The removal of toxic metals from liquid effluents by ion exchange resins. Part XII: Mercury(II) /H+/Lewatit SP112

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ABSTRACT: Mercury(II) was eliminated, from acidic aqueous solutions, by the cationic ion exchange resin Lewatit SP112. Various experimental conditions were tested in the investigation, such as, stirring speed (275–1000 min^{-1}), temperature (20–60 °C), pH of the aqueous solution (0–4) and resin dosage (0.05–0.4 g·L^{-1}). Mercury(II) uptake onto the resin decreased with the increase of the temperature (exothermic reaction) in a spontaneous process, whereas the moving boundary model represented the metal uptake in the 20–60 °C temperatures range. Moreover, the experimental data fitted to the second order kinetic model (275 min^{-1}) or the pseudo-second order kinetic model (500–1000 min^{-1}), though maximum metal uptake was not dependent on the stirring speed applied to the system. The experimental results responded well to the Langmuir type-2 isotherm. The Hg(II)-loading ability of Lewatit SP112 was compared against that of other resins and non-functionalized multiwalled carbon nanotubes. Mercury(II) loaded onto the resin can be eluted by means of various eluants, furher, zero valent mercury was yielded from the eluates.

KEYWORDS: Lewatit SP112; Liquid effluents; Mercury(II); Multiwalled carbon nanotubes; Removal

RESUMEN: *La eliminación de metales tóxicos presentes en efluentes líquidos mediante resinas de cambio iónico. Parte XII: Mercurio(II)/H+/Lewatit SP112.* El mercurio(II) puede ser eliminado de disoluciones acuosas acidas mediante la resina de intercambio catiónico Lewatit SP112. Se ha investigado la influencia de distintas variables experimentales sobre la carga del mercurio(II) en la resina: velocidad de agitación (275–1000 min^{-1}), temperatura (20–60 °C), valor de pH del medio acuoso (0–4) y dosificación de la resina (0.05–0.4 g·L^{-1}). La carga de mercurio(II) en la resina disminuye con el aumento de la temperatura (reacción exotérmica) en un proceso espontaneo, mientras que el modelo de núcleo recesivo representa al mecanismo de carga del metal en el rango de temperaturas investigado. Los datos experimentales se ajustan al modelo cinético de segundo orden (275 min^{-1}) o al modelo de pseudo segundo orden (500–1000 min^{-1}), aunque la carga máxima del metal en la resina no depende de la velocidad de agitación. Los datos experimentales se ajustan a la isoterma tipo-2 de Langmuir. Se ha comparado la carga de mercurio(II) con distintas resinas y con nanotubos de carbono de pared múltiple. El mercurio(II) puede ser eluido con distintos eluyentes, pudiéndose obtener mercurio en estado de oxidación 0 a partir de las disoluciones de elución conteniendo al Hg(II).

PALABRAS CLAVE: Efluentes líquidos; Eliminación; Lewatit SP112; Mercurio(lI); Nanotubos de carbono de pared múltiple

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1. INTRODUCTION

Mercury is, together with gold, silver, lead, copper and iron, one of the six elements known and used by the Mankind from the beginning, however, and unlike the others, mercury had gained a bad reputation of harmfulness and toxicity, despite the fact that under centuries it had various medical uses. Consequently, mercury is banned in the European Union and most industrialized countries, with more strict regulation from January 1, 2010. Together with the recycling of mercury, the metal and compounds are nowadays still consumed in fluorescent lamps, electronic devices, industrial chemicals, and the chloralkali and dental industries. Besides the above, the barely legal or illegal gold-mining industry appeared to be one of today´s greater mercury consumer in the world. Taking into consideration the above, mercury bans and uses, it is not quite rare that actually worldwide mercury production is around 3500 ton/year (Table 1) with near 20 countries involved in the total mercury production (USGS, 2019). Major mercury reserves seemed to be located in China, Kyrgyzstan and Peru, with Spain having appreciable estimated mercury resources.

Considering only inorganic mercury, organic mercury is another world, this element is basically found in aqueous solutions in the form of Hg^{2+} cation, or forming a number of complexes i.e. $HgCl_4^{2-}$, $Hg(CN)_4^{2-}$, $Hg(Tu)_2^{2+}$, etc. Thus, and based in the above, the elimination of Hg(II) from aqueous streams is a topic of interest from researchers, which explored new systems to achieve this goal, This interest is reflected in the number of articles published in the 2106–2019 period years regarding the removal of mercury(II) using adsorbents/ion exchangers; the number of articles surpassed well the articles devoted to the use of liquid-liquid extraction or liquid membranes technologies for such removal (Table 2).

Following on 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; Alguacil, 2019c), in this work the removal of Hg(II) from acidic aqueous solutions by using the cationic exchange resin Lewatit SP112 is investigated. Several variables affecting mercury(II) uptake onto the resin are studied, as well as the performance of various resins and multiwalled carbon nanotubes on Hg(II) uptake. The elution of mercury(II) from metal-loaded Lewatit SP112 resin by different eluants is also tested, and also the precipitation of zero valent mercury as end product of the process.

2. EXPERIMENTAL

Lewatit SP112 (Fluka) is a macroporous strongly acidic resin, which presented the form of spheres with a high degree of crosslinked polystyrene matrix containing sulfonic groups; the bead size is in the 0.4–1.25 mm range. Other chemicals, including the various cations exchange resins used in the experimental work are of AR grade. The multiwalled carbon nanotubes (MWCNTs) have the characteristics given elsewhere (Alguacil *et al.*, 2016).

The experimental investigation, in batch form both in loading and elution steps, was carried out in a glass reactor vessel (250 mL), containing the Hg(II) aqueous solution and the corresponding resins/adsorbents dosage. The system was stirred *via* a four blades glass impeller at 500 min^{-1} and 20 °C, except when these variables were investigated.

Mercury in the aqueous solutions was analysed by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES), whereas mercury loaded onto the resins/adsorbent was calculated by the mass balance.

3. RESULTS AND DISCUSSION

As it was mentioned in the Introduction section, this investigation was based in the removal of Hg^{2+} species from aqueous solutions, and being Lewatit SP112 a cationic exchange resin, metal uptake onto the resin can be represented by the next equilibrium:

$$2\left[-(SO_3Na) + Hg_{aq}^{2+} \Leftrightarrow \left[-(SO_3^-)_2 Hg_r^{2+} + 2Na_{aq}^+ \right.\right. \quad (1)$$
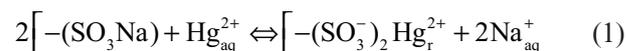
where [- represented the unreactive part of the resin, and r and aq are the species present in the resin and in the aqueous solution, respectively.

TABLE 1. Top mercury producers countries

Country	2017 year	2018 year
China	3380	3000
Mexico (export)	197	200
Tajikistan	100	100
Total production	3790	3400

TABLE 2. Hg^{2+} publications related to its removal from aqueous solutions

Year	Adsorption/ion exchange	Liquid-liquid extraction	Liquid membranes
2016	104	1	nil
2017	78	2	nil
2018	89	nil	1
2019[a]	115	1	nil

[a]Web of Science as 3rd September 2019

3.1. Mercury(II) uptake onto Lewatit SP112 resin

Along the works of this series, it was mentioned the importance that the stirring speed, applied to a system, may have on the corresponding metal uptake, and that this was an experimental variable to consider in every exchange-adsorption system. In the present case, experiments to investigate the influence of this variable on metal uptake had been carried out using aqueous solutions of 0.01 $g \cdot L^{-1}$ Hg(II) at pH 4, and resin concentrations of 0.05 $g \cdot L^{-1}$. Results derived from these sets of experiments were shown in Fig. 1, and it can be deduced from these results that maximum mercury removal from the solution was 45% (90 $mg \cdot g^{-1}$ uptake) for the range of stirring speeds investigated. Thus, this variable had not any appreciable influence on metal loading, but it had an influence on the time to achieve equilibrium; accordingly, as the stirring speed was increased the variation of the $[Hg]_{s,t}/[Hg]_{s,0}$ relationship had a more pronounced slope. The experimental results were fitted to various kinetic models, and the results indicated that at 275 min^{-1}, the second order kinetic model (Ho, 2006) best fitted the data:

$$\frac{1}{[Hg]_{s,t}} = \frac{1}{[Hg]_{s,0}} + kt \qquad (2)$$

with $r^2 = 0.9982$ and $k = 4.6 \times 10^{-4}$ L/mg min, whereas in the 500–1000 min^{-1} the experimental data were well explained by the pseudo-second order kinetic model (Fu et al., 2019):

$$\frac{1}{[Hg]_{r,t}} = \frac{1}{k[Hg]_{r,e}^2} + \frac{1}{[HG]_{r,e}} t \qquad (3)$$
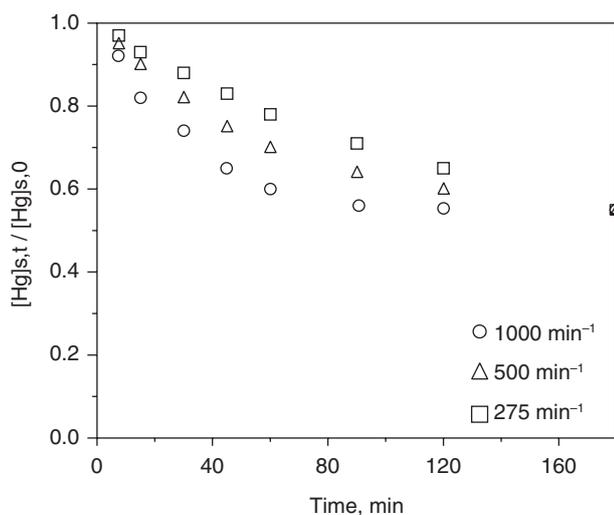
with $r^2 = 0.9938$ and 0.9871, and k values of 8.5×10^{-4} and 1.6×10^{-3} g/mg min) for the stirring speeds of 500 and 1000 min^{-1}, respectively. In Eqs. (2) and (3), $[Hg]_{s,t}$, $[Hg]_{r,t}$, $[Hg]_{s,0}$ and $[Hg]_{r,e}$ were the mercury concentrations in the solution and in the resin at an elapsed time t, and the metal concentrations in the initial solution and in the resin at equilibrium, respectively. In the present experimental conditions, in the 275–1000 min^{-1} range, the system reached a minimum in the thickness of the solution boundary layer and the metal uptake reached a maximum.

Temperature was another variable which had been investigated in the 20–60 °C range, and the results were given in Table 3, being D defined as:

$$D = \frac{[Hg]_{r,e}}{[Hg]_{s,e}} \qquad (4)$$

where $[Hg]_{r,e}$ had the same significance that in Eq. (3), and $[Hg]_{s,e}$ is the mercury concentration in the solution at the equilibrium. From these values it can be seen that the metal uptake onto the resin decreased (lower D value) with the increase of the temperature, with ΔH° and ΔS° values of −15 $kJ \cdot mol^{-1}$ and −23 $J \cdot mol^{-1}K$, respectively, derived from the plot of log D versus 1000/T. The value of ΔG° for the system was estimated as -8 $kJ \cdot mol^{-1}$. Thus, the metal uptake was exothermic and spontaneous, whereas the negative entropy values indicated an exchange process with decreased its randomness. The experimental data, derived from studying the influence of the temperature on mercury loading onto the resin, were used to estimate the model which explained the exchange process; in the 20–60 °C temperature range, the data fitted well with the moving boundary model (López Díaz-Pavon et al., 2014):

$$3 - 3(1-F)^{2/3} - 2F = kt \qquad (5)$$

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

$$F = \frac{[Hg]_{r,t}}{[Hg]_{r,e}} \qquad (6)$$

FIGURE 1.   Non-dimensional variation $[Hg]_{s,t}/[Hg]_{s,0}$ at different stirring speeds. Temperature: 20 °C.

TABLE 3.   Influence of temperature on Hg^{2+} uptake onto Lewatit SP112

Temperature, °C	log D
20	1.43
40	1.26
60	1.11

Aqueous solution: 0.01 $g \cdot L^{-1}$ Hg(II) at pH 4. Resin dosage: 0.1 $g \cdot L^{-1}$.
Stirring speed: 500 min^{-1}. Time: 3 h

with r^2 values of 0.9841, 0.9881 and 0.9966 and k values of 5.3×10^{-3}, 1.4×10^{-2} and 1.3×10^{-2} min^{-1}, for 20, 40 and 60 °C, respectively.

The variation of the aqueous phase pH value on Hg^{2+} using resin dosages of 0.1–0.4 g·L^{-1}, and aqueous solutions containing 0.01 g·L^{-1} mercury(II) at different pH values (0 to 4). The results from this investigation were shown in Fig. 2, plotting the percentage of mercury(II) loaded onto the resin versus pH. These results showed that the percentage value decreased as the value of the pH decreased; this behaviour was repeated for every resin dosage used in the experimentation, though this effect was less pronounced as the resin dosage increased.

Various resin dosages (0.05–0.4 g·L^{-1}) were used to investigate their influence on Hg(II) load onto the resin. In these series of experiments, the aqueous solution was of 0.01 g·L^{-1} Hg^{2+} at pH 4, whereas the temperature was of 20 °C and the stirring speed of 500 min^{-1}. The results were plotted in Fig. 3, where the y-axe represented the non-dimensional $[Hg]_{s,t}/[Hg]_{s,0}$ relationship, and the x-axe the time. From these plots it is observed that the increase of the resin dosage produced an increase of the mercury left in the solution, at every time. From these experimental results, in Table 4 the equilibrium results, from which the fit of the data were done on Langmuir or Freundlich isotherms, was given. The data from this Table best fitted (r^2= 0.9932) to the Langmuir type-2 isotherm (Haghdoost *et al.*, 2017):

$$\frac{1}{[Hg]_{r,e}} = \frac{1}{[Hg]_m} + \frac{1}{k[HG]_m[Hg]_{s,e}} \qquad (7)$$

with k= 0.3 L·mg^{-1} and $[Hg]_m$= 152 mg·g^{-1} being this last value the maximum metal uptake onto the resin. The dimensionless separation factor:
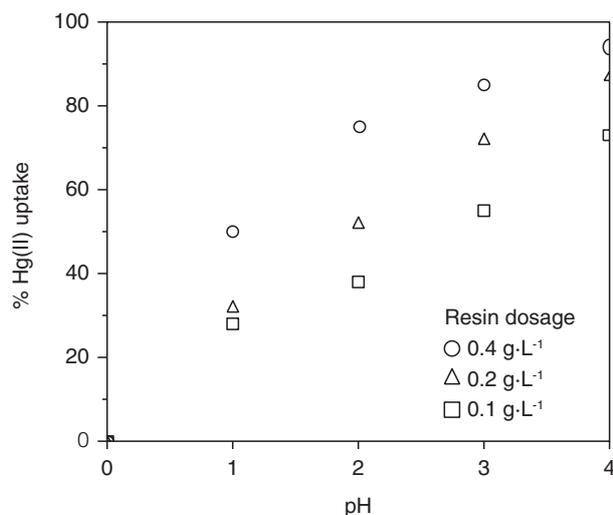
FIGURE 2.   Percentage of Hg(II) loaded onto the resin versus pH; Temperature: 20 °C; Stirring speed: 500 min^{-1}; Time: 3 h.

$$R = \frac{1}{1 + k[Hg]_{s,0}} \qquad (8)$$

was estimated as 0.25, thus, the exchange process was favourable, since R value wass greater than zero and lower than one.

The removal of mercury(II), from the aqueous solution of pH 4, using other potential agents for this task also investigated. The results derived from these experiments were summarized in Table 5. It can be seen that, under the present experimental conditions, Lewatit SP112 results compared well with the obtained with the others exchangers/adsorbent used in the present work.

3.2. Mercury(II) elution

The elution of Hg(II) loaded onto the resin was evaluated using two types of solutions, i) acid solution, ii)Hg(II)-complexant bearing solutions. Results from this investigation were summarized in Table 6. In the case of acid (HNO$_3$) solution, the variation
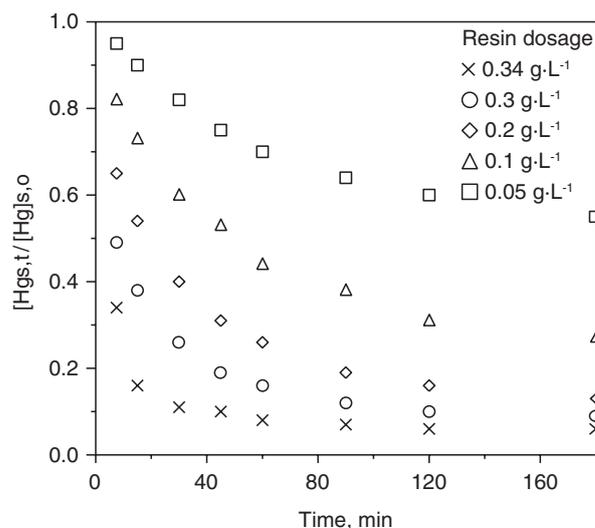
FIGURE 3.   Non-dimensional variation $[Hg]_{s,t}/[Hg]_{s,0}$ versus≈time at different resin dosages.

TABLE 4.   Influence of Lewatit SP112 dosage on Hg^{2+} uptake onto the resin

Lewatit SP112 (g·L^{-1})	[a]Hg^{2+} in solution (mg·L^{-1})	[a]Hg uptake (mg·g^{-1})
0.05	5.5	90
0.1	2.7	73
0.2	1.3	44
0.3	0.9	30
0.4	0.6	24

[a]After 3 h. Temperature: 20 °C. Stirring speed: 500 min^{-1}

TABLE 5.   Hg^{2+} uptake using different cation exchangers/adsorbent

Exchanger/adsorbent	Type	Active group	[a]Hg^{2+} uptake (mg·g^{-1})
Lewatit OC1026	acid ester	di-2ethylhexylphosphate (adsorbed)	34
Lewatit K2621	strongly acid	sulfonic/H$^+$	39
Lewatit TP214	chelating	thiourea	33
Amberlite IR120	strongly acid	sulfonic/H$^+$	25
Amberlite IRC50	weakly acid	carboxylic/H$^+$	40
Lewatit SP112	strongly acid	sulfonic/Na$^+$	44
Multiwalled carbon nanotubes	adsorbent	none	31

Aqueous solution: 0.01 g·L^{-1} Hg^{2+} at pH 4. Resin/adsorbent dosage: 0.2 g·L^{-1}. Temperature: 20 °C. Stirring speed: 500 min^{-1}. [a]Time: 3 h

TABLE 6.   Hg^{2+} elution

Solution	Volume solution/ resin (weight)	% Hg^{2+} elution
0.1 M HNO$_3$	2000	84
0.1 M HNO$_3$	1000	80
0.1 M HNO$_3$	500	78
0.1 M NaSCN	2000	65
0.1 M EDTA	2000	54
0.1 M Tu	2000	50

Resin loaded with 19 mg·g^{-1}. Temperature: 20 °C. Time: 40 min

of the solution volume/resin weight relationship had little influence on mercury elution, averaging near 80%, but obviously had an influence on the metal concentration resulting in the eluate: the lower solution volume/resin weight relationship used the higher Hg(II) concentration in the eluate. In the case of the solutions containing Hg-complexant agents (thiocianate, ethylendiaminotetraacetic acid and thiourea), the results are more or less of the same magnitude order, a little better with the NaSCN solution, but, in the present conditions, were lower values than in the case of the acid solution. With this acid solution, the elution step responded to the next equilibrium:

$$|-(SO_3^-)_2 Hg^{2+} + 2H_{aq}^+ \Leftrightarrow 2[-(SO_3H) + Hg_{aq}^{2+} \qquad (9)$$
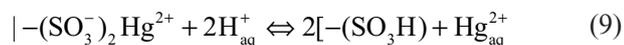
where the subscript aq, represented the elution phase. In order to recycle back the resin to the Na$^+$ form, it is necessary a further wash of it with NaOH solution.

3.3. Post-treatment of the Hg-bearing eluate

After being mercury(II) recovered in the eluate, it seemed necessary to treat the solution in order to end the process of mercury removal from a given liquid effluent. One option, was to recover the metal in one of its more stable form, such as zero valent mercury, and this was done by putting into contact the eluate containing 0.03 g·L^{-1} Hg(II) in 0.1 M HNO$_3$ medium with solid sodium borohydride. This salt was a strong reducing agent because its hydrolysis in acidic medium released hydrogen:

$$BH_4^- + 4H_2O \rightarrow B(OH)_4^- + 4H_2 \qquad (10)$$

Hydrogen reacted with mercury(II), to reduce it to the zero valent oxidation state:

$$Hg^{2+} + H_2 \rightarrow Hg^0 + 2H^+ \qquad (11)$$

and the released Hg^0 can be safely dumped. Figure 4 showed zero valent mercury nanodrops (bright points) obtained from this precipitation. It can observed how bigger drops were formed by coalescence of smaller ones.

4. CONCLUSIONS

The use of the cationic exchange resin Lewatit SP112 allows to the removal of Hg(II) from liquid wastes. The agitation speed has not influence on the maximum metal loading (90 mg·g^{-1} under the experimental conditions), but has an influence on the time to reach this maximum. Moreover, the kinetic model representing experimental data is the second order in the case of using 275 min^{-1} as agitation speed, and the pseudo-second order for agitation speeds of 500–1000 min^{-1}. Mercury(II) uptake onto the resin is exothermic and spontaneous. In the 20–60 °C temperatures range, the data fit well with the moving boundary model. Mercury(II) load onto the resin decreases with the decrease of the pH value from 4 to zero, however, as the resin dosage increases, from 0.1 to 0.4 g·L^{-1}, this negative influence is less
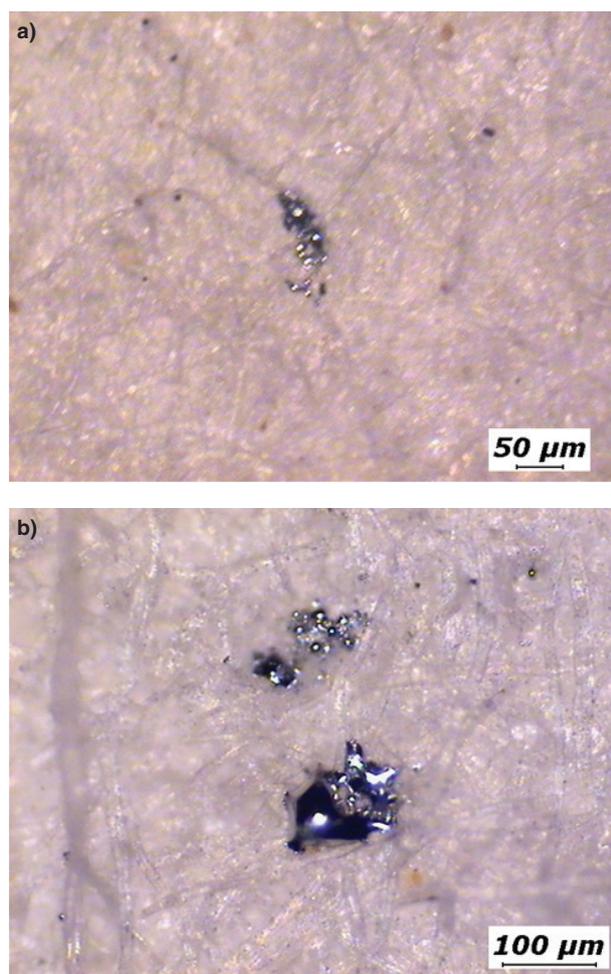
FIGURE 4. Images of the zero valent mercury nanodrops (bright points) obtained from the precipitation of mercury(II)-bearing eluate with sodium borohydride. a) ×50, b) ×100.

evident. At pH zero, no mercury(II) uptake is found for every resin dosage tested. At pH 4, metal loading experiments show that the experimental data fit well (r^2= 0.9932) with the Langmuir type-2 isotherm, and the maximum mercury(II) uptake onto the resin is estimated in the 15 mg·g^{-1} order in a favourable exchange process (R= 0.25).

Mercury(II) elution is best performed using acidic (nitric acid) medium, and from the eluate, zero valent mercury yields as final product.

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