

Chitosan Sphere Adsorption Mechanisms for Ni, Mo, and Their Mixtures**C.L. Martinez-Gonzalez¹, S.D. Perez-Sanchez¹, J.O. Rivera-Gonzalez², L.T. Salazar-Bustos¹**¹Universidad Autónoma de Nuevo León, Facultad de Ingeniería Mecánica y Eléctrica, Ave. Universidad No. 1000, San Nicolás, N.L., México²Centro de Investigación en Energía, Universidad Nacional Autónoma de México, Coyoacán, Ciudad de México, México

Keywords: *Sorption, equilibrium, Kinetics, chitosan gel beads.***ABSTRACT**

In this work, chitosan gel beads (spheres) were prepared using a phase inversion method. They were used to study the process of sorption of nickel and molybdenum ions in aqueous solutions by means of equilibrium analysis and sorption kinetics. The results obtained establish that both metals as a function of the variation of the concentration, obey the Freundlich model with values of load capacity of 2.49 mg g⁻¹ for Ni and 41.84 mg g⁻¹ for Mo. The sorption results of the Ni (II), Mo (VI) and Ni (II) / Mo (VI) mixtures with chitosan beads showed that both ions are extracted, obtaining extraction percentages of 36.64% for Ni (II) and 68.9% for Mo (VI). For the case of the mixture, a percentage of 74.22% is reported. This result, which is shown above the values of individual extraction, yields a synergistic process. Obtaining the most efficient extraction for the Mo (VI) in simple system, this is ratified with the capacity value (qm) obtained from the Freundlich model.

INTRODUCTION

With the increase in industrialization and mining processes, environmental contamination with heavy metal ions has increased to an alarming level. Heavy metal contaminants exist in the air, soil and water waste streams of many industries.

Heavy metal contamination of water sources is dangerous for plants, animals and microorganisms and can be carcinogenic to humanity [1,2].

The removal of heavy metal ions from drinking water is a real challenge due to its minimal amounts, the formation of complexes with natural organic matter and the toxic effect even at very low concentrations [3].

Hydrogels have attracted great interest due to their diverse applications in sorption, biomedical materials, tissue engineering, biosensor membranes, etc., due to their similar structure to the extracellular matrix, as well as their excellent biological, physical and chemical properties. Variety of hydrogels have been prepared from synthetic polymers or natural polymers such as chitosan [4].

During the last three to four decades, biopolymers have been extensively studied due to their interactions with metal ions. Chitosan are the most widely studied and reported biopolymer for the metal ions sorption [5].

Chitosan is characterized by a high affinity for metal ions due to its high content of amine groups. The mechanism of sorption depends both on the protonation of these amine groups and metal ions speciation. Metal cations can be adsorbed at pH close to neutrality by a chelation mechanism, while metal anions can be adsorbed in acidic solutions through ionic interactions with protonated amine groups [6].

In the present work, gel beads (spheres) of crab shell chitosan, at a concentration of 2 wt.%, were prepared to carry out studies on the sorption process of Nickel and Molybdenum ions in aqueous solutions by means of equilibrium analysis and sorption kinetics.

MATERIALS AND METHODS**Materials**

Crab shell chitosan with a degree of deacetylation of 85% was used, from batch 91k1265, as received from Sigma Aldrich, as well as glacial acetic acid (99.8% purity). The metal salts used were (NH₄)₆Mo₇O₂₄ · 4 H₂O (Ammonium heptamolybdate) and Ni(NO₃)₂ (Nickel nitrate) Fermont brand.

Methods

Chitosan solution preparation

The solution was prepared by dissolving 2 wt. % of chitosan in 2 wt. % of acetic acid. This solution was magnetically stirred until completely dissolved at room temperature. Finally, it was filtered under pressure with a medium filter to eliminate residues of undissolved material.

Procedure to obtain the chitosan gel beads (spheres)

The polymeric solution was transferred to a syringe and needle pump was used, where it was dripped at a flow of 20 ml/h into a beaker containing 2M NaOH solution which was slowly stirred with a magnetic stirrer. Chitosan is insoluble in alkali, hydrogel beads of chitosan were formed in NaOH solution. The gel beads remained in the solution for 24 h for hardening. Subsequently the gel beads were washed in bidistilled water to remove the NaOH until a neutral pH was obtained, then were stored in bidistilled water at room temperature for the following sorption experiments.

Ion metal sorption onto chitosan gel beads (spheres)

Solutions were made at concentrations of 200 ppm Ni at pH = 5, Mo at pH = 1, 3, and 5 and NiMo at pH = 5 (controlled adding microvolume of sulfuric acid and sodium hydroxide concentrated solutions), equal amounts of gel beads (spheres) were added (5 gr) in beakers with 50 ml of the obtained solutions and left in constant agitation at 100 rpm, the necessary adjustments were made in the pH, until no longer achieving any pH variation in the solutions, this was done to analyze the pH optimal for the following experiments. Solutions were prepared at 2000, 1000, 500, 300, 200, 100 and 50 ppm of the Ni, Mo and NiMo metals at pH 5, and the same procedure was carried out for each of the solutions, samples were subsequently taken for the corresponding analyzes. The samples were analyzed by emission spectroscopy with inductively coupled plasma (ICP-OES) with the Perkin Elmer Analyst 300 equipment.

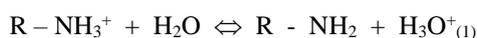
Sorption kinetics for ni, mo and nimo

In beakers, 250 ml of Ni, Mo and NiMo solutions were prepared at 2000 ppm, 50 grams of chitosan gel beads were added at each solution in constant agitation, solution samples were taken respectively at consecutive times of 0, 3, 6, 15, 30, 45, 60, 90, 120 min, 3, 4, 5 and 24 h, these samples were used for their respective concentration analyzes and used to construct the sorption kinetics.

RESULTS AND DISCUSSION

Ph effect on the metal ion sorption

The sorption of metal ions with chitosan is produced by interactions between the metal ion and the amino group of chitosan, this is a weak base and the equilibrium of dissociation depends on the pH (equation 1), some authors establish that at pH 6 ($pK_a \cong 6.20$), about 50% of the amino groups have the protonated form as NH_3^+ [7,8].



It is known that nickel ions can be extracted at pH 5 [9,10] and for molybdenum ions at pH of 1, 3 and 5 [11, 12, 13], taking into account these parameters in Figure 1 is presented the sorption process of Mo (VI) to different pH values, it is observed that the highest sorption percentage is achieved at pH 3 however considering that the extraction of Ni (II) is at 5, we choose pH 5 where it is obtained the maximum extraction of Ni (II), extraction of Mo (VI) greater than 65%, and the possibility of having the chitosan with a good percentage of active sites that propitiate the sorption of the species in both simple and mixed systems.

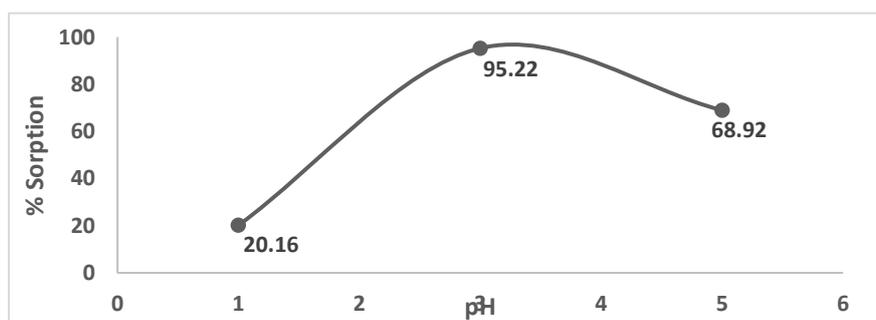


Figure 1. Percentage of Mo sorption at 200 mg L⁻¹ at pH values of 1, 3 and 5.

Effect of metal concentration, ni (II) and mo (VI).

The Langmuir model describes the adsorption process in monolayers without lateral interactions between the adsorbate molecules, this due to the sorption-desorption equilibrium, on the other side Freundlich's model considers that the interactions are on an energetically heterogeneous surface. In equations 2 and 3, both models are presented as a function of the sorption capacity for chitosan.

$$q = \frac{q_m b C_{eq}}{1 + b C_{eq}} \quad (2)$$

$$q = K_f C_{eq}^{1/n} \quad (3)$$

where q is the sorption capacity ($\text{mg M}^+ \text{g}^{-1}$, or $\text{mmol M}^+ \text{g}^{-1}$) in equilibrium with C_{eq} ($\text{mg M}^+ \text{L}^{-1}$, or $\text{mmol M}^+ \text{L}^{-1}$), q_m is the sorption capacity at saturation of the monolayer coverage ($\text{mg M}^+ \text{g}^{-1}$, or $\text{mmol M}^+ \text{g}^{-1}$), b is the affinity coefficient (L mg^{-1} , or L mmol^{-1}), K_f is capacity coefficient and n is intensity coefficient. The parameters of the model have been obtained by non-linear regression in order to diminish the statistics bias, compared to the linearization/linear regression method [14]. Figure 2 shown the modeling of experimental data with the Langmuir and Freundlich models using the parameter values summarized in Table 1.

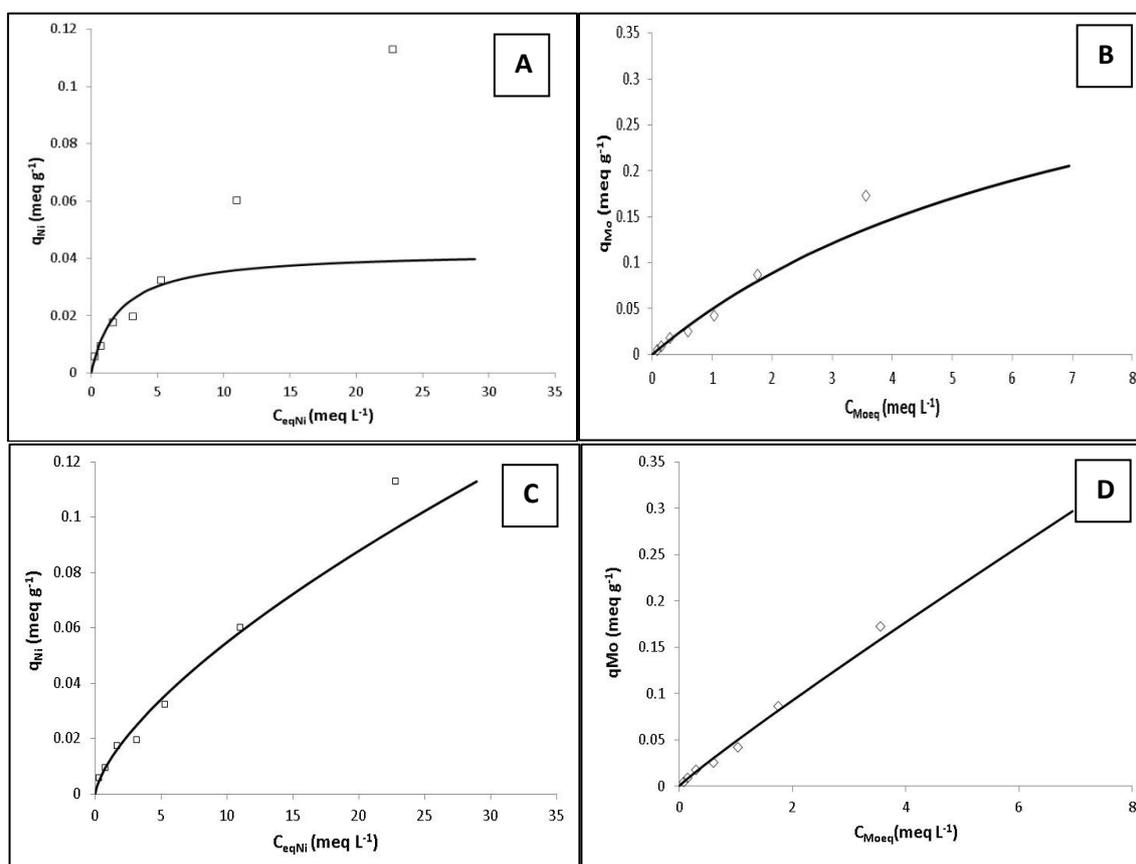


Figure 2. Sorption isotherms of Ni and Mo A) Model Langmuir Ni, B) Model Langmuir Mo, C) Model Freundlich Ni and D) Freundlich Mo

According to Figure 2 the sorption process of Ni (A and C) and Mo (B and D) on chitosan gel beads is more accurately adjusted to Freundlich (Figure 2, C and D) with sorption capacities of 2.49 mg g^{-1} for Ni and 41.84 mg g^{-1} for Mo, different authors report that the processes of sorption of transition metals are governed by Langmuir [15, 16, 17] the values of the correlation coefficient (R^2) do not show substantial differences as to rule out the possibility of having combined behaviors, that is to say that they resemble Freundlich, in this case it is observed in Figure 2 (A-D) at low concentrations of metals the adjustment to both models is adequate and it is precisely at this point where both models coincide, on the other hand at high concentrations we have that Freundlich presents a better fit with smaller deviations of the coefficient (R^2). With these results it is

established that the sorption on the chitosan beads is in a monolayer system but that it presents high energy sites when working at high concentrations.

Table 1. Parameters of equilibrium for simple systems.

Quitosano	Langmuir			Freundlich		
	q_m (mg M ⁺ g ⁻¹)	b (L mg ⁻¹)	R ²	K _f	n	R ²
Ni (II)	2.49	0.0084	0.95	0.0426	1.473	0.98
Mo (VI)	41.84	0.0013	0.99	0.0642	1.067	0.99

Regarding the extraction process of metals, in Table 1, it is observed that the load capacity for Mo (41.84 mg g⁻¹) is greater than that of Ni (2.49 mg g⁻¹), so that the surface is used more effectively by molybdenum, this is due to the size of the ion that is extracted, that is to say of the extracted species depending on the conditions of the study, in this case pH = 5, which has been reported by different authors as the ideal one since the majority of the active centers of chitosan are available for the process. Is known [6,7] that the total number of active sites in chitosan gel beads is high (\cong 90% of the total available sites) and it also suggests that the mechanism of extraction of Ni and Mo is by ion exchange.

Effect of the concentration on the sorption of ni (II) / mo (VI) mixtures

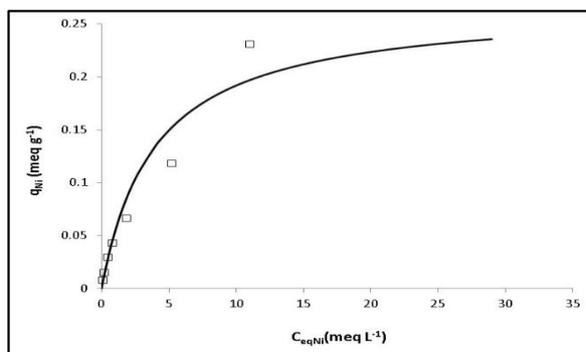
For the case of the sorption of binary mixtures, the behavior is different from the single study, it is possible to find masking mechanisms that is to say that one metal is favored over the other, or synergy. Several authors have reported the use of chitosan for the separation of mixtures selectively, Matus et al. [18], studied the sorption of Cu (II) and Hg (II), finding that chitosan although adsorbed the two metals but is more related to the extraction of Cu (II). Other reports the sorption of Ni (II) in the presence of Cu (II), with results that establish that the extraction of Cu (II) is favored over Ni (II) [19]. On the other hand, Benavente et al. [20], verified that the experimental data of the sorption equilibrium of Cr (VI) and Ni (II) are adjusted to the Langmuir model, with maximum capacity of Ni sorption of 83.31 mg/g chitosan.

According to the results presented in Table 2, the sorption process for a mixture of Ni (II) / Mo (VI) in chitosan gel beads is set in the case of nickel to both Langmuir and Freundlich models, a phenomenon that differs if Metal (Ni (II)) is used alone, with a loading capacity (q_m) of the order of 14.95 mg g⁻¹, higher than that obtained for simple sorption (2.49 mg g⁻¹).

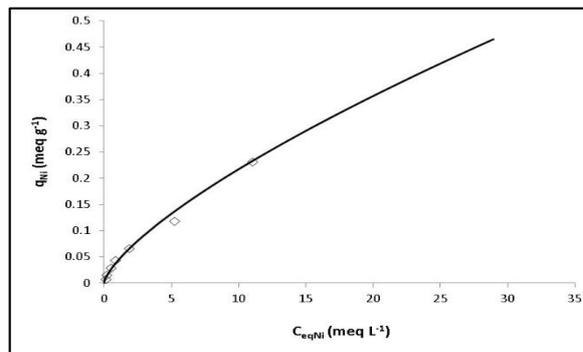
Table 2. Parameters of equilibrium for combined systems Ni (II) / Mo (VI)

Quitosano	Langmuir Ni(II)/Mo(VI)			Freundlich Ni(II)/Mo(VI)		
	q_m (mg M ⁺ g ⁻¹)	b (mg M ⁺ g ⁻¹)	R ²	K _f	n	R ²
Ni (II)	14.95	0.0043	0.99	0.1314	1.3941	0.98
Mo (VI)	-3.10	-0.02933	0.71	0.0429	0.6308	0.92

On the other hand, molybdenum only fits Freundlich both individually and in a mixture with Ni (II). With the obtained result it can be established that while the Ni (II) adheres to the chitosan in a monolayer system, the increase in its concentration affects the sorbate energy, while the molybdenum seems to adjust to the fact that its sorption process is given on an energetically heterogeneous surface.



A



B

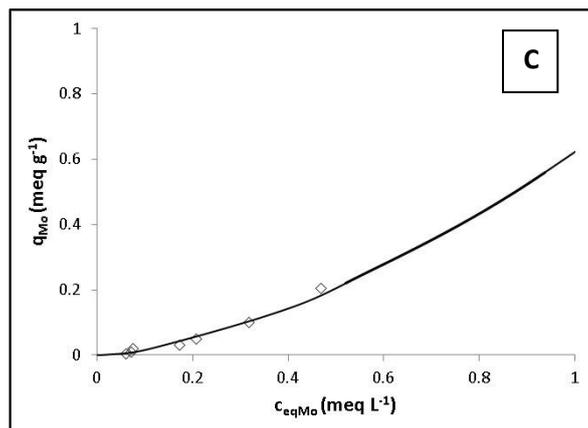


Figure 3. Sorption isotherms of Ni and Mo A) Model Langmuir Ni, B) Model Freundlich Ni, C) Model Freundlich Mo.

The sorption results of the Ni (II), Mo (VI) and Ni (II) / Mo (VI) mixtures with chitosan beads showed that both ions are extracted, obtaining extraction percentages of 36.64% for Ni (II) and 68.9% for Mo (VI), see Figure 4. On the other hand, for the case of the mixture, a percentage of 74.22% is reported. This result, which is shown above the values of individual extraction, yields a synergistic process, observed by other authors for systems involving Ni (II) [18], it is important to take into account the conditions of the system in addition to the ions involved. Obtaining the most efficient extraction for the Mo (VI) in simple system, this is ratified with the capacity value (q_m) obtained from the model.

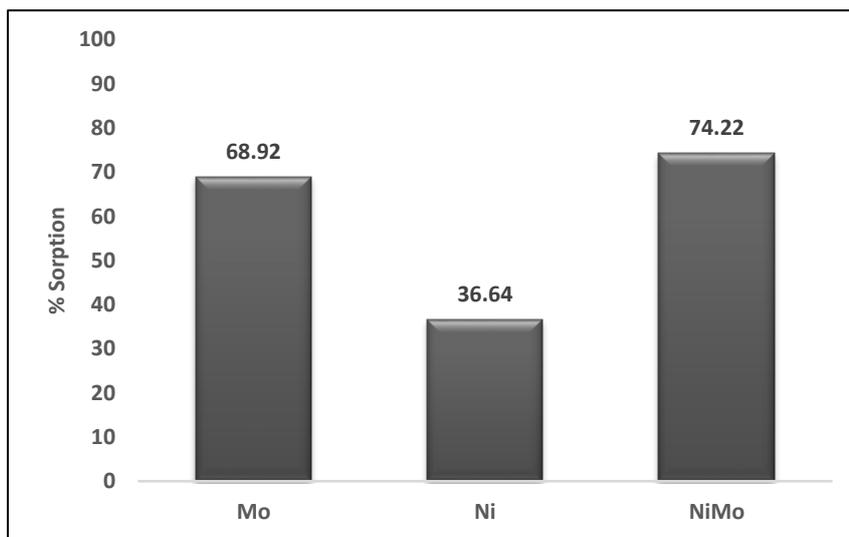


Figure 4. Extraction percentages of Ni (II), Mo (VI) and the mixture Ni (II) / Mo (VI).

CONCLUSIONS

The results obtained establish that both metals as a function of the variation of the concentration, obey the Freundlich model with values of load capacity of 2.49 mg g^{-1} for Ni and 41.84 mg g^{-1} for Mo. The results of sorption of the Ni (II), Mo (VI) and Ni (II) / Mo (VI) mixtures with chitosan beads showed that both ions are extracted, obtaining extraction percentages of 36.64% for Ni (II) and 68.9% for Mo (VI). For the case of the mixture, a percentage of 74.22% is reported. This result, which is shown above the values of individual extraction, yields a synergistic process. Obtaining the most efficient extraction for the Mo (VI) in simple system, this is ratified with the capacity value (q_m) obtained from the model.

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REFERENCES

1. VM Boddu, K Abburi, AJ Randolph, ED Smith. *Separation Science and Technology*, 2008, 43, 1365–1381.
2. CF Francisco, FCF Barros, FW Sousa, RM Cavalcante, TV Carvalho, FS Dias, DC Queiroz, LCG Vasconcellos, RF Nascimento. *Clean*, 2008, 36, 292–298.
3. KH Chu. *Journal of Hazardous Materials*, 2002, B90, 77–95.
4. Y Zhao, L Ma, R Zeng, M Tu, J Zhao. *Carbohydrate Polymers*, 2016, 151, 237–244.
5. S Chauhan. *Journal of Chemical and Pharmaceutical Research*, 2015, 7(4):49-55
6. R Navarro, J Guzmán, I Saucedo, J Revilla, E Guibal. *Macromolecular Bioscience*, 2003, 3, 552-561.
7. E Guibal. *Separation and Purification Technology*, 2004, 38, 1, 43-74.
8. JA Flores, AE Navarro, KP Ramos, L Chang, N Ale, M Ly, HJ Maldonado. *Rev. Soc. Quím. Perú*, 2005, 71, 1, 17-25.
9. L Pivarč'iova', O Roskopfova', M Galambos', P Rajec. *J Radioanal Nucl Chem*, 2014, 300, 361–366.
10. M Aliabadi, M Irani, J Ismaeili, H Piri, MParnian. *Chemical Engineering Journal*, 2013, 220, 237–243.
11. CYChen, TH Chang, JT Kuo, YF Chen, YC Chung. *Bioresource Technology*, 2008, 99, 7487–7494.
12. A Kufelnicki, ME Lichawska, KHBodek. *Journal of Applied Polymer Science*, 2009, 114, 1619–1625.
13. LZhang, JXue, X Zhou, X Fei, Y Wang, Y Zhou, L Zhong, X Han. *Carbohydrate Polymers*, 2014, 114, 514–520.
14. D Kinniburgh. *Environ. Sci. Technol.* 1986, 20 (9), 895–904.
15. C Milot, J McBrien, S Allen, E Guibal. *Journal of Applied Polymer Science*, 1998, 68, 571–580.
16. C Tejada, A Herrera, E Ruiz. *Revista Ciencia en Desarrollo*, 2016, 7, 31-36.
17. S Castro, R Cerda, N Betanco, F Canelo, X López, A García, M Benavente. *Revista científica*, 2013, 26, 56-68.
18. I Matus, L Paniagua, M Benavente. *Revista científica*, 2011, 24, 1, 20-32.
19. I Vold, K Vårum, EGuibal, OSmidsrød. *Carbohydrate Polymers*, 2003, 54,4,471-477.
20. M Benavente. *Licentiate Thesis. The Royal Institute of Technology (KTH), Stockholm, Sweden, (2008)*