

The removal of toxic metals from liquid effluents by ion exchange resins. Part VII: Manganese(VII)/H⁺/Amberlite 958

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ABSTRACT: The anionic exchange resin Amberlite 958 was used to remove manganese(VII), as permanganate ion, from aqueous solutions of different pH values. Besides the aqueous pH, other variables involved in the exchange process were investigated, including, stirring speed of the system, temperature, ionic strength and resin concentrations. The non-linear fit of the experimental points, indicated that the equilibrium isotherm is best explained by the Langmuir equation, whereas the anion exchange equilibrium is endothermic and non-spontaneous. The Mn(VII) loading performance of Amberlite 958 resin was compared with that of other anion exchangers and multiwalled carbon nanotubes. The elution of the Mn(VII) loaded onto Amberlite 958 was investigated using hydrazine sulphate solutions, which render manganese to the eluate as the somewhat less hazardous form of Mn(II).

KEYWORDS: Amberlite 958; Liquid effluents; Manganese(VII); Multiwalled carbon nanotubes; Removal

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RESUMEN: La eliminación de metales tóxicos presentes en efluentes líquidos mediante resinas de cambio iónico. Parte VII: Manganeso(VII)/H⁺/Amberlite 958. Se ha utilizado la resina de intercambio aniónico Amberlite 958 para la eliminación de manganeso(VII) de aguas con distintos valores de pH. Además de esta variable, se han investigado otras que pueden afectar al proceso de carga del metal en la resina: velocidad del sistema, temperatura, fuerza iónica del medio y concentración de la resina. El modelo no lineal de la isoterma de carga responde mejor al modelo de Langmuir, mientras que el equilibrio se relaciona con un sistema endotérmico y no espontáneo. Se ha comparado la carga del metal con la de otras resinas de intercambio aniónico y con la nanotubos de carbono de pared múltiple. El proceso de elución del metal se ha abordado con disoluciones de sulfato de hidracina, que además permiten obtener al metal en la disolución de elución como la especie menos tóxica Mn(II).

PALABRAS CLAVE: Amberlite 958; Efluentes líquidos; Eliminación; Manganeso(VII); Nanotubos de carbono de pared múltiple

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1. INTRODUCTION

Manganese occurs naturally in the II or III oxidation states. Being manganese(II) the only manganese oxidation state stable in waters, the presence of manganese(VII) in the environment is only due to antropogenic causes.

The manganese(VII) oxidation state has a double character, to one side, its oxidative powder makes to this element a powerful decontaminant for wastes containing harmful compounds (Zhang *et al.*, 2013; Lee *et al.*, 2014; Guo *et al.*, 2016), on the other hand, and having the same toxicological aspects than manganese(II) (O'Neal and Zheng, 2015), this oxidative character makes to manganese(VII) to be a little more hazardous for life than manganese(II). Thus, its removal from aqueous wastes is mandatory to comply with the regulatory laws issued by industrialized countries (Mahmoud *et al.*, 2016; Mohy Eldin *et al.*, 2017).

Following in the series of articles published in this Journal about the use of ion exchange resins in the removal of hazardous metals (Alguacil *et al.*, 2002; Alguacil, 2002; Alguacil, 2003; Alguacil, 2017a; Alguacil, 2017b; Alguacil, 2018), the present work investigates about the use of the anionic exchange resin Amberlite 958 on the removal of manganese(VII) from aqueous solutions. The experimental results were fitted to models in order to a better understanding of the exchange process.

2. EXPERIMENTAL

Amberlite 958 (Fluka) has the characteristics shown in Table 1. Other resins and chemical used in the investigation were of AR grade. The multiwalled carbon nanotubes (MWCNTs) presented the next characteristics: carbon content > 98%, outer diameter: 10nm±1nm, inner diameter: 4.5 nm±0.5 nm, length: 3-6 µm) (Alguacil *et al.*, 2016).

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.

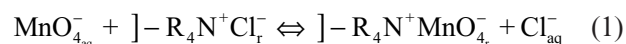
TABLE 1. Characteristics of Amberlite 958 resin

Active group	quaternary ammonium salt in chloride form
Matrix	macroreticular acrylic copolymer
Particle form and particle size	Spheres, 13-45 mesh

3. RESULTS AND DISCUSSION

3.1. Manganese load onto the resin

Manganese(VII) or the permanganate ion MnO_4^- , which is the form in which Mn(VII) is normally found in aqueous solutions, loads onto the resin *via* an anion exchange reaction, which can be represented by the next equilibrium:



where the subscripts aq and r referred to the aqueous and resin phases, respectively, and]- to the non-reactive matrix of the resin.

The effect of varying the stirring speed on Mn(VII) loading onto the resin was investigated using aqueous phases of 0.01 g·L⁻¹ Mn(VII) at pH 5, and resin doses of 0.5 g·L⁻¹. The stirring speed was varied between 350 and 1200 rpm. The results derived from this investigation were shown in Fig.1, plotting the percentage of manganese loaded onto the resin *versus* time. It can be seen that a maximum in metal adsorption is achieved at 1000 rpm, though the variation between 1000 and 1200 rpm is quite small. Thus, all the experiments were carried out at 1000 rpm, where the system reached a minimum in the thickness of the aqueous feed layer.

In the case of the temperature, the influence of this variable on metal uptake by the resin was investigated using the same aqueous solution as above, but with a resin dose of 0.25 g·L⁻¹. The results from

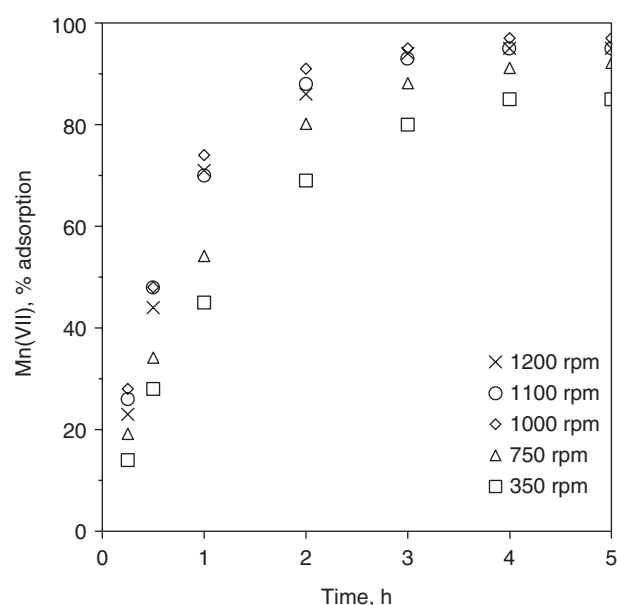


FIGURE 1. Influence of stirring speed on Mn(VII) loading onto the resin. Aqueous phase: 0.01 g·L⁻¹ Mn(VII) at pH 5. Resin dosage: 0.5 g·L⁻¹. Temperature: 20 °C.

this study were summarized in Table 2. It can be seen that the metal uptake onto the resin increased as the temperatures is increased from 20 °C to 60 °C, thus, the anionic exchange reaction was endothermic with ΔH° , ΔS° and ΔG° values estimated as 31.1 kJ·mol⁻¹, 59.3 J·mol⁻¹ K and 13.8 kJ·mol⁻¹, respectively. The above numbers suggested that the metal uptake onto the resin is not spontaneous and that the process increased its randomness.

The influence of the pH on metal load onto the resin at various aqueous pH was investigated with resin doses of 0.5 g·L⁻¹ and aqueous solutions of 0.01 g·L⁻¹ Mn(VII) at pH values from 1 to 5. The results were shown in Fig. 2, it can be seen that this variable changed dramatically the manganese uptake onto the resin, decreasing this load as the pH of the solution decreased from 5 to 1. The above being attributable to the resin performance with varying the pH of the solution and its non-capacity to exchange anions, or particularly this

anion, with the chloride ions from the resin at this pH range.

The variation of the resin concentration and its influence on metal uptake were investigated with resin doses of 0.075-1 g·L⁻¹ and aqueous solutions of 0.01 g·L⁻¹ Mn(VII) at pH 5. The results showed in Fig. 3 indicated that the percentage of metal loaded onto the resin is greatly dependent of the resin dose, but with more of the 70% of the maximum Mn(VII) loading reached in the two firsts hours of reaction for every resin dose.

The kinetics of manganese(VII) loaded onto the resin was derived from the results obtained with the resin dose of 0.25 g·L⁻¹. The model fit to the experimental data indicated that under the given experimental conditions, the kinetics of manganese(VII) uptake is governed by the pseudo-first order rate law (Hallajiqomi and Eisazadeh, 2017) ($r^2 = 0.997$):

$$\ln([Mn(VII)]_{e,r} - [Mn(VII)]_{t,r}) = \ln[Mn(VII)]_{e,r} - k_1 t \quad (2)$$

where $[Mn(VII)]_{e,r}$ and $[Mn(VII)]_{t,r}$ are the manganese concentrations in the resin at equilibrium and at elapsed time, respectively, t is the time and k_1 is the rate constant. From the fit data, k_1 is 0.011 min⁻¹ and $\ln[Mn(VII)]_{e,r} = 3.59$ which compares well with the experimental value of 3.56.

An equilibrium isotherm was generated from the experimental loading results, and this isotherm is shown in Fig. 4, together with the non-linear fits to the Langmuir and Freundlich approaches

TABLE 2. Manganese(VII) load at various temperatures

T, °C	[Mn(VII)] (mg·L ⁻¹)	[Mn(VII)] (mg·g ⁻¹)	D ^a
20	1.25	35.0	28.0
40	0.70	37.2	53.1
60	0.28	38.9	138.9

Aqueous phase: 0.01 g·L⁻¹ Mn(VII) at pH 5, resin dosage: 0.25 g·L⁻¹, Time: 5 h

^aCalculated as $[Mn(VII)]_{e,r}/[Mn(VII)]_{e,aq}$

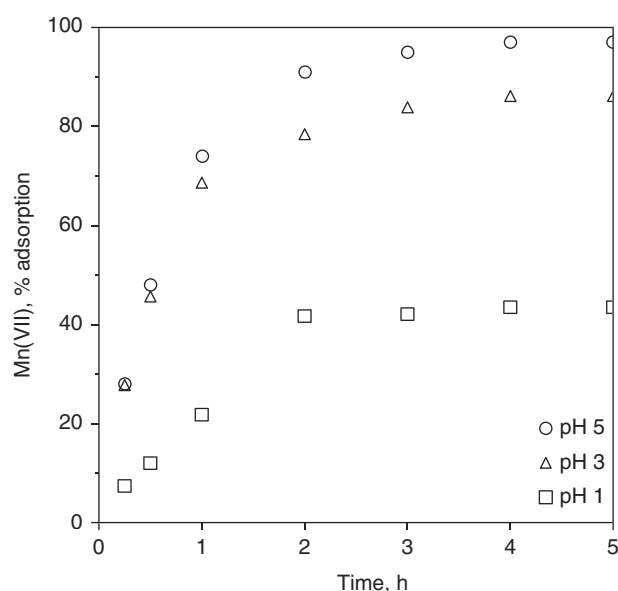


FIGURE 2. Influence of aqueous pH on Mn(VII) loading onto the resin. Aqueous phase: 0.01 g·L⁻¹ Mn(VII) at various pH values. Resin dosage: 0.5 g·L⁻¹. Temperature: 20 °C. Stirring speed: 1000 rpm.

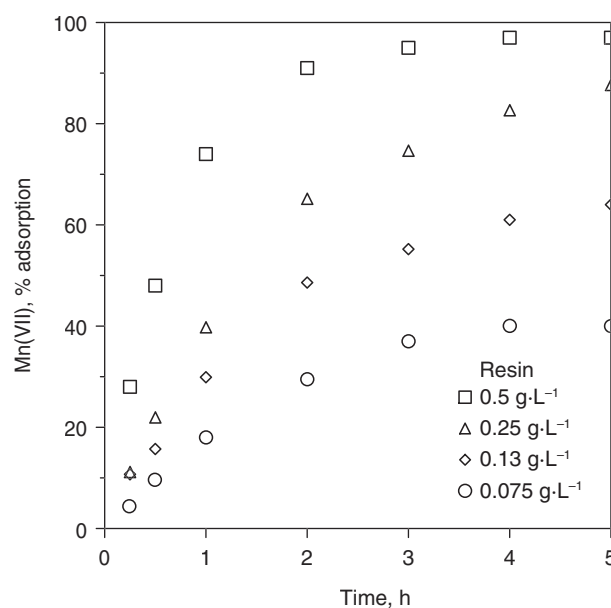


FIGURE 3. Influence of resin dosage on Mn(VII) uptake. Rest of experimental conditions as in Fig. 2.

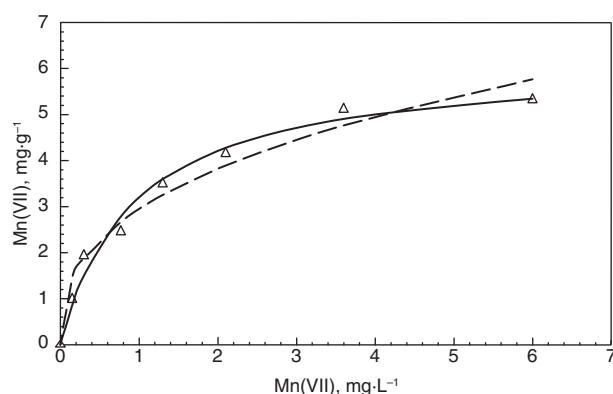


FIGURE 4. Equilibrium loading isotherm of Mn(VII) onto Amberlite 958 resin and its fit to the Langmuir and Freundlich models. Experimental points: Δ , Langmuir model: continuous line, Freundlich model: broken line. Temperature: 20 °C. Stirring speed: 1000 rpm.

(Wang *et al.*, 2017). The isotherm responded better to the Langmuir model ($r^2 = 0.985$):

$$[\text{Mn(VII)}]_{e,r} = \frac{Q^0 [\text{Mn(VII)}]_{e,aq}}{(1 + b [\text{Mn(VII)}]_{e,aq})} \quad (3)$$

where $[\text{Mn(VII)}]_{e,r}$ and $[\text{Mn(VII)}]_{e,aq}$ are the manganese concentrations in the resin and in the aqueous solution at equilibrium, respectively, whereas Q^0 represented the amount of solute required to form a monolayer, accordingly to the present fit $66.3 \text{ mg} \cdot \text{g}^{-1}$, and b is a constant, in the present case with a value of 1.07.

The manganese (VII) load onto the resin can be also affected by the ionic strength presented by the aqueous solution. Thus, this variable was also investigated using aqueous solutions of $0.01 \text{ g} \cdot \text{L}^{-1}$ Mn(VII) and different amount of inorganic salts, the resin dose was in all the cases of $0.25 \text{ g} \cdot \text{L}^{-1}$. The results of these set of experiments are summarized in Table 3, showing that the presence of

TABLE 3. Influence of the feed ionic strength on Mn(VII) exchange

Ionic strength (M)	Mn(VII) load ^a (%)
1M LiCl	7.8
0.1 LiCl	25.0
0.1 Li NO ₃	32.0
0.1 NaCl	36.1
0.1 NaClO ₄	26.2
0.1 Li ₂ SO ₄	31.2

^aTime: 5 h

these salts, or the increase in the ionic strength of the aqueous medium decreased the percentage of manganese(VII) uptake, 87.5% when no salt is present in the feed against the figures presented in the Table.

Several others exchangers or adsorbents were tested in order to compare the capacity of Amberlite 958 to load manganese(VII) with that of these. In this case, the exchange resins or the adsorbents doses were of 0.25 g with aqueous feeds of $0.01 \text{ g} \cdot \text{L}^{-1}$ Mn(VII) at pH 5. The results obtained from these set of experiments being shown in Table 4. It can be seen, that in the present case the best percentage of metal adsorption and therefore the higher metal uptake is obtained with the MWCNT, following by Amberlite 958, Ionac SR7 and >Lewatit MP64. Lewatit EP-63, with an apparent high adsorption characteristics, did not load any appreciable amount of manganese(VII).

The experimental data from which manganese(VII) is uploaded onto Amberlite 958, Ionac SR7 and the MWCNT was tested against various models in order to gain knowledge of how this metal species is loaded onto the above three. From this fit, it is obtained that with either with Amberlite 958 and Ionac SR7, both acting as anionic exchangers, the metal load can be explained by the film-diffusion controlled process (Amberlite 958 $r^2 = 0.997$, rate constant = 0.011 min^{-1} , Ionac SR7 $r^2 = 0.990$, rate constant = 0.014 min^{-1}):

$$\ln(1 - F) = -kt \quad (4)$$

where as in the case of the non-functionalized MWCNT adsorbent, the manganese(VII) load is best explained by the particle-diffusion controlled model ($r^2 = 0.985$, rate constant 0.13 min^{-1})

$$\ln(1 - F^2) = -kt \quad (5)$$

TABLE 4. Mn(VII) load with different types of exchanger-adsorbents

Exchanger-adsorbent	Active group ^a	Mn (VII) load (%)	Mn(VII) uptake (mg·g ⁻¹)
Amberlite 958	QAS	87.5	35.0
MWCNT	none	93.0	37.2
Ionac SR7	QAS	69.0	27.6
Lewatit EP-63	none	nil	nil
Lewatit MP-64	QAS	20.3	8.1

Temperature: 20 °C, Time: 5 h, ^aQAS: quaternary ammonium salt

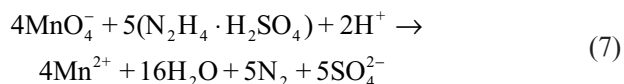
In the above equations, F is the factorial approach to the equilibrium, calculated as:

$$F = \frac{[\text{Mn(VII)}]_{\text{t,r}}}{[\text{Mn(VII)}]_{\text{e,r}}} \quad (6)$$

where both manganese concentrations have the same significance as above, and k is the rate constant (López Díaz-Pavón *et al.*, 2014).

3.2. Metal elution from the loaded resin

Different elution solutions were examined, in the case of 1M NaCl solution, there is not any appreciable removal from the metal loaded onto the resin well after 1 hour of reaction. In the case of 1 M HCl solution, the situation is a little better but the yield is not above 30% manganese recovery in the solution after 2 hours of reaction. The above is not the case, if solutions of hydrazine sulphate are used as eluant for the present system. In these cases, using various experimental conditions, i.e. $5 \text{ g} \cdot \text{L}^{-1}$ hydrazine sulphate solution, resin loaded with 14 mg Mn(VII)/g resin and liquid/resin ratios of $100\text{--}200 \text{ mL} \cdot \text{g}^{-1}$, the percentage of manganese recovery in the eluate is quantitative even at 15 min of contact. In the same experimental conditions that above, but using a $2.5 \text{ g} \cdot \text{L}^{-1}$ hydrazine sulphate solution as eluant, the recovery is 80% at 7.5 min and quantitative at 10 min of reaction. Moreover, using these hydrazine sulphate solutions, manganese is obtained in the eluate as the less hazardous form of Mn(II):



4. CONCLUSIONS

Various experimental conditions that influence the manganese(VII) uptake onto Amberlite 958 resin were investigated. With a stirring speed of 1000 rpm, maximum metal loading was achieved, indicating that at this speed a minimum in the thickness of the aqueous layer is attained, whereas an increase of the temperature from 20°C to 60°C increased the metal uptake in the resin, being this indicative of an endothermic process ($\Delta H^\circ = 31.1 \text{ kJ} \cdot \text{mol}^{-1}$). An equilibrium loading isotherm was experimentally obtained, and its better fit is to the Langmuir model, whereas the metal loading process responded well to the pseudo-first order kinetic law. The manganese(VII) uptake had been compared between various anion exchanger resins and adsorbents without any specific interchangeable group such as multiwalled carbon nanotubes and Lewatit EP-63 resin. The experimental results indicated that

best manganese(VII) uptake results were obtained with the carbon nanotubes and Amberlite 958 resin, and metal loading responded to the particle-diffusion (carbon nanotubes) or film-diffusion (Amberlite 958) controlled models. Best elution results were obtained with hydrazine sulphate solutions, and manganese released in the eluant as the less toxic form of Mn(II).

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