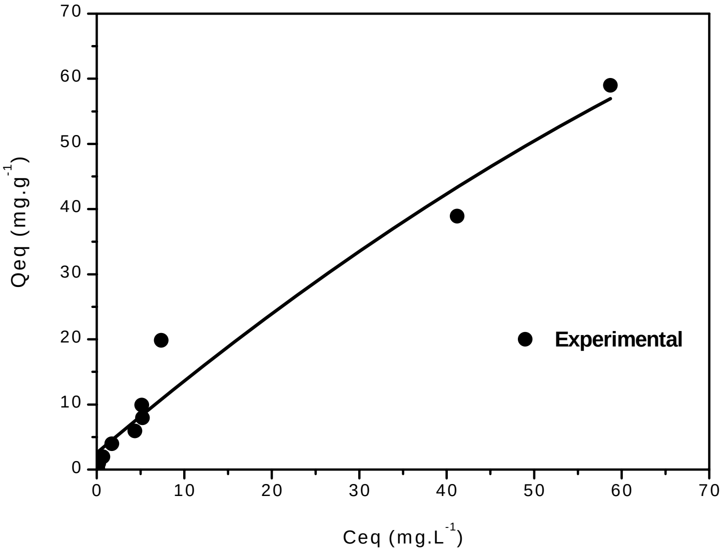

Figure 3. Adsorption equilibrium isotherm of the Mo (VI) on the PMQd from the nitric solution, pH 1.

These data were evaluated using Langmuir and Freundlich model linear equations, respectively, shown in Fig. 4 and 5, and the parameter values were calculated and are presented in Table 2. The models were able to fit the equilibrium data obtained experimentally, getting through the adjustment parameters of adsorption, as shown in Fig.6.

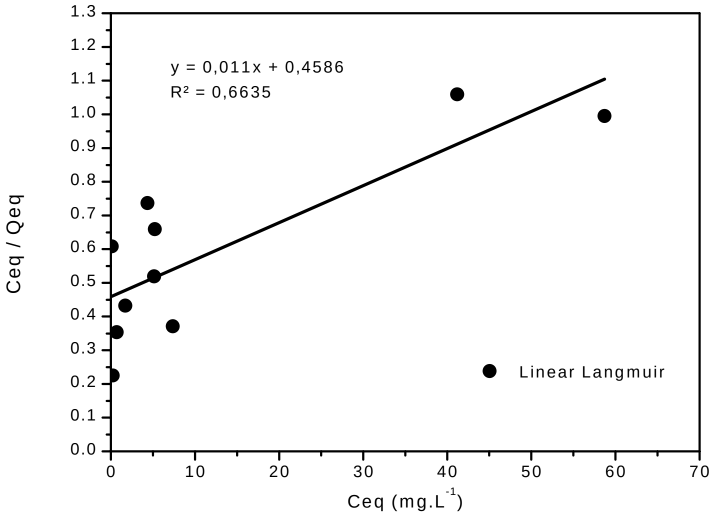

Figure 4 - Langmuir linear isotherm for the adsorption of Mo(VI) ions on the PMQd.

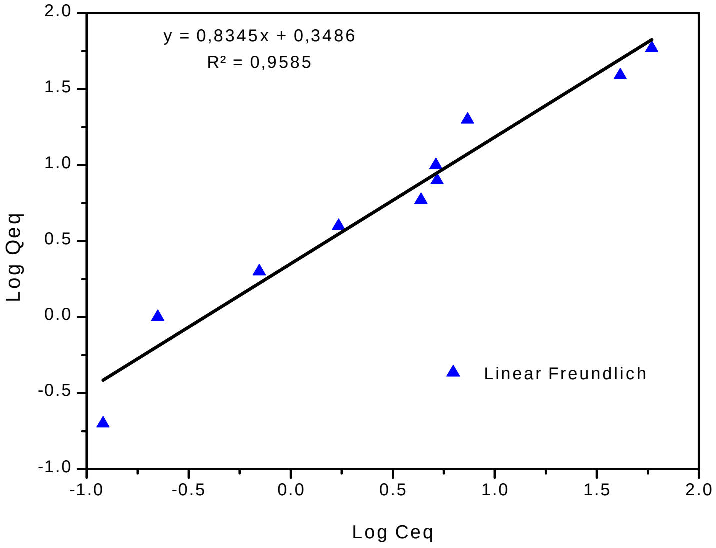

Figure 5. Freundlich Linear isotherm for the adsorption of Mo(VI) ions on the Mo PMQd.

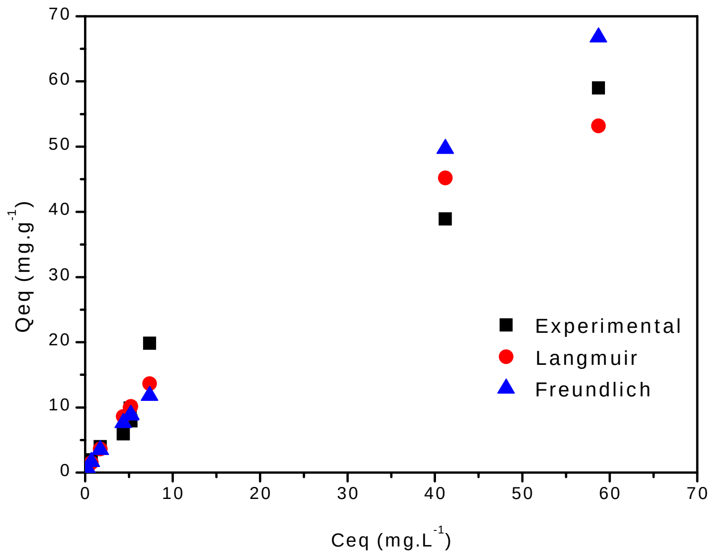

Figure 6. Comparison between the experimental isotherm and models of Langmuir and Freundlich for Mo(VI) ions on the PMQd.

Table 2 shows that the correlation coefficient (r^2) of the model of Freundlich was higher than that found for Langmuir, and close to unity, suggesting that in this concentration range of Mo, the Freundlich model described better the relationship of the equilibrium adsorption isotherm of Mo(VI) ions. According to the Langmuir model, the maximum adsorption capacity of the PMQd for Mo ions was 91 mg.g^{-1}.

Table 2. Parameters of the Langmuir and Freundlich models for adsorption of Mo(VI) ions on the PMQd.

	R^2	K_L (L.mg^{-1})	Q_{max} (mg.g^{-1})	K_F (mg.g^{-1}) (L.g^{-1})	1/n
Langmuir	0.6635	0.0240	91	----	----
Freundlich	0.9585	----	----	2.2315	0.8345

4. CONCLUSIONS

The results showed that the magnetite particles coated with chitosan (PMQd) are an excellent adsorbent of Mo(VI) ions from the aqueous solution from pH 0.5 to 9. In pH 1, the maximum adsorption capacity was 91 mg.g^{-1} according to the Langmuir model, and Freundlich model described better the equilibrium adsorption isotherm. This adsorbent showed great potential of application as magnetic adsorbent where the technique of magnetic separation proved be viable when subjected to an external magnetic field, accelerating the process of separation between the liquid phase and solid phase.

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