# The removal of toxic metals from liquid effluents by ion exchange resins. Part XIII: Zinc(II)/H<sup>+</sup>/Lewatit OC-1026

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**ABSTRACT:** Zinc(II) was removed, from aqueous solutions, by the ion exchange resin Lewatit OC-1026 (having di-2-ethylhexyl phosphoric acid as adsorbed functional group). Different experimental variables influencing metal uptake, such as, stirring speed ( $400-1200 \text{ min}^{-1}$ ), temperature (20-60 °C), pH of the aqueous solution (1–4) and resin dosage ( $0.05-1 \text{ g} \cdot \text{L}^{-1}$ ) were investigated. The concentration of zinc(II) loaded onto the resin decreased with the increase of the temperature (exothermic reaction) in a spontaneous process, whereas equilibrium was achieved at shorter times as the temperature was increased. The experimental values fitted to the second order kinetic model (60 °C) or the pseudo-second order kinetic model (20 °C). The ion exchange process was pH-dependent, decreasing the percentage of zinc(II) loading onto the resin from pH 4 to pH 1. At pH 4, the rate law was best fitted to the particle diffusion model, and to the Langmuir type-2 isotherm. Zinc(II) removal from the aqueous solution using this resin is by far better than when oxidized or non-oxidized multiwalled carbon nanotubes were used as adsorbents for zinc(II). This element can be eluted from zinc-loaded resin using acidic solutions.

KEYWORDS: Lewatit OC-1026; Liquid effluents; Multiwalled carbon nanotubes; Removal; Zinc(II)

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**RESUMEN:** La eliminación de metales tóxicos presentes en efluentes líquidos mediante resinas de cambio iónico. Parte XIII: Zinc(II)/H<sup>+</sup>/Lewatit OC-1026. La resina de intercambio catiónico Lewatit OC-1026 (que tiene como grupo activo al acido di-2-etilhexil fosfórico adsorbido) se ha utilizado para la eliminación de zinc(II) de disoluciones acuosas. Esta eliminación se ha investigado bajo diferentes condiciones experimentales: velocidad de agitación (400-1200 min<sup>-1</sup>), temperatura (20-60 °C), pH del medio acuoso (1-4) y concentración de la resina (0,05-0,4 g·L<sup>-1</sup>). La carga de zinc(II) en la resina disminuye con el aumento de la temperatura (reacción exotérmica) en un proceso espontaneo, alcanzándose el equilibrio en tiempos mas cortos al aumentar esta variable. A 20 °C, los datos experimentales se ajustan a la cinética de pseudo-segundo orden, mientras que a 60 °C el modelo cinético que mejor representa la carga del metal en la resina es el de segundo orden. El proceso de cambio iónico depende del valor de pH del medio acuoso, disminuyendo el tanto por ciento de la carga del metal en la resina con la disminución de este valor (de 4 a 1); a pH 4, la carga del metal responde al modelo de difusión en la partícula y a la isoterma tipo-2 de Langmuir. La resina Lewatit OC-1026 presenta mejores características, respecto a la eliminación de zinc(II), que los nanotubos de carbono funcionarizados (grupos carboxí-licos) y sin funcionalizar. El zinc(II) cargado en la resina puede ser eluido mediante el uso de disoluciones ácidas.

PALABRAS CLAVE: Efluentes líquidos; Eliminación; Lewatit OC-1026; Nanotubos de carbono de pared múltiple; Zinc(II)

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### **1. INTRODUCTION**

Zinc is an essential element for life, though and excess in zinc exposure (*ingesta*) is detrimental for human health because it causes nausea, diarrhea, headaches and losses of essential copper and iron in human body (Chasapis *et al.*, 2012; Maret, 2013).

There are not stringent regulations about maximum zinc allowance in drinking water, though from a zinc concentration above 3 mg·L<sup>-1</sup>, water tends to be opalescent, develops a greasy film when boiled, and has an undesirable astringent taste (WHO, 2020). In the USA, there was not also a general rule about zinc allowances in waters, i.e. i) if the effluent comes from an electroplating facility, the daily limit for zinc is 0.6 mg·L<sup>-1</sup>, ii) if the facility is engaged in chemical etching and milling, the daily limit is 164 mg·L<sup>-1</sup>, and iii) in the steam electric power generating industry, the daily limit is 1.0 mg·L<sup>-1</sup>. These differences are a function of the ability of the specific industry to treat its wastewater and remove the pollutants using technology applicable to that industry at the time that USEPA studied the industry (Walker Jr., 2020).

Despite the above, several procedures aimed to the removal of this element from aqueous solutions had been already reported (Abdelrahman *et al.*, 2019; Aliyu, 2019; Gümüş, 2019; Sakalova *et al.*, 2019; Mirjavadi *et al.*, 2019; Zand and Abyaneh, 2019; Ahmad *et al.*, 2020; Wieszczycka *et al.*, 2020; Zhang *et al.*, 2020), all of them are based in the adsorption of  $Zn^{2+}$  onto different adsorbents.

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; Alguacil and Escudero, 2020), in this work, the adsorption of zinc(II) from acidic aqueous solutions by using Lewatit OC-1026 resin is investigated. This resin has an organic phosphorous derivative (di-2ethylhexyl phosphoric acid) adsorbed in the resin matrix. Various experimental variables influencing zinc(II) loading onto the resin are studied, as well as the performance of various resins and multiwalled carbon nanotubes on zinc(II) uptake. The elution of zinc(II) from metal-loaded resin by acidic solutions is also described.

#### 2. EXPERIMENTAL

Lewatit OC-1026 resin, consisted in white spherical beads of styrene-DVB matrix with adsorbed di-2-ethylhexyl phosphate groups and particle size in the 0.3–1.25 mm range. Other resins used in this investigation were purchased from Fluka, whereas all the chemicals used in the experimental work are of AR grade. The characteristics of the multiwalled carbon nanotubes (MWCNTs) and oxidized multiwalled carbon nanotubes (ox-MWCNTs) were given elsewhere (Alguacil *et al.*, 2016; Alguacil *et al.*, 2017).

Batch, loading and elution, experiments were done in a glass reactor vessel (250 mL), containing the Zn(II) (metals) solution and the corresponding resins/adsorbents dosage. Agitation of the system was provided *via* a four blades glass impeller.

The analysis of zinc and the accompanying metals in the aqueous solutions was done by Atomic Absorption Spectrometry, and the metal loaded onto the resins/adsorbent was calculated by the mass balance.

### **3. RESULTS AND DISCUSSION**

A distinctive difference of this resin with others used in these series of works, is that in the present case, Lewatit OC-1026 has a liquid-liquid extraction reagent adsorbed in the resin matrix as functional group, which in the present case (Fig. 1) is an organic phosphorous derivative (D2EHPA), thus, in the case of zinc(II), metal uptake onto the resin is represented by the next equilibrium:

$$2((RO)_2 PO(OH))_r + Zn_{aq}^{2+} \Leftrightarrow$$

$$((RO)_2 POO^{-})_r Zn_r^{2+} + 2H_{aq}^{+}$$
(1)

which is a cation exchange reaction, releasing protons to the aqueous solution. In the above equation, r and aq subscripts represented to the species in the resin and the aqueous phase, respectively, and R represented the 2-ethylhexyl chain associated to the phosphorous derivative.

#### 3.1. Zinc(II) uptake onto LewatitOC-1026 resin

The stirring speed applied to the system is a experimental variable often neglected in many ion exchange/adsorption investigations, however, it can varies the quantitative data of a given system. In this work, and to investigate the influence of this variable on zinc(II) uptake onto the resin, aqueous solutions of 0.01 g·L<sup>-1</sup> Zn(II) at pH 4, were put into contact with a resin dosage of 0.25 g·L<sup>-1</sup>, at 20 °C,



FIGURE 1. Structure of D2EHPA.

and various stirring speeds ranging from 400 to  $1200 \text{ min}^{-1}$ . The results derived from this investigation, Table 1, showed that there was a continuous increase of the metal uptake with the increase of the stirring speed from 400 to 800 min<sup>-1</sup>, and then zinc uptake levels off at about 21.6 mg·g<sup>-1</sup>, with a further decrease of this values for stirring speeds around  $1200 \text{ min}^{-1}$ . These results can be explained by a first decrease of the thickness of the aqueous boundary layer, until a minimum was obtained at  $800-1000 \text{ min}^{-1}$ . The further decrease in metal uptake are the result of the formation of local equilibria between the solution and the resin beads, causing the decrease of zinc(II) loaded onto the resin. Based in the above, a stirring speed of 900 min<sup>-1</sup> was used throughout all the experimentation.

By the use of aqueous solutions of  $0.01 \text{ g} \cdot \text{L}^{-1}$ Zn(II) at pH 4, and resin doses of 0.25 g·L<sup>-1</sup>, the effect of the variation of the temperature on zinc(II) uptake was investigated. The results from this set of experiments were summarized in Table 2. It can be seen that there was a continuous decrease in the zinc(II) loaded onto the resin with the increase of the temperature. From the experimental values it was estimated that the ion exchange reaction represented in Eq. (1) had an exothermic character ( $\Delta H^{\circ}$ = -16 kJ·mol<sup>-1</sup>) in an spontaneous process, and with  $\Delta S^{\circ}$  estimated as -44 J/mol K, thus, the exchange process decreased its randomness. This variable also influenced the time in which the system reached the equilibrium, i.e. at 20 °C, this time was of 5 h, at 40 °C decreased to 30 min, and at 60 °C 15 min of reaction time was needed to reach equilibrium conditions. At 20 °C, the kinetics was best represented ( $r^2 = 0.9966$ ) by the pseudo-second order model (Chen et al., 2019):

TABLE 1. Influence of the stirring speed on Zn(II) uptake

Stirring speed, min <sup>-1</sup>	$[\mathbf{Zn}]_{r,e}, \mathbf{mg} \cdot \mathbf{g}^{-1}$
400	17.6
800	21.6
1000	21.7
1200	18.0

Time: 5 h;  $[Zn]_{r,e}$ : zinc concentration in the resin at the equilibrium

TABLE 2. Variation of Zn(II) uptake with the temperature

Temperature, °C	$[\mathbf{Zn}]_{r,e}, \mathbf{mg} \cdot \mathbf{g}^{-1}$
20	21.6
30	18.0
40	15.2
50	14.2
60	13.6

$$\frac{t}{[Zn]r,t} = \frac{1}{K[Zn]_{r,e}^{2}} + \frac{1}{[Zn]_{r,e}}t$$
(2)

being  $[Zn]_{r,t}$  and  $[Zn]_{r,e}$  the zinc concentrations in the resin at an elapsed time and at the equilibrium respectively, and k the rate constant, estimated as  $1.6 \times 10^{-3}$  g/mg min. Moreover, from the model it was estimated that  $[Zn]_{r,e}$  was of 22 mg·g<sup>-1</sup>, which fitted very well with the experimentally found value of 21.6 mg·g<sup>-1</sup>. At 60 °C, the experimental data fitted well (r<sup>2</sup>= 1.00) with the second order kinetic model (Ho, 2006):

$$\frac{t}{[Zn]_{aq,t}} = \frac{1}{[Zn]_{aq,0}} + kt$$
(3)

where  $[Zn]_{aq,t}$  and  $[Zn]_{aq,0}$  represented the zinc concentrations in the aqueous solution at an elapsed time t and the initial one, respectively, and k being the corresponding kinetic constant, estimated as  $4 \times 10^{-3}$  L/mg min. In this case, the model estimated  $[Zn]_{aq,0}$  as 0.01 g·L<sup>-1</sup>, which again matched to the experimental value.

The pH of the aqueous solutions is another parameter to consider in these ion exchange/adsorption systems, and in the removal of zinc(II) from solutions using Lewatit OC-1026 resin, the influence of this variable on zinc uptake was investigated using aqueous solutions of 0.01 g·L<sup>-1</sup> Zn(II) at various pH values (1 to 4) and a resin dosage of 0.5 g·L<sup>-1</sup>. Figure 2 showed the variation of the metal loaded onto the resin *versus* the pH of the aqueous solution, and it was evident that a decrease of this pH value resulted, accordingly to the equilibrium of Eq. (1), in a decrease of the metal uptake. Probably, this effect, again accordingly with Eq. (1), will be



FIGURE 2. Influence of the aqueous pH on Zn(II) uptake onto the resin. Temperature: 20 °C, Time, 5 h.

less evident as the resin dosage increased. At pH 4, the experimental results best fitted ( $r^2 = 0.9900$ ) to the particle diffusion model (López Díaz-Pavón *et al.*, 2014):

$$\ln(1-F)^2 = -Kt \tag{4}$$

with F calculated as:

$$F = \frac{[Zn]_{r,t}}{[Zn]_{r,r}}$$
(5)

and k, the rate constant, estimated as  $9.5 \times 10^{-3}$  min<sup>-1</sup>.

The influence of the variation of the aqueous ionic strength on zinc(II) uptake was also investigated, and in this case the resin dosage was of 0.25 g·L<sup>-1</sup> and the aqueous solutions contained 0.01 g·L<sup>-1</sup> Zn(II) and various concentrations of LiCl. As it can be seen from Table 3, the increase of the ionic strength also decreased the metal uptake onto the resin.

Zinc(II) uptake onto the resin was also investigated using various resin concentrations  $(0.05-1.0 \text{ g}\cdot\text{L}^{-1})$ . The results derived from this experimentation were resumed in Table 4, and as it was somewhat expected, the metal uptake onto the resin decreased as the resin dosage increased. These data were used to estimate the loading isotherm which represented the equilibrium of Eq. (1). It was found, that this best fit (r<sup>2</sup>= 0.9861)

 TABLE 3.
 Zn(II) uptake at various ionic strengths of the aqueous solution

Ionic strength, M	$[\mathbf{Zn}]_{\mathbf{r},\mathbf{e}}, \mathbf{mg} \cdot \mathbf{g}^{-1}$
no LiCl addition	21.6
0.06	18.0
0.12	16.0
0.25	10.4
0.5	9.1

Aqueous solution: pH 4; Temperature: 20 °C; Time: 5 h

was on the Langmuir type-2 isotherm (Abd El Salam and Zaki, 2019):

$$\frac{1}{[Zn]_{r,e}} = \frac{1}{[Zn]_{r,m}} + \frac{1}{k[Zn]_{r,m}} \frac{1}{[Zn]_{aq,e}}$$
(6)

being  $[Zn]_{r,m}$  the maximum zinc loading onto the resin (46 mg·g<sup>-1</sup>) and k the corresponding estimated Langmuir constant. (0.25 L·mg<sup>-1</sup>). The separation factor:

$$\mathbf{R} = \frac{1}{1 + \mathbf{k} [Zn]_{ao.0}} \tag{7}$$

was estimated as 0.29, thus, the exchange process was favourable, since R value was lower than 1 and greater than zero.

Different resins and multiwalled carbon nanotubes were used to investigate their performance in zinc(II) uptake, expressed as the distribution coefficient:

$$D = \frac{[Zn]_{r,e}}{[Zn]_{aq,t}}$$
(8)

and the results showed in Table 5. Generally speaking, ion exchange resins resulted in greater distribution coefficient values, thus better zinc uptakes, than multiwalled carbon nanotubes.

Several experiments were done in order to evaluate the use of Lewatit OC-1026 in the separation of zinc(II) from other accompanying metals in the aqueous solutions. Thus, experiments were carried out on binary solutions having zinc/metal equimolar concentrations of  $1.5 \times 10^{-4}$  M, and resin dosages of  $0.25 \text{ g} \cdot \text{L}^{-1}$ . The results from this set of experiments were given in Table 6, in the form of the separation factor, defined as:

$$\beta_{Zn/M} = \frac{D_{zn}}{D_M}$$
(9)

Resin concentration, g·L <sup>-1</sup>	<sup>a</sup> Zn(II) in solution, mg·L <sup>-1</sup>	<sup>a</sup> Zn(II) loading, mg·g <sup>-1</sup>
0.05	8.3	34.0
0.13	6.5	28.0
0.25	4.6	21.6
0.50	2.2	15.6
0.75	1.4	11.5
1.0	0.2	9.8

TABLE 4. Influence of Lewatit OC-1026 concentration on Zn(II) loading onto the resin

Aqueous solution: 0.01 g·L<sup>-1</sup> Zn(II) at pH 4; <sup>a</sup>After 5 h; Temperature: 20 °C

Resin/adsorbent	Active group	D, $L \cdot g^{-1}$
Lewatit OC-1026	D2EHPA	49
Lewatit K2621	sulfonic acid, H <sup>+</sup> form	12
Lewatit SP112	sulfonic acid, Na <sup>+</sup> form	7
Lewatit TP208	iminodiacetate, Na <sup>+</sup> form	5
Lewatit TP260	aminomethyl phosphonic acid, di-Na <sup>+</sup> form	3
ox-MWCNTs	carboxylic acid	0.85
MWCNTs	none	0.11

TABLE 5. Zn(II) uptake using various cation exchangers/adsorbent

Aqueous solution: 0.01 g·L<sup>-1</sup> Zn(II) at pH 4; Resin/adsorbent dosage: 1 g·L<sup>-1</sup>; Temperature: 20 °C; Time: 5 h.

TABLE 6. Separation of Zn(II) from other metals

System	βzn/M
Zn(II)-Cu(II)	8
Zn(II)-Fe(III)	0.86
Zn(II)-Ni(II)	28
Zn(II)-In(III)	0.21
Zn(II)-Cr(III)	3
Zn(II)-Mn(II)	17
Zn(II)-Co(II)	12

Temperature: 20 °C; Time: 5 h

Solution	Volume solution/resin weight	% Zn(II) elution
0.1 M HCl	400	76
0.1 M HCl	200	70
0.1 M H <sub>2</sub> SO <sub>4</sub>	200	76

Resin loaded with 1.4 mg·g<sup>-1</sup>; Temperature: 20 °C; Time: 60 min

It was shown, that under the present experimental conditions, zinc(II) can be separated,  $\beta$  values greater than 1, from Cu(II), Ni(II), Cr(III), Mn(II) and Co(II), however, Fe(III) and In(III) were loaded onto the resin preferably to zinc(II).

## 3.2. Zinc(II) elution

Accordingly with the equilibrium represented in Eq. (1), zinc(II) elution is possible by shifting it to the left, thus acidic solutions are used to elute zinc from the resin. Resin with zinc uptakes of  $1.4 \text{ mg} \cdot \text{g}^{-1}$  were used in the experiments, and both sulphuric and hydrochloric acid solutions were used as eluting agents. The results from these experiments were shown in Table 7, and it can be seen that zinc(II) was effectively eluted from the resin using these acidic solutions, whereas neither the change of the acid nor the variation in the liquid/solid ration had a great influence on the recovery of zinc from the metal-loaded resin. Based in these results, it appeared to

be possible to concentrate the zinc solution at least five times with respect the initial zinc aqueous solution feeding the loading step.

#### 4. CONCLUSIONS

Lewatit OC-1026 is useful in the removal of zinc(II) aqueous solutions. The influence of several variables on this removal can be summarized as:

- Stirring speed. A maximum in zinc(II) loading is observed in the 800–1000 min<sup>-1</sup> range, thus, a minimum in the aqueous thick layer is obtained.
- Temperature. The increase of this variable from 20 to 60 °C has a detrimental effect on zinc(II) uptake, however, the increase of the temperature allows to achieve the equilibrium at shorter times. At 20 °C, the data fit to the pseudosecond order kinetic model, whereas at 60 °C, the second order kinetic model best represents the adsorption data.
- Aqueous pH value. The decrease of the aqueous pH value from 4 to 1 has also a detrimental effect on the removal of zinc(II) from the solution. At pH 4, the rate law governing the ion exchange process is represented by the particle diffusion model and the Langmuir type-2 isotherm.
- The performance of this resin, with respect to zinc(II) removal from the solution, compares very well against the use of other resins, having different active groups, and specially against the use of multiwalled carbon nanotubes.
- The resin was selective for zinc against the presence of other elements in the solution, but not in the case of In(III) and Fe(III). Based in the values of the separation factor, an apparent adsorption order was established as: In(III)> Fe(III)>Zn(II)>Cr(III)>Cu(II)>Co(II)>Mn (II)>Ni(II), which resembled the solvent extraction order of these elements by D2EHPA.
- Elution. Zinc(II) can be eluted from loaded resin by the use of acidic solutions, allowing to the concentration of zinc(II), in the corresponding eluate, of at least five times with respect to the initial feed, i.e. from 0.01 to 0.05 g  $\cdot$ L<sup>-1</sup>.

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