

The removal of toxic metals from liquid effluents by ion exchange resins. Part VI: Manganese(II)/H⁺/Lewatit K2621

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ABSTRACT: In this sixth part of the series, Manganese(II) was removed from aqueous solutions by the cationic exchange resin Lewatit K2621. The investigation was performed under various experimental conditions such as the stirring speed associated with the system, aqueous pH, temperature, resin dosage and the ionic strength of the solution. The performance of the resin against the loading of metals from metal-binary solutions as well as the removal of Manganese(II) from the solutions using multiwalled carbon nanotubes and functionalized (carboxylic groups) multiwalled carbon nanotubes, were also investigated. Experimental results fit well with the pseudo-first kinetic order model, whereas fit of the data show that at 20 °C the process responded well to the diffusion controlled model, and that at 60 °C, the system is controlled by the moving boundary model. Adsorption data is better related to the Freundlich isotherm. Elution of the Manganese(II) loaded onto the resin was investigated using acidic (H₂SO₄ or HCl) solutions.

KEYWORDS: Lewatit K2621; Liquid effluents; Manganese(II); Multiwalled carbon nanotubes; Removal

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RESUMEN: *Eliminación de metales tóxicos presentes en efluentes líquidos mediante resinas de cambio iónico. Parte VI: Manganeso(II)/H⁺/Lewatit K2621.* En esta sexta parte de la serie de trabajos sobre la eliminación de metales tóxicos de disoluciones acuosas, se presentan datos sobre el sistema manganeso(II)-Lewatit K2621. La investigación se ha llevado a cabo empleando diferentes condiciones experimentales como son la velocidad de agitación asociada al sistema, el pH del medio acuoso, la temperatura, la adición de distintas cantidades de resina a la disolución acuosa que contiene Manganeso(II) y la fuerza iónica de esta disolución. El comportamiento de la resina Lewatit K2621 respecto a la eliminación del Manganeso(II) se ha evaluado en presencia de otros elementos metálicos en la disolución acuosa, asimismo se ha comparado el comportamiento de la resina frente a la utilización de otros potenciales adsorbentes para el metal como son los nanotubos de carbono de pared múltiple sin funcionalizar o funcionalizados con grupos carboxílicos. El modelo cinético de pseudo-primer orden explica los resultados cinéticos del proceso de intercambio catiónico, el aumento de temperatura hace que el modelo de cambio iónico responda a dos procesos diferentes, a 20 °C es del tipo de difusión en el medio acuoso y a 60 °C el modelo es el de núcleo recesivo. La isoterma de Freundlich se adapta mejor a los resultados obtenidos respecto a la carga del metal en la resina. La elución del Manganeso(II) cargado en la resina se ha investigado mediante el uso de disoluciones ácidas (H₂SO₄ o HCl).

PALABRAS CLAVE: Efluentes líquidos; Eliminación; Lewatit K2621; Manganeso(II); Nanotubos de carbono de pared múltiple

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1. INTRODUCTION

Manganese is a natural occurring element, that as many others metallic elements is essential to human health. In fact, manganese is a normal component of human tissues and fluids, but as can be expected, manganese overexposure can be toxic.

Manganese(II) intake by humans can be done *via* air, water or food, and health effects of inorganic manganese on humans include: death, systemic, neurologic and developmental (US ATSD, 2012). In the case of waters, and particularly drinking waters, the intake limit established by the World Health Organization is of $400 \mu\text{g}\cdot\text{L}^{-1}$ in a daily basis, whereas concentrations about $0.05 \text{ mg}\cdot\text{L}^{-1}$ is normally acceptable for consumption, though the presence of the element in waters can be somewhat objectionable if causes water discoloration, black staining and bitter metallic taste (WHO, 2011; USEPA, 2017). Manganese is non-classified as human carcinogenic (group D). A number of disclosures and future developments on manganese toxicity related to humans can be found elsewhere (O'Neal and Zheng, 2015).

Having manganese(II) these hazardous characteristics, recently, several authors reported about the removal of this ion from aqueous solutions using different types of methodologies (Coskun *et al.*, 2016; Li *et al.*, 2016; Zue *et al.*, 2016; Alexander *et al.*, 2017; Kebabi *et al.*, 2017; Vries *et al.*, 2017).

Next in the series of articles published by the author about the use of ion exchange technology in the removal of toxic metals (Alguacil *et al.*, 2002; Alguacil, 2002; Alguacil, 2003; Alguacil, 2017a; Alguacil, 2017b), the present work reports about the use of the cationic exchange resin Lewatit K2621 on the removal of manganese(II) from aqueous solutions. The experimental results were fitted to models in order to a better understanding of the exchange process.

2. EXPERIMENTAL

Lewatit K2621 (Fluka) has the characteristics shown in Table 1. Other chemical used in the investigation were of AR grade, whereas the experimental procedure used here was the same as described in previous works of this series. The multiwalled carbon nanotubes (MWCNTs) presented the next characteristics: carbon content > 98%, outer diameter: $10\text{nm}\pm 1\text{nm}$, inner diameter: $4.5 \text{ nm} \pm 0.5 \text{ nm}$, length: $3\text{-}6 \mu\text{m}$ (Alguacil *et al.*, 2016), whereas the

TABLE 1. Characteristics of Lewatit K2621 resin

Active group	Sulfonic in H^+ form
Matrix	Crosslinked styrene-DVB
Particle form and particle size ^a	Spheres, $0.4 \text{ mm} < \text{particle size} < 1.3 \text{ mm}$

^a minimum 90%

carboxylic functionalized multiwalled carbon nanotubes (MWCNTs-ox) presented >8% carboxylic acid functionalized, 9.5 nm average diameter and 1.5 μm length.

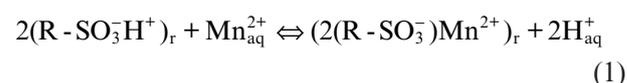
All the loading experiments were carried out in a glass reactor using 200 mL of the aqueous solution, 1200 rpm and 20 °C, except when these variables were investigated.

Metals in solution were analysed by AAS spectrophotometry, whereas metals load in the resin was calculated by the mass balance.

3. RESULTS AND DISCUSSION

3.1. Manganese uptake onto the resin

The equilibrium which represented the loading of Manganese(II) onto the resin Lewatit K2621 can be represented by a cationic exchange between protons of the sulfonic group of the resin and Mn^{2+} from the aqueous solution, thus:



where R is the non-reactive part of the resin, and *r* and *aq* represent to the resin and the aqueous solution, respectively.

To investigate the effect of the stirring speed on metal loading onto the resin, aqueous solutions containing $0.01 \text{ g}\cdot\text{L}^{-1}$ manganese(II) at pH 5 were put into contact with $0.5 \text{ g}\cdot\text{L}^{-1}$ of the resin at 20 °C and various stirring speeds, ranging from 250 to 1400 rpm. The results of this set of experiments being shown in Fig. 1, it can be seen (Fig.1 top) that the percentage of metal loaded onto the resin increased as the stirring speed of the system is increased, however in the 1000-1400 rpm range, and specially in the 1200-1400 rpm, this difference is, if any, negligible. Thus, in the 1200-1400 rpm a maximum in metal loading is achieved and a minimum in the thickness of the aqueous boundary layer is reached. Fig. 1 bottom represented the variation of the fractional approach to equilibrium (F) versus time. F values were calculated accordingly with the next expression:

$$F = \frac{[\text{Mn}]_{\text{t,r}}}{[\text{Mn}]_{\text{e,r}}} \quad (2)$$

where $[\text{Mn}]_{\text{t,r}}$ and $[\text{Mn}]_{\text{e,r}}$ represented the manganese concentrations in the resin at an elapsed time *t* and at equilibrium, respectively. When the fractional approach to equilibrium is considered, it can be seen that there is an initial influence of the stirring speed on the F value, but after 1 h of reaction, in all cases, near or more than 50% of the metal loading is achieved, being practically the F value

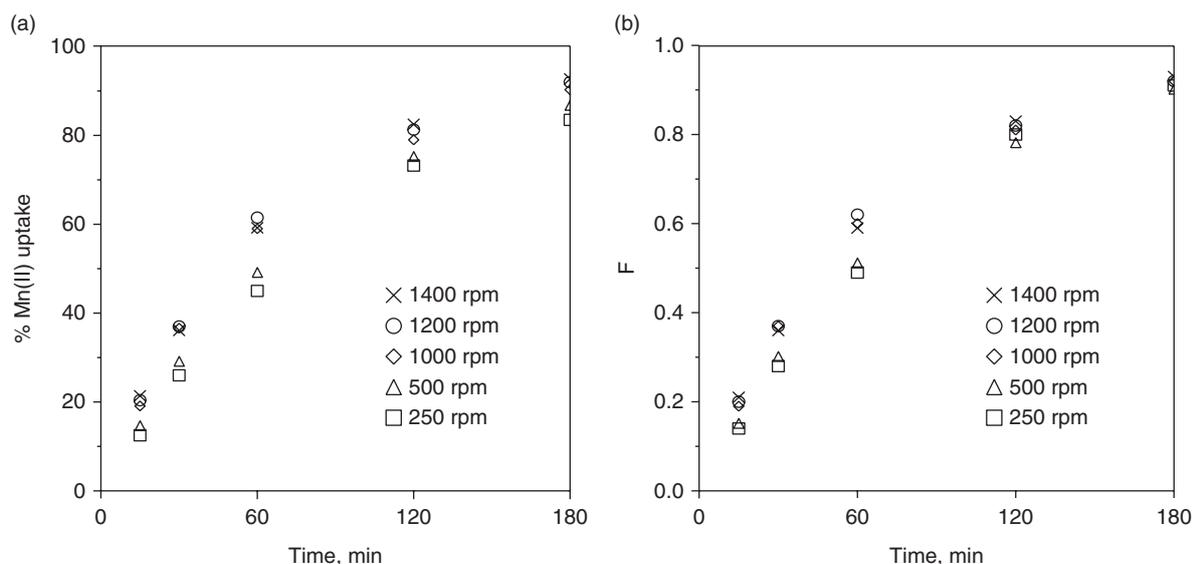


FIGURE 1. a) Influence of stirring speed on manganese(II) uptake, and b) influence of stirring speed on the factorial approach to equilibrium.

independent of the stirring speed after 2 h or 3 h of reaction (near 80% of 90% of the total metal loading, respectively), this means that at these times, the rate of metal uptake is independent of the stirring speed, being this independence also evident for stirring speeds greater than 1000 rpm and shorter contact times. Experimental data at 1200 rpm were used to investigate the loading kinetics followed by this system. Thus, data were fit to the pseudo-first or pseudo-second kinetics order models, the results of this fitting showed that the system responded better to the pseudo-first kinetic order model ($r^2 = 0.998$):

$$\ln([\text{Mn}]_{e,r} - [\text{Mn}]_{t,r}) = \ln[\text{Mn}]_{e,r} - kt \quad (3)$$

where $[\text{Mn}]_{e,r}$ and $[\text{Mn}]_{t,r}$ are the manganese concentrations in the resin at equilibrium and at elapsed time, respectively, k is the rate constant and t the elapsed time. From the numerical data the value of k was estimated as 0.014 min^{-1} .

Metal loading onto the resin was also investigated as a function of the temperature. In this case, the resin dosage was of $0.25 \text{ g}\cdot\text{L}^{-1}$, whereas the aqueous solution contained $0.01 \text{ g}\cdot\text{L}^{-1}$ Mn(II) at pH 5. From results showed in Table 2, it can be seen that with the increase of the temperature the metal uptake in the resin increases. In this table, the values of the distribution coefficient D were calculated accordingly with:

$$D = \frac{[\text{Mn(II)}]_{e,r}}{[\text{Mn(II)}]_{e,s}} \quad (4)$$

TABLE 2. Manganese uptake at various temperatures

T, °C	[Mn(II)], mg·L ⁻¹	[Mn(II)], mg·g ⁻¹	log D ^a
20	1.5	34.0	1.4
40	0.15	39.4	2.4
60	0.01	40.0	3.6

^a Time: 5 h

where $[\text{Mn(II)}]_{e,r}$ and $[\text{Mn(II)}]_{e,s}$ are the manganese concentrations in the resin and in the solution at equilibrium, respectively. From the experimental values, ΔH° was calculated as $102.1 \text{ kJ}\cdot\text{mol}^{-1}$, being the exchange reaction endothermic. The values of ΔG° and ΔS° calculated for the present system are $-6.5 \text{ kJ}\cdot\text{mol}^{-1}$ (spontaneous system) and $374.2 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ (increase of the process randomness), respectively.

Various models were used to investigate the influence of the temperature on the mechanism in which manganese is loaded onto the resin (López Díaz-Pavon *et al.*, 2014). From this fitting, it is showed that at 20 °C, the metal loading onto the resin is better explained by the aqueous diffusion, whereas at 60 °C the data best fit to the moving boundary model (Table 3).

The variation of the metal loaded onto the resin when the pH of the solution changes was also considered, and for these experiments solutions containing $0.01 \text{ g}\cdot\text{L}^{-1}$ manganese(II) at pH values of 5 or 1, resin concentrations of $0.5 \text{ g}\cdot\text{L}^{-1}$ were used. Fig. 2 showed the variation in the Manganese(II) concentration in the aqueous solution versus time at these pH values. The pH of the solution clearly influences the removal of Manganese(II) from the

TABLE 3. Model fits for manganese uptake at different temperatures

T, °C	model	r ²	k, min ⁻¹
20	ln(1-F) = -kt	0.994	9.8x10 ⁻³
60	3-3(1-F) ^{2/3} -2F = kt	0.993	4.9x10 ⁻³

F: calculated as in Eq. (2)

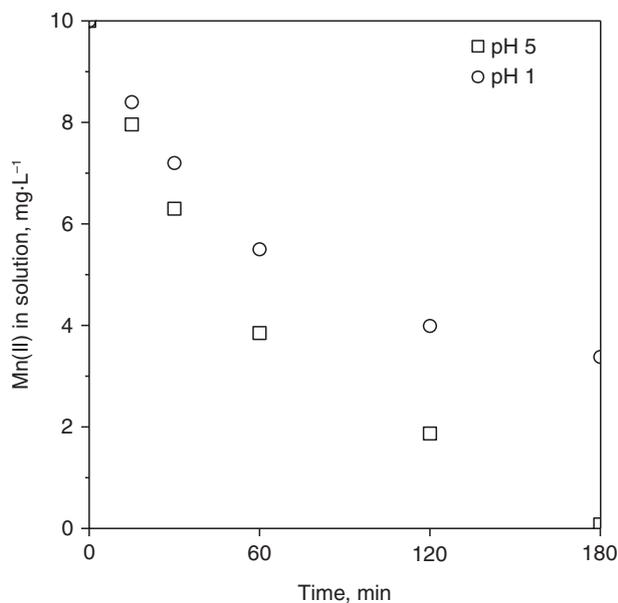


FIGURE 2. Influence of the aqueous pH on manganese(II) remained in the aqueous solution.

TABLE 4. Influence of the aqueous ionic strength on manganese uptake

Ionic strength, M	manganese uptake, mg·g ⁻¹ *
1	1.5
0.5	1.9
0.25	6.0
0.13	12.0
7.2x10 ⁻⁴	34.0

*Time: 5 h

solution, increasing the remaining Mn(II) concentration in the solution as the pH of the solution becomes more acidic. Metal uptakes at equilibrium are 14.4 and 19.9 mg·g⁻¹ at pH values of 1 and 5, respectively, for Manganese(II) concentration in the solution of 2.8 and 0.04 mg·L⁻¹.

The ionic strength of the aqueous solution is another variable which potentially can affect to the exchange reaction and thus the Manganese(II) loads onto the resin. These experiments were carried out with resin doses of 0.25 g·L⁻¹ and aqueous solutions containing 0.01 g·L⁻¹ Mn(II) and various concentrations of LiCl, as the source for the ionic strength variation. Table 4 summarized the results

TABLE 5. Manganese uptake at various resin doses

Resin, g·L ⁻¹	[Mn(II)], mg·L ⁻¹	[Mn(II)], mg·g ⁻¹
0.5	0.04	19.9
0.25	1.5	34.0
0.13	4.5	44.0
0.05	6.8	64.0

Time: 5 h

from these experiments. It can be seen how clearly the increase of the ionic strength influences the metal uptake, specially when compared with solutions in which no LiCl are present, thus, with ionic strength almost zero a maximum in metal uptake (34.0 mg·g⁻¹) is reached.

Resin concentrations in the 0.05-0.5 g·L⁻¹ range were used to investigate the influence of the resin dosage on metal uptake, when aqueous solutions containing 0.01 g·L⁻¹ Mn(II) at pH 5 were used as the source for Mn²⁺ ions. The results of this investigation are summarized in Table 5, as can be expected, the decrease in the resin concentration resulted in an increase of the metal uptake onto the resin, but at the same time, the residual Mn²⁺ concentration in the solution increases. The experimental data better responded to the Freundlich model (r² = 0.901):

$$\ln[\text{Mn}]_{e,r} = \ln K_F + \frac{1}{n} \ln[\text{Mn}]_{e,s} \quad (5)$$

where [Mn]_{e,r} and [Mn]_{e,s} are the manganese concentrations at equilibrium in the resin and in the aqueous solution, respectively, K_F is a Freundlich constant and 1/n is a parameter. For the present system ln K_F = 3.6 and 1/n = 0.199.

The selectivity of the resin respect to Manganese(II) when other metals are present in the aqueous solution was studied using binary solutions of Manganese(II) and a given metal in equimolar concentrations. Table 6 summarized these results in the form of the experimental separation factors, β_{Mn/metal}:

$$\beta = \frac{D_{\text{Mn}}}{D_{\text{Metal}}} \quad (6)$$

where D represented the distribution coefficient for the metals, calculated as in Eq. (4). From these results it can be deduced that this resin presented a bad selectivity with respect to manganese(II), since this element only is exchanged favourably in the presence of zinc(II) and indium(III), β > 1, whereas the others metals experimented in this work are exchanged in preference to manganese(II) (β < 1). The differences in selectivity may be attributed, among others, to:

TABLE 6. Separation factors (β) for various metals-binary solutions using Lewatit K2621 resin as cation exchanger

System	$\beta_{Mn/M}$
Mn(II) Cr(III)	0.89
Mn(II) Co(II)	0.78
Mn(II) Pb(II)	0.78
Mn(II) Ni(II)	0.65
Mn(II) Cu(II)	0.57
Mn(II) In(III)	1.2
Mn(II) Zn(II)	2.3

Aqueous solution: 0.17 mmol·L⁻¹ each metal at pH 5; Resin dosage: 0.25 g·L⁻¹; Temperature: 20 °C; Time: 7 h

TABLE 7. Metal uptake obtained with different types of exchanger-adsorbents

Exchanger-adsorbent	Mn(II) uptake, mg·g ⁻¹
Lewatit K2621	19.9
MWCNTs	2.5
MWCNTs-ox	8.0

Aqueous solution: 0.01 g·L⁻¹ Mn(II) at pH 5; Resin or carbon nanotubes dosage: 0.5 g·L⁻¹; Temperature: 20 °C; Time: 5 h

i) The easiness (affinity) in which the cation is exchanged with the proton from the resin, resulting in greater metal uptake.

ii) The different rate of the metal loading onto the resin.

Also the exchange capacities of the resin with respect to other smart metal-adsorbents or exchangers, as functionalized and non-functionalized multi-walled carbon nanotubes are examined. The results of this investigation are shown in Table 7, it can be seen that the results obtained within the resin are far better than those obtained with the two types of multiwalled carbon nanotubes.

3.2. Metal elution from the loaded resin

Hydrochloric acid and sulfuric acid were used as eluents for the present system. The elution step in this system can be related to an exchange of the manganese ions loaded onto the resin with the correspondent concentration of protons released from the acids, that is a shifting of Eq. (1) to the left.

The use of both acids results in an acceptable yield in the recovery of manganese, 85.0 % and 92.3% for sulfuric and hydrochloric acid, respectively.

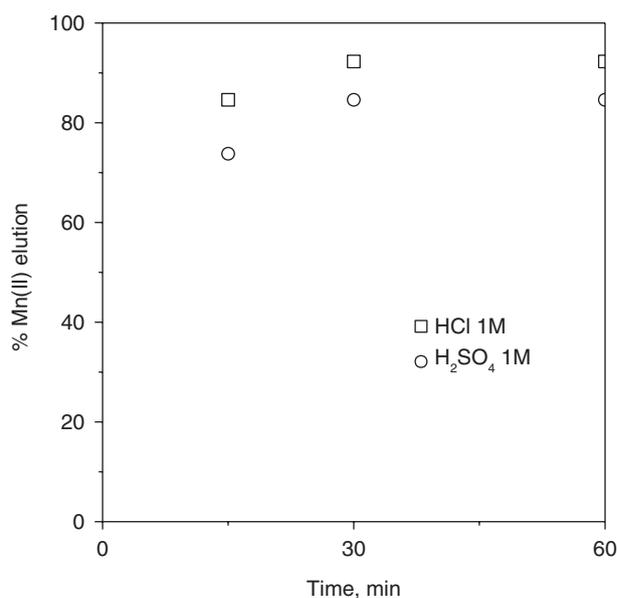


FIGURE 3. Influence of the acid on manganese(II) elution from Mn(II)-loaded resin.

 TABLE 8. Elution of Mn(II) using H₂SO₄ solution as eluent

Liquid/resin ratio, mL·g ⁻¹	% elution	[Mn(II)], g·L ⁻¹
250	85.0	0.06
125	84.6	0.11

Aqueous solution: H₂SO₄ 1 M; Resin: 0.1 g; loaded with 1.6 mg Mn(II); Time: 1 h; Temperature: 20 °C

Reaching the equilibrium, also in both cases, within 30 min of contact between the Mn(II)-loaded resin and the respective elution solution (Fig. 3). The conditions for the above experiments were: 0.1 g resin loaded with 1.6 mg Mn(II), aqueous solution: the corresponding acid, liquid/resin ratio: 125/1 mL·g⁻¹, temperature: 20 °C, time: 15, 30 and 60 min. The effect of varying the solution/resin ration was also investigated in the case of H₂SO₄ in order to evaluate if this variation has any effect on the percentage of Manganese(II) elution. The results from these tests are shown in Table 8, and it can be seen that this variation has not any influence in the recovery of the metal from the loaded resin. In any case it can be observed that near a ten-fold increase in the concentration of Manganese(II) in the solution, with respect to the initial one, can be achieved using the proper liquid volume/resin weight ratio.

4. CONCLUSIONS

- The resin Lewatit K2621 can be used in the removal of manganese(II) from solutions of pH 5 or near this value, the decrease of the aqueous pH dramatically hampered the use of this resin in the removal of this element. Also the increase

of the aqueous ionic strength and the decrease of the temperature (the exchange reaction being endothermic) are detrimental for the manganese uptake onto the resin.

- The variation of the temperature also produced a change in the adsorption model, at 20 °C, the aqueous diffusion model best explained the experimental results (rate constant estimated as $9.8 \times 10^{-3} \text{ min}^{-1}$), whereas at 60 °C the metal loading process is best explained by the moving boundary model (rate constant $4.9 \times 10^{-3} \text{ min}^{-1}$).
- The loading of the metal can be related to the Freundlich equation and the pseudo-first kinetic order equation (rate constant estimated as 0.014 min^{-1}).
- The Lewatit K2621 resin is only selective with respect to manganese when zinc(II) or indium(III) are presented in the aqueous solution, in the presence of Cr(III), Co(II), Pb(II), Ni(II) and Cu(II), the above elements are loaded onto the resin preferably to manganese(II). This resin presented better removal characteristics (greater metal uptake) with respect to manganese(II) than those presented by the carboxylic-functionalized or non-functionalized multiwalled carbon nanotubes tested in this work. Manganese(II) can be recovered from the loaded resin by the use of mineral acids, such as HCl or H₂SO₄ solutions, the recovery is fast (30 min) and the yield is around 90% for both acids, ten-fold increasing concentration, with respect to the initial manganese(II) concentration, can be reached, i.e.: $0.11 \text{ g} \cdot \text{L}^{-1}$ against the initial $0.01 \text{ g} \cdot \text{L}^{-1}$.

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