The removal of toxic metals from liquid effluents by ion exchange resins. Part XI: Cobalt(II) /H⁺/Lewatit TP260

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ABSTRACT: The removal of cobalt(II) from aqueous solutions by ion exchange with Lewatit TP260 resin was investigated. The experimental variables investigated in the present work were: stirring speed (300-1400 min^{-1}), temperature (20-60 ºC), pH of the aqueous solution (1-5), resin dosage (0.07-0.5 $g \cdot L^{-1}$) and the aqueous ionic strength. Cobalt(II) was loaded onto the resin by a cation exchange reaction in an endothermic and spontaneous process. Metal uptake was defined by the aqueous diffusion rate law and the pseudo-first order kinetic model (20 ºC) and the pseudo-second order kinetic model (60 ºC), whereas the experimental results responded well to the Langmuir isotherm. Several resins as well as non-oxidized and oxidized multiwalled carbon nanotubes were tested in order to compare the uptake results with that of Lewatit TP260, whereas the selectivity of the Co(II)-Lewatit TP 260 system was compared against the presence of other cations (Co-metal binary solutions) in the aqueous phase. Cobalt(II) can be recovered from metal-loaded resin by the use of acidic solutions (HCl or H_2SO_4).

KEYWORDS: Cobalt(II); Lewatit TP260; Liquid effluents; Multiwalled carbon nanotubes; Removal

RESUMEN: *La eliminación de metales tóxicos presentes en efluentes líquidos mediante resinas de cambio iónico. Parte XI: Cobalto(II)/H⁺/Lewatit TP260.* Este trabajo investiga sobre la eliminación de cobalto(II) presente en medios acuosos mediante la resina de cambio iónico Lewatit TP260. El sistema se estudia bajo distintas condiciones experimentales: velocidad de agitación (300-1400 min^{-1}), temperatura (20-60 ºC), pH del medio acuoso (1-5), dosificacion de la resina (0.07-0.5 $g \cdot L^{-1}$) y fuerza iónica de la disolución acuosa. El metal se carga en la resina mediante una reacción de intercambio catiónica en un proceso endotérmico y espontáneo. Esta reacción de intercambio se define por un proceso de difusión en la disolución acuosa y el modelo cinético de pseudo-primer orden (20 ºC) y el modelo cinético de pseudo-segundo orden (60 ºC), asimismo los resultados experimentales se ajustan bien a la isoterma de Langmuir. Los resultados experimentales del sistema se han comparado con los obtenidos con otras resinas de intercambio cationico y también con nanotubos de carbono de pared multiple oxidados y sin oxidar. Se estudia la selectividad del sistema Co(II)-Lewatit TP260 con respecto a la presencia de otros cationes (disoluciones binarias Co-metal) en el medio acuoso). El cobalto(II) cargado en la resina se puede fluir con disoluciones ácidas (HCl o H_2SO_4).

PALABRAS CLAVE: Cobalto(II); Efluentes líquidos; Eliminación; Lewatit TP260; Nanotubos de carbono de pared múltiple

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1. INTRODUCTION

Cobalt is an element necessary for human life, in fact, a biochemical key cobalt-bearing product is vitamin B_{12} or cyanocobalamin. However in excess, cobalt became toxic for humans. Upon ingesta, cobalt distributed in all tissues and liver, kidney and bones, thus it is responsible for a series of diseases, and also based on the animal data, the International Agency for Research on Cancer (IARC) had considered that this metal has a great possibility to produce cancer in humans (ATSDR, 2004; Kim *et al.*, 2006; Leyssens *et al.*, 2017).

Thus, the removal of this element from different environments is of a practical necessity. In aqueous media, cobalt is normally found as cobalt(II) or Co^{2+}, and the treatment of solutions containing it, included, as recent literature shows, ion exchange, adsorption, solvent extraction and liquid membranes processing (Ashtari and Pourghahramani, 2018; Bozecka *et al.*, 2018; Devi *et al.*, 2018; Farag *et al.*, 2018; Hayati *et al.*, 2018; Kara *et al.*, 2018; Ma *et al.*, 2018; Omelchuk and Chagnes, 2018; Song *et al.*, 2018; Vafaei *et al.*, 2018; Xavier *et al.*, 2018; Yuan *et al.*, 2018; Zherebtsov *et al.*, 2018; Anirudhan *et al.*, 2019; Rodriguez *et al.*, 2019).

In this new article of the series (Alguacil *et al.*, 2002; Alguacil, 2002; Alguacil, 2003; Alguacil, 2017a; Alguacil, 2017b; Alguacil, 2018a; Alguacil 2018b; Alguacil and Escudero, 2018; Alguacil 2019a; Alguacil 2019b), the removal of cobalt(II) from aqueous solutions by the use of the cationic exchanger Lewatit TP260 resin is investigated. Several experimental parameters affecting the metal loading onto the resin are considered, and also competitive cobalt-metals systems as well as the use of various resins and smart adsorbents are studied in terms of cobalt uptake. The elution of this metal from cobalt-loaded resin by different eluants is also investigated.

2. EXPERIMENTAL

Lewatit TP260 (Fluka) is a macroporous weakly acidic resin with di-Na^+ substituted (aminomethyl) phosphonic acid groups. Other cations exchange resins and chemicals used in the experimentation are of AR grade. The oxidized and non-oxidized multiwalled carbon nanotubes (MWCNTs) have the characteristics given elsewhere (Alguacil *et al.*, 2016; Alguacil *et al.*, 2017).

Batch experiments (loading and elution) were carried out in a glass reactor (250 mL), containing the aqueous solution of cobalt(II) and the resins/adsorbents, and was stirred *via* a four blades glass impeller at 1200 min^{-1} and 20 ºC, except when these variables were investigated.

Cobalt (and metals) in the aqueous solutions were analysed by AAS, whereas cobalt (and metals) loaded onto the resins/adsorbent were calculated by the mass balance.

3. RESULTS AND DISCUSSION

Since Lewatit TP260 is a cationic exchanger resin, it is logical to attribute the metal uptake onto the resin to the next equilibrium:

$$\left[-\left(Na^+\right)_{2_r} + Co^{2+}_{aq} \Leftrightarrow \left[-Co^{2+}_r + 2Na^+_{aq}\right.\right.\quad (1)$$
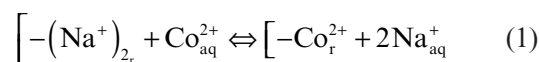
where [- represented the non-reactive part of the resin, and r and aq refereed to the species in the resin and in the aqueous solution, respectively.

3.1. Cobalt(II) loading onto Lewatit TP260

The variation of the stirring speed may have a key influence in the load of a given metal onto a given resin/adsorbent, though the investigation of this variable in these systems is very often neglected by researchers. Considering its experimental importance, in the present system the influence of this variable on cobalt(II) uptake onto the resins was first investigated by the use of aqueous solutions containing 0.01 g·L^{-1} Co(II) at pH 4 and resin dosages of 0.25 g·L^{-1}. The results obtained from this investigation being summarized in Table 1. It can be seen that the metal uptake increases from 28 mg·g^{-1} to 32 mg·g^{-1} when the stirring speed of the system increases from 300 to 1200 min^{-1}, and then remained constant. Thus, in the 1200-1400 min^{-1} range, the system reached a minimum in the thickness of the feed solution boundary layer and the metal uptake maximizes.

Using the results at 1200 min^{-1}, it was estimated the rate law for cobalt(II) uptake. The best fit (r^2= 0.9795) corresponded to the aqueous diffusion (Lopez Diaz-Pavon *et al.*, 2014):

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

TABLE 1. Influence of the stirring speed on cobalt(II) uptake onto the resin

Stirring speed, min^{-1}	[a]Metal uptake, mg·g^{-1}
300	28
600	30
1200	32
1400	32

[a]After 5 h (equilibrium conditions). Temperature: 20 ºC

with k estimated as 0.012 min⁻¹. In the above equation, t was the elapsed time, and F was calculated as:

$$F = \frac{[Co(II)]_{r,t}}{[Co(II)]_{r,e}} \qquad (3)$$

being $[Co(II)]_{r,t}$ and $[Co(II)]_{r,e}$ the cobalt concentrations in the resin at an elapsed time and at equilibrium, respectively.

The influence of the temperature (20-60 ºC range) on cobalt(II) loading onto the resin was investigated using the same aqueous solution and resin dose as above, and stirring speeds of 1200 min⁻¹. After 5 hours contact time, time in which the system achieved the equilibrium for all the range of temperatures investigated, the percentage of metal loading onto the resin is increased with the increase of the temperature, i.e., 80% at 20 ºC and 92% at 60 ºC, which corresponded to cobalt(II) uptakes of 32.0 and 36.8 mg·g⁻¹, respectively. Thus, it is concluded that the metal loading onto the resin is endothermic, with ΔHº estimated as 21 kJ·mol⁻¹, whereas ΔSº is 95 J·mol⁻¹ K⁻¹, representative of a process which incremented its randomness, and ΔGº -7 kJ·mol⁻¹, indicative of an spontaneous equilibrium. Moreover, the variation of the temperature indicated that the system reached the equilibrium at shorter contact times as the temperature is increased, i.e. 5 h at 20 ºC against 3 h at 60 ºC, and the results were fitted to the usual kinetics models. The results from this fit indicated that at 20 ºC, the pseudo-first order kinetic model (Hemavathy et al., 2019) best represented the experimental results (r²= 0.9763):

$$\ln\left([Co(II)]_{r,e} - [Co(II)]_{r,t}\right) = \ln[Co(II)]_{r,e} - kt \qquad (4)$$

with k of 0.012 min⁻¹ and ln $[Co(II)]_{r,t}$ of 3.4, value which compared well with the experimentally obtained of 3.5. At 60 ºC, the experimental results were best fitted to the pseudo-second order kinetic model (Alguacil, 2018c) (r²= 0.9718):

$$\frac{t}{[Co(II)]_{r,t}} = \frac{1}{k[Co(II)]_{r,e}^2} + \frac{t}{[Co(II)]_{r,e}} \qquad (5)$$

with k in the 5x10⁻⁴ min⁻¹ magnitude order.

The influence of the aqueous pH value on cobalt(II) uptake onto the resin was investigated using aqueous solutions of 0.01 mg·L⁻¹ Co(II) at various pH values (1-5) and resin dosages of 0.5 g·L⁻¹. The results from these set of experiments were summarized in Table 2, in which it can be seen that in the 3-5 pH interval range the metal loading was practically the same, but at the more acidic pH value the metal loads was nil, indicating that cobalt(II) was not recovered from the aqueous solution.

The influence of the continuous variation of the resin dosage onto the metal loads was investigated using the same aqueous solution that in previous experiments and resin dosages in the 0.07-0.5 g·L⁻¹ range. Table 3 showed the results obtained from these experiments, and it was concluded that the variation of the resin dosage produced an increment in the percentage of cobalt(II) loaded onto the resin, but at the same time the metal uptake decreased. These results were used to estimate the equilibrium isotherm, and the results from this fit indicated that the experimental results were best represented by the Langmuir model (r²= 0.9612) (Daraei and Mittal, 2017; Rahmani et al., 2017):

$$\frac{1}{[Co(II)]_{r,e}} = \frac{1}{Q^0} + \frac{1}{bQ^0}\frac{1}{[Co(II)]_{aq,e}} \qquad (6)$$

being $[Co(II)]_{aq,e}$ the metal concentration in the aqueous solution at the equilibrium. The value of b was estimated as 0.13 L·mg⁻¹, and the constant separation factor or equilibrium parameter, R_L was estimated using the next equation:

$$R_L = \frac{1}{1 + b[Co(II)]_0} \qquad (7)$$

TABLE 2. Influence of the aqueous pH on cobalt(II) uptake onto the resin

pH	ªCobalt uptake, mg·g⁻¹
1	NIL
3	19.6
5	19.9

ªAfter 5 h (equilibrium conditions). Temperature: 20 ºC. Stirring speed: 1200 min⁻¹

TABLE 3. Influence of the resin dosage on cobalt(II) uptake onto the resin

Resin dosage, g×L⁻¹	ª% Cobalt uptake	ªMetal uptake, mg·g⁻¹
0.50	99.5	19.9
0.38	87.0	23.2
0.25	80.0	32.0
0.18	73.5	42.0
0.13	70.2	56.0
0.07	40.1	62.0

ªAfter 5 h (equilibrium conditions). Temperature: 20 ºC. Stirring speed: 1200 min⁻¹

being $[Co(II)]_0$ the initial metal concentration in the aqueous solution. Thus, R_L, from the present system, is of 0.44, indicating a favourable system.

The increase the ionic strength (I) of the aqueous solution and its effect on cobalt(II) uptake was investigated using aqueous solutions of 0.01 g·L⁻¹ Co(II) and various LiCl concentrations, and resin dosages of 0.25 g·L⁻¹. Table 4 showed the decrease in metal loading as the ionic strength of the solution was increased.

In order to compare the performance of Lewatit TP260 with respect to cobalt(II) removal from aqueous solutions, different cationic exchangers were examined and also non-oxidized and oxidized multiwalled carbon nanotubes. The experimental conditions used were of aqueous solutions containing 0.01 g·L⁻¹ Co(II) at pH 4, exchangers/adsorbents dosages of 0.5 g·L⁻¹ and temperature of 20 ℃. Table 5 showed the results obtained from these sets of experiments. It can be seen that metal uptake is similar in the case of Lewatit SP112 and Lewatit TP260 resins, both acidic and in Na⁺ form though with different active group, and with near half the metal uptake in the case of oxidized-multiwalled carbon nanotubes. In the case of Lewatit OC1026 resin, cobalt uptake is about six times lower than those exhibited with SP112 and TP260 resin, and this uptake is even lower in the case of using multiwalled carbon nanotubes as adsorbent for cobalt(II).

The competitive removal of cobalt(II) in presence of other cations in the aqueous solution was also investigated. In this case, the aqueous solutions contained 1.7×10^{-4} M of each element (binary solutions) at pH 4 and the Lewatit TP260 dosage was of 0.25 g·L⁻¹. The results obtained in these sets of experiments being summarized in Table 6 in the form of the separation factor Co/Metal ($\beta_{Co/M}$), calculated. as:

$$\beta_{Co/M} = \frac{D_{Co}}{D_{Metal}} \qquad (8)$$

and where, D is the distribution coefficient (cobalt or metals) between the resin and the aqueous solutions, defined as:

$$D = \frac{[Co]_{r,e}}{[Co]_{r,aq}} \qquad (9)$$

and where $[Co]_{r,e}$ and $[Co]_{r,aq}$ are the cobalt (metals) concentrations in the resin and in the aqueous solution at equilibrium, respectively. Accordingly with the results presented in Table 6, only in the case of the Co-Mn and Co-Zn pairs, cobalt is separated selectively from the accompanying metal ($\beta>1$). In all the other cases, the accompanying metal is exchanged preferably to cobalt(II) ($\beta<1$). In these cases, it should be better accomplish a non-selective metals

TABLE 4. Influence of the aqueous ionic strength (I) on cobalt(II) uptake onto the resin

I, M	ᵃMetal uptake, mg·g⁻¹
-	32.0
0.05	29.6
0.13	16.0
0.25	14.8

ᵃAfter 5 h (equilibrium conditions). Temperature: 20 ℃. Stirring speed: 1200 min⁻¹

TABLE 6. Separation factors Co/Metal from binary solutions

System	ᵃβCo/M
Co(II)-Pb(II)	0.36
Co(II)-Zn(II)	1.5
Co(II)-Mn(II)	1.1
Co(II)-Ni(II)	0.95
Co(II)-Cr(III)	0.33
Co(II)-Cu(II)	0.84

ᵃAfter 5 h (equilibrium conditions). Temperature: 20 ℃. Stirring speed: 1200 min⁻¹

TABLE 5. Cobalt(II) uptakes using different ion exchangers/adsorbents

Exchanger/adsorbent	Active group	ᵃMetal uptake, mg·g⁻¹
Lewatit OC1026	Di-2ethylhexylphosphate	3.1
Lewatit SP112	(adsorbed)	19.8
Lewatit TP260	Strongly acidic in Na⁺ form	19.9
Oxidized-multiwalled carbon	This work	8
nanotubes	carboxylic groups	1.6
Multiwalled carbon	none	
nanotubes		

ᵃAfter 5 h (equilibrium conditions). Stirring speed: 1200 min⁻¹

Eluant	Eluant volume/ resin weight	Time, min	% Co elution
1 M HCL	100	5-15	94
1 M HCL	200	15-30	96
1 M HCL	2000	5-60	94
1 M H$_2$SO$_4$	100	5-15	93
1 M NaCL	100	15-60	5

Temperature: 20º C. Stirring speed: 300 min^{-1}

load onto the resin, and then separate them by selective or controlled elution process (Cerpa *et al.*, 2017). It should be noted here that in the case of cobalt(II), these multielmental systems demonstrated that the cobalt(II) uptake decreased with respect to the uptake resulted in the removal of the metal from a cobalt monoelemental solution, this should be attributed to interactions between the ions presented in the aqueous solution.

3.2. Cobalt (II) elution from Co(II)-loaded Lewatit TP260 resin

Elution experiments were performed with resin loaded with 14 mg Co/g under various experimental conditions. Table 7 showed that the variation of the volume of eluant versus resin weight had a negligible effect on the percentage of cobalt eluted using 1 M HCl solutions as eluant. In the same Table, was presented the result obtained when the eluant solution was changed from HCl to H$_2$SO$_4$ or NaCl solutions. This change in the solution composition produced a dramatic change in the results, since with 1 M sulphuric acid the percentage of cobalt eluted is the same than that obtained with 1 M HCl solution, but when 1 M NaCl solution was used, the percentage of cobalt recovered in the solution was of a mere 5%. From the above results, it is seemed clear that the elution responded to the next equilibrium:

$$\left[-Co^{2+} + 2H_{aq}^+ \Leftrightarrow \left[-H_2^+ + Co_{aq}^{2+}\right.\right. \tag{10}$$
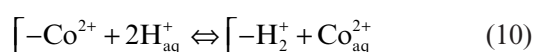
where the subscript aq, represented the elution phase. Thus, a washing of the resin with NaOH solution is needed in order to recycle back to the Na$^+$ form.

4. CONCLUSIONS

– Cobalt(II) is removed from aqueous solutions by the use of Lewatit TP260 resin. The removal of the metals is attributed to a cation exchange mechanism which released Na$^+$ ions to the aqueous solution. A minimum thickness of the aqueous diffusion layer is reached with agitation speeds of around 1200 min^{-1}, in this conditions cobalt uptake onto the resin is a maximum, and the metal uptake onto the resin responded to the aqueous diffusion model.

– The exchange process is endothermic and spontaneous ($\Delta H°= 21$ kJ·mol^{-1} and $\Delta G°= -7$ kJ·mol^{-1}), whereas the metal upload result in an increase disorder of the system ($\Delta S°= 95$ J·mol^{-1}K^{-1}). At 20 °C, the experimental results fit well to the pseudo-first order kinetic model, but at 60º C the best fit corresponded to the pseudo-second order kinetic model. At acidic pH values the resin does not remove the metal from the solution, however in the 3-5 pH range, and under the experimental conditions used in this work, the load is 19.6 mg·g^{-1}.

– The increase of the aqueous ionic strength decreased the metal removal from the solution, however, an increase in the resin dosage increase this removal from 40% to 99.5% for 0.07 to 0.5 g·L^{-1} resin dosages, respectively.

– The resin performed well, in the removal of cobalt(II) from aqueous solutions, against oxidized and non-oxidized multiwalled carbon nanotubes, however, the resin does not performed well, with respect to its selectivity towards Co^{2+}, in the presence of a series of accompanying-metal ions in the aqueous solution. Cobalt is eluted from the loaded resin by the use of acidic solutions.

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