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The removal of toxic metals from liquid effluents by ion exchange resins. Part X: Antimony(III) /H^+/Ionac SR7

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ABSTRACT: The present work investigates the removal of Sb(III) from acidic aqueous solution by the ion exchange resin Ionac SR7. Several experimental parameters were considered in the study: stirring speed of the system (280–1000 min^{-1}), temperature (20–60 °C), aqueous acidity (0.1–2 M HCl), resin dosage (2.5–20 $g\cdot L^{-1}$) and the source of the aqueous ionic strength. The load of Sb(III) onto the resin is attributable to an anion exchange reaction, being this process exothermic and spontaneous. Based in the experimental data, several modes were tested to explain loading kinetics, loading mechanism and loading isotherm, which respectively are the pseudo-second order kinetic model, the particle-diffusion controlled model and the Freundlich isotherm. The performance of the resin with respect to antimony load was compared against other anion exchanger resins and multiwalled.carbon nanotubes. It was found that water is an effective medium to remove antimony(III) from the metal-loaded resin.

KEYWORDS: Antimony(III); Ionac SR7; Liquid effluents; Multiwalled carbon nanotubes; Removal

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RESUMEN: *La eliminación de metales tóxicos presentes en efluentes líquidos mediante resinas de cambio iónico. Parte IX: Antimonio(III))/H^+/Ionac SR7.* Este trabajo presenta los resultados obtenidos en el estudio de la eliminación de Sb(III) de disoluciones acuosas acidas utilizando la resina de cambio iónico Ionac SR7. En el estudio se consideran diferentes variables experimentales: la velocidad de agitación (280–1000 min^{-1}), la temperatura (20–60 °C), la concentración de ácido en la disolución acuosa (0,1–2 M HCl), la concentración de resina (2,5–20 $g\cdot L^{-1}$), y el tipo de sal empleado en los ensayos a fuerza iónica constante. La carga de Sb(III) en la resina responde a una reacción de intercambio aniónico, siendo esta exotérmica y espontánea. Los resultados experimentales se han utilizado para estimar el modelo cinético, el modelo y la isoterma de carga del metal en al resina, encontrándose que estos responde a un modelo cinético de pseudo-segundo orden, a un modelo de difusión en partícula y a la isoterma de Freundlich, respectivamente. Los resultados obtenidos en la resina Ionac SR7 se han comparado con los obtenidos con otras resinas de intercambio aniónico y con nanotubos de carbono de pared múltiple. El antimonio cargado en al resina se puede eluir de forma efectiva usando agua como eluyente.

PALABRAS CLAVE: Antimonio(III); Efluentes líquidos; Eliminación; Ionac SR7; Nanotubos de carbono de pared múltiple

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1. INTRODUCTION

Probably not as famous, in terms of hazardourness, as mercury, lead, cadmium, etc., antimony is an element with a potential health-risk when it is present in the air, waters or soils.

Similarly to others metals, antimony toxicity is dependent on different factors including: exposure and duration doses, route of inhalation, sex, age, etc. However, there is a general lacks of information about the effects that antimony inhalation had on human organisms, but based in these scarce data, it can be determined that oral inhalation of this element had several effects: systemical, neurological, developmental and cancer (ATSDR, 2017). It must be noted here, that this author, while consulting the previous document, find one repeated sentence: *no studies were located regarding effects in humans after exposure to antimony*.

In the case of waters, antimony can be found due to contamination from mining and smelters, shooting ranges and road sides that contain dust from brake pads and tires. It was recommended that the antimony concentration in drinking waters did not exceeded 5 $\mu g \cdot L^{-1}$ (WHO, 2011), thought a great exposure can be possible when one drinks water from PET (polyethylene phthalate) water bottles. Antimony is considered as a hazardous substance in water (USEPA, 2011).

From a chemical point of view, and similarly to arsenic, Sb(III) is more toxic than Sb(V) and the inorganic compounds are more toxic than the organic ones.

Thus, several technologies are being used to remove antimony from liquid effluents, wastewaters, etc. Recent investigation included: coagulation/flotation, membrane processes, etc. (Ungureanu *et al.*, 2015), liquid-liquid extraction with ionic liquids (Dupont and Binnemans, 2016), precipitation or adsorption with iron based compounds (Multani *et al.*, 2016; Qi and Pichler, 2016; Deng *et al.*, 2017; Yang *et al.*, 2017; Mitrakas *et al.*, 2018), bacterial treatment (Zhu *et al.*, 2018), and various adsorbents, i.e. chitosan-modifies pumice, calcined hydrotalcite (Sari *et al.*, 2017; Constantino *et al.*, 2018).

Following in the series of articles devoted to the removal of toxic metals from aqueous solutions using ion exchange resins (Alguacil, 2002; Alguacil *et al.*, 2002; Alguacil, 2003; Alguacil, 2017a; Alguacil, 2017b; Alguacil, 2018a; Alguacil, 2018b; Alguacil, 2018c; Alguacil and Escudero, 2018), the present investigation deeps in the use of Ionac SR7 ion exchange resin to eliminate antimony(III) from solutions under various experimental conditions. Moreover, the performance of the resin was compared against other potentials adsorbents/exchangers for this metal or metalloid.

2. EXPERIMENTAL

Ionac SR7 (Fluka) has as active group a quaternary ammonium salt, the resin beads presented particle sizes in the 15–50 µm range. Other resins and chemical used in the investigation are of AR grade, whereas the source for Sb(III) solutions was a commercially available AAS standard. The multiwalled carbon nanotubes (MWCNTs) has the characteristics given elsewhere (Alguacil *et al.*, 2016).

The loading and elution experiments were carried out in a glass reactor (250 mL), where the aqueous solutions containing Sb(III) in HCl medium and the resin were stirred *via* a four blades glass impeller at 750 min^{-1} and 20 °C, except when these variables are investigated.

Antimony(III) in the aqueous solutions was analysed by AAS whereas antimony(III) uptake onto the resin was calculated by the mass balance.

3. RESULTS AND DISCUSSION

3.1. Antimony(III) uptake onto Ionac SR7

The influence of the stirring speed on Sb(III) loading onto the resin was first study, and the results derived from this investigation were shown in Table 1, together with the experimental conditions used in this set of experiments. It can be seen that Sb(III) uptake increased with the increase of the stirring speed up to 750 min^{-1} and then decreased. These results indicated that as the stirring speed increased the thickness of the aqueous boundary layer decreased reaching a minimum at 750 min^{-1} (maximum loading). The decrease of Sb(III) loads onto the resin at 1000 min^{-1} can be attributable to the formation of local equilibria in the system which results in finding a lower antimony(III) concentration in the resin.

The results obtained at 750 min^{-1} were used to estimated the kinetics of the exchange reaction, from this calculation it was found that the present system best responded to the pseudo-second order kinetic model (Wang *et al.*, 2017):

$$\frac{t}{[Sb]_{r,t}} = \frac{1}{k[Sb]_{r,e}^{2}} + \frac{t}{[Sb]_{r,e}} \quad (1)$$

TABLE 1. Effect of stirring speed on antimony(III) uptake onto the resin

Stirring speed (min^{-1})	Metal uptake ($mg \cdot g^{-1}$)
280	0.46
500	0.48
750	0.51
1000	0.44

Aqueous solution: 0.01 $g \cdot L^{-1}$ Sb(III) and 0.5 M HCl; Resin dosage: 10 $g \cdot L^{-1}$; Temperature: 20 °C; Time: 3 h with r^2= 0.9993 and k= 0.15 g mg^{-1} min^{-1}. In the above equation, k is the rate constant, $[Sb]_{r,t}$ and $[Sb]_{r,e}$ are the antimony(III) concentration in the resin at elapsed time and equilibrium, respectively and t is the elapsed time.

Moreover, the data at 750 min^{-1} were also used to model the loading process, and best fit was obtained with the particle-diffusion controlled model (López Diaz-Pavón *et al.*, 2014):

$$\ln\left(1-F^2\right)=-kt \tag{2}$$

where F is the factorial approach to equilibrium, defined as:

$$F=\frac{\left[Sb\right]_{r,t}}{\left[Sb\right]_{r,e}} \tag{3}$$

The rate constant value k is 0.026 min^{-1} and r^2 = 0.9908.

The influence of the temperature (20–60 °C) on Sb(III) uptake onto the resin was also studied using the same experimental conditions as above and 750 min^{-1} as stirring speed. The results obtained from this experimentation being summarized in Table 2. It is observed that the increase of the temperature results in a decrease of the metal loaded onto the resin, but as can be seen in Fig. 1, plotting $[Sb]_{r,t}/[Sb]_{r,e}$ versus time, the equilibrium was reached at shorter times as the temperature of the system was increased, the above was specially sound at the beginning of the experiment, i.e. 69% at 60 °C, versus 50% and 41% at 40 °C and 20 °C, respectively, and 7.5 min of elapsed time. By using the well known thermodynamics relationships the next values was obtained for ΔH°, ΔS° and ΔG°, −2.3 kJ·mol^{-1}, −27 J·mol^{-1} K and −1.5 kJ·mol^{-1}, respectively. This indicated that the exchange reaction is exothermic, whereas the negative entropy change can be attributed to a decrease of randomness at the solid-liquid interface during the anion exchange process. The negative ΔG° value indicated a spontaneous system.

The effect of aqueous acidity on metal uptake was investigated in the 0.1–2 M HCl concentrations range, and the results were shown in Fig. 2, plotting the metal uptake onto the resin against time. It can be seen that the load of antimony(III) onto the resin increased with the increase of the aqueous acidity from 0.1 to 2 M HCl, being this behaviour attributable to the formation of the $SbCl_4^-$ species in the aqueous solution (Fig. 3), which is exchanged with the chloride ion of the resin, thus, the antimony(III) was loaded onto the resin *via* an anion exchange mechanism:

Table 2. Influence of temperature on antimony(III) uptake onto the resin

Temperature (° C)	Metal uptake (mg·g^{-1})
20	0.51
40	0.49
60	0.47

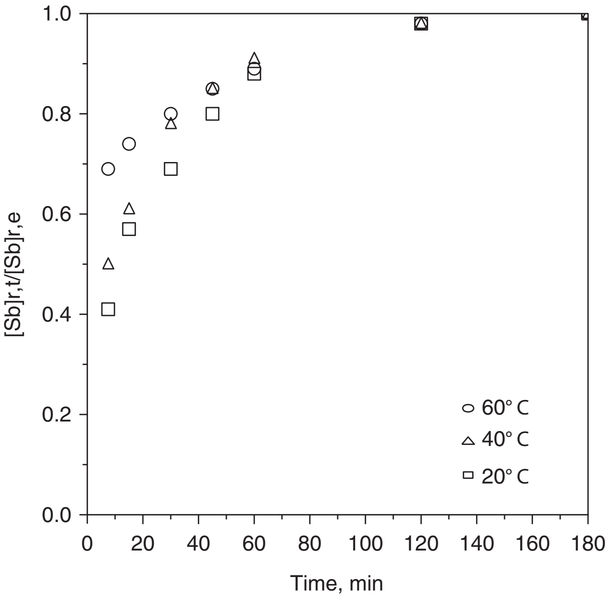

Figure 1. Influence of temperature on time to achieve equilibrium.

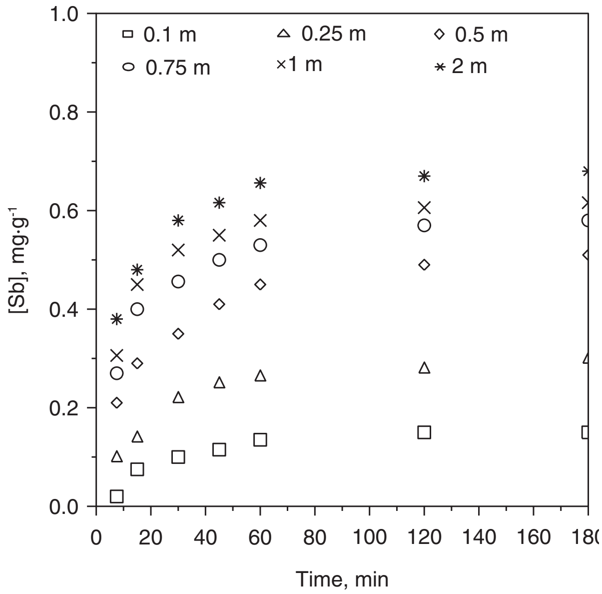

Figure 2. Sb(III) uptake onto the resin at different HCl concentrations in the aqueous phase. Aqueous solution: 0.01 g·L^{-1} Sb(III) and HCl; Resin dosage: 10 g·L^{-1}; Temperature: 20 °C; Stirring speed: 750 min^{-1}.

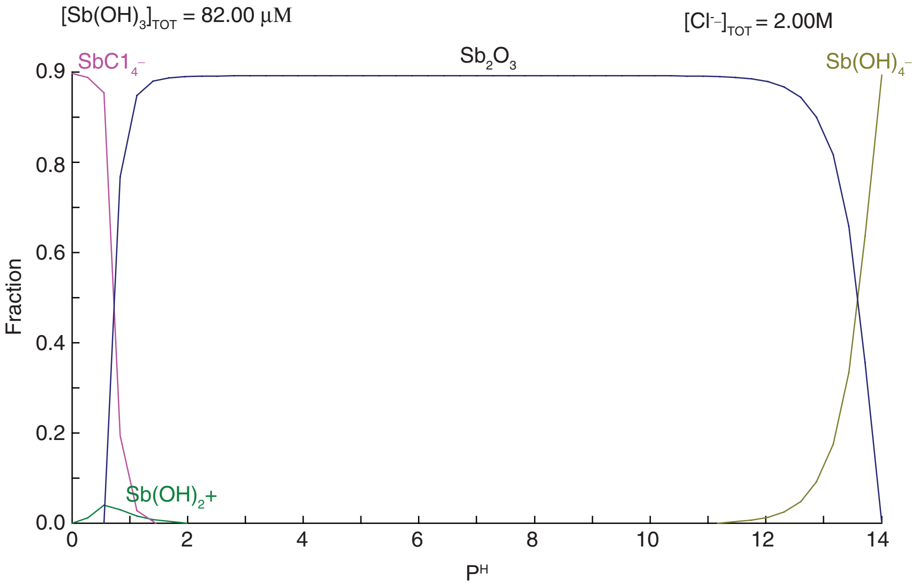

FIGURE 3. Sb(III) speciation at 2 M HCl.

$$SbCl^-_{4_{aq}} + \left[-Cl^-_r \Leftrightarrow \left[-SbCl^-_{4_r} + Cl^-_{aq}\right.\right. \quad (4)$$

where [- represented to the non-reactive part of the resin and the subscripts aq and r to the aqueous and resin phases.

Several resin doses (2.5–20 g·L^{-1}) were used to investigate their influence of antimony(III) uptake onto the resin. The aqueous solution was of 0.01 g·L^{-1} Sb(III) and 0.5 M HCl, whereas the temperature and the stirring speed were 20 °C and 750 min^{-1}. The results were summarized in Table 3, showing that the percentage of antimony(III) loaded onto the resin increased with the increase of the resin dosage. These equilibrium values were used to model the loading isotherm for the present system, both the Langmuir and Freundlich isotherms were tested. Accordingly with this approach, it was found that the load of Sb(III) in 0.5 HCl medium best fits the Freundlich isotherm (Naghizadeh *et al.*, 2017):

$$\ln\left[Sb\right]_{r,e} = \ln K_F + \frac{1}{n}\ln\left[Sb\right]_{aq,e} \quad (5)$$

with a discrete r^2= 0.8950 and ln K_F = −2,04 and 1/n of 0.81.

The source for maintaining a constant ionic strength and its effect on antimony(III) loading onto the resin was investigated by the use of a resin dosage of 10 g·L^{-1} and aqueous solutions of 0.01 g·L^{-1} Sb(III) at constant I= 0.5 M. In this series of experiments, the temperature was of 20 °C and the stirring speed was fixed at 750 min^{-1}. The results, Table 4, showed a definitive influence of the source of the ionic strength, since best results were obtained with HCl, against the presence of salts in the aqueous solution.

The performance of Ionac SR7 resin with respect antimony(III) uptake was compared against the use of others anion exchange resins containing quaternary ammonium chloride active groups and also

TABLE 3. Equilibrium values for antimony(III) loading at various resin doses

Resin dosage (g·L^{-1})	**% Sb(III) loading**	**$[Sb]_{aq}$ (mg·L^{-1})**	**$[Sb]_r$ (mg·g^{-1})**
2.5	22	7.8	0.88
5	34	6.6	0.68
7.5	44	5.6	0.59
10	51	4.9	0.51
15	58	4.2	0.39
20	64	3.6	0.32

TABLE 4. Antimony(III) uptake onto the resin at constant ionic strength, I= 0.5 M, in the aqueous solution. Influence of the source electrolyte

Electrolyte	**Sb(III) uptake (mg·g^{-1})**
HCl	0.51
LiCl	0.10
NaCl	-
NH_4Cl	0.06
$CrCl_3$	-

Time: 3 h

Table 5. Antimony(III) uptake onto different anion exchange resins and multiwalled carbon nanotubes

Exchanger/adsorbent	Sb(III) uptake (mg·g^{-1})
Ionac SR7	0.55
Dowex 1x8	0.37
Amberlite IRA958	0.03
Multiwalled carbon nanotubes	0.64

Aqueous solution: 0.01 g·L^{-1} Sb(III) and 0.5 M HCl; Exchanger/adsorbent dosage: 7.5 g·L^{-1}; Temperature: 20 °C; Stirring speed: 750 min^{-1}; Time: 1 h

Table 6. Results of the elution step

Volume eluant/resin weight (mL·g^{-1})	% Sb(III) elution	[Sb(III)] (mg·L^{-1})
12.5	80	29.8
25	99	17.8
50	99	8.9
100	98	4.4

Eluant: water; Resin loaded with 0.45 mg Sb(III)/g Temperature: 20° C; Time: 1 h

against multiwalled carbon nanotubes. The results from this set of experiments were summarized in Table 5. It can be seen from these results that, in the present experimental conditions, best antimony(III) loading was firstly achieved with the multiwalled carbon nanotubes and secondly with Ionac SR7 resin.

3.2. Antimony(III) elution from Sb(III)-loaded resin

In this system, the elution step was performed surprisingly easy, since water was an effective eluant for Sb(III)-loaded resin. The results from this investigation are summarized in Table 6, it can be seen how yields for this step are around 98% for most of the experimental conditions used, and only this yield decreased to 80% when using the lowest volume of eluant/resin weight relationship. Very probably, in the elution step antimony(III) was released to the aqueous solution as $SbCl_3$ or Sb^{3+} and $3Cl^-$, whereas the resin is regenerated to its chloride form.

4. CONCLUSIONS

- Antimony(III) can be effectively removed from acidic (HCl) aqueous solutions by the use of ion exchange technology using the anionic exchanger resin Ionac SR7. The exchange process is dependent upon various experimental variables:
    - the stirring speed. An increase in the stirring speed increased Sb(III) uptake onto the resin up to 750 min^{-1}, at higher stirring speed this uptake decreased due to the formation of local equilibria which inhibited the anion exchange process.
    - the HCl concentration in the aqueous solution. Antimony(III) uptake increase with the increase of the acid concentration in the solution.
    - the resin dosage. The increase of the resin dosage increased the percentage of Sb(III) loaded onto the resin, however, the Sb(III) uptake onto Ionac SR7 decreased as the resin doses increased.
    - the source of the aqueous ionic strength. Sb(III) uptake onto the resin is greatly influenced by this variable. When HCl is present in the aqueous phase, Sb(III) load is higher than when the source from Cl^- ions are inorganic salts
- The increase of the temperature (20–60 °C) produced a slight decrease of the Sb(III) uptake onto the resin, the exchange process is thus exothermic and spontaneous. The uptake of Sb(III) onto the resin best responded to the pseudo-second kinetic order model and to the Freundlich isotherm. Antimony(III) uptake can be represented by the particle-diffusion controlled model.
- Multiwalled carbon nanotubes produced a higher Sb(III) uptake than Ionac SR7.
- Antimony(III) can be recovered from Sb(III)-loaded Ionac SR7 resin by the use of water as eluant.

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