



## Removal of Cd and Zn from inorganic industrial waste leachate by ion exchange

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### Abstract

This paper presents a study of the removal of Cd and Zn present in the leachate from an inorganic industrial waste landfill using cationic exchange resins (Amberlite 200, 252-C, IR-120, Duolite C-464), a chelating resin, Amberlite IRC 718, and an adsorbent resin, XAD-2. The chelating resin Amberlite IRC 718 presented the higher removal in batch experiments for both metals (93% for Zn and 50% for Cd). Five hundred ten bed volumes of leachate were treated in column experiments using this material, reducing the concentrations of Cd and Zn from 18 mg/dm<sup>3</sup> to 0.1 and 1.0 mg/dm<sup>3</sup>, respectively. Regeneration of the saturated bed was achieved with 11 BV of 2 M HCl.

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**Keywords:** Leachates; Landfill; Industrial waste; Ion exchange; Heavy metal removal

### 1. Introduction

The disposal of waste in landfills constitutes the last option in the so-called “options hierarchy” in waste management in the European Union. Nevertheless, it still remains widely used for both municipal and industrial solid waste. One of the problems arising from this form of waste disposal is the generation of leachate. The composition of this leachate depends on the type of waste being disposed of, landfill design, local rainfall, etc. Whereas the characterization and treatment of leachate from municipal solid waste has been widely studied [1–4], the leachate from security landfills for industrial waste has been studied to a much lesser degree [5].

In inorganic waste landfills, the main process that takes place as a result of rainfall is the solubilization and subsequent run-off of the components present. The leachate generated at this type of landfill is characterized by relatively high initial concentrations of salts; sulphates and chlorides may be

found in concentrations of around 15,000 mg/l. The content in organic matter, however, usually presents COD values of below 1000 mg/l [6,7].

In the Principality of Asturias, the management of the waste produced in this region is carried out by the Consortium for Waste Management of Asturias (its Spanish acronym, COGERSA). Among other facilities, it has security landfills for municipal solid waste [8], organic industrial waste, and inorganic industrial waste.

The waste admitted to this last landfill is: solid inorganic waste, with less than 65% moisture, carbonates and bicarbonates, asbestos (dust and filters), filter press cakes, waste containing heavy metals, and ion exchange resins. The following waste is not admitted to the landfill: radioactive waste, explosives, inflammable products (Flash Point < 55 °C), self-inflammable products, solvents, liquid waste and waste that alters the system of impermeabilization.

According to the information facilitated by COGERSA, the leachate generated at this security landfill presents a high concentration of salts, such as chlorides (in concentrations of up to 11,000 mg/l) and sulphates (up to

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Table 1

Limit emission values established in the Spanish regulations for Zn and Cd

Metal ion	Limit values into watercourses (mg/l)	Limit values into sewage system (mg/l)
Zn	3	10
Cd	0.1	0.5

Table 2

Analytical characteristics of the leachates employed in the ion exchange experiments

Parameter	Concentration			
	Batch	Column		
		L1	L2	L3
pH	7.5	7.2	7.7	8.0
Conductivity ( $\mu\text{S}/\text{cm}$ )	19900	9180	27700	27200
Alkalinity (mg $\text{CaCO}_3/\text{l}$ )	3971	360	1700	1620
COD (mg/l)	244	62.3	288	289
$\text{Cl}^-$ (mg/l)	11680	3065	7240	7545
$\text{SO}_4^{2-}$ (mg/l)	1223	648	1987	1993
$\text{Ca}^{2+}$ (mg/l)	1007	161	n.d.	n.d.
$\text{Mg}^{2+}$ (mg/l)	687	33	75	93
$\text{Na}^+$ (mg/l)	4517	1575	9088	8270
$\text{K}^+$ (mg/l)	700	275	595	594
$\text{Cd}^{2+}$ (mg/l)	2.2	18.3	14.8	9.7
$\text{Zn}^{2+}$ (mg/l)	5.4	18.4	8.4	7.1
$\text{N-NH}_4^+$ (mg/l)	150	74.5	284	179

n.d.: not detected.

## 2. Materials and methods

### 2.1. Composition of the leachates

The leachate used in both the batch and column experiments came from COGERSA's security landfill for inorganic industrial waste. It was collected from the homogenization pond in which it is stored. Its composition is given in Table 2.

The same leachate was used in batch experiments in order to select the best exchange material. In the column experiments, leachates with different compositions were used which had been collected at different times of the year. The aim was to take representative samples of the different compositions that this wastewater may present throughout the year due to the different types of waste being disposed of.

### 2.2. Chemical analyses

The parameters analyzed in the leachates were: pH, conductivity, total alkalinity (TA), chemical oxygen demand (COD), chlorine, sulphate, ammonium nitrogen and metals. pH was determined at 20 °C using a CRISON Mod. 507 pH meter. Determination of conductivity was carried out at 20 °C using a CRISON Mod. 524 conductivimeter. Hardness was determined by the EDTA titrimetric method. Alkalinity was determined by the potentiometric titration method with sulphuric acid 0.1N. Determination of COD was carried out by means of the colorimetric method with closed reflux, using a HACH Mod. DR/2010 spectrophotometer. Chloride was determined by the argentometric method. Sulphate was measured by the gravimetric method, with drying of the residue. Ammonia nitrogen, nitrate nitrogen and nitrite nitrogen were determined by the selective electrodes method using an Orion Mod. 95-12 ammonia-selective electrode, an Orion Mod. 93-07 nitrate-selective electrode and an Orion Mod. 93-46

1200 mg/l), a slightly alkaline pH of around 8, slight ammonium contamination, metals, etc. On analyzing the evolution of the concentrations of Cd and Zn in the leachate generated during the years 2000, 2001 and 2002, it was found that the concentrations of these metals in the leachate exceeded the limits established in both state regulations with respect to direct discharge into watercourses (Royal Decree 606/2003, of 23rd May) as well as regional regulations (Law 5/2002, of 3rd June) with respect to discharge into public sewage systems, which means that some kind of treatment is required. The characteristics that the water to be discharged must fulfill are shown in Table 1, and if the water is discharged into a watercourse, these characteristics are a function of the characteristics of the receiving medium.

Ion exchange is one of the most widely used conventional techniques for removing heavy metals, achieving high yields in the removal of metals and other constituents present in industrial effluents [9–16].

There are a variety of different types of exchange materials, which may be mineral in nature (aluminas, carbons, silicates and aluminosilicates) or synthetic (synthetic zeolites, resins). Zeolites can act as highly efficient porous media in ion exchange or adsorption processes. They are made up of highly hydrated aluminosilicates in which some silicon atoms have been substituted by aluminum atoms. The presence of aluminum atoms leads to a deficiency in the local electrical charge. This translates into the appearance of acid centers that will be occupied by cations such as Na, K, Ca, etc., thus conferring ion exchange properties on the material [17–19]. Ion exchange resins are formed by a matrix, made from a polymeric material, to which functional ion groups of an acid, basic or chelate-forming nature, are fixed. Resins are distinguished on the basis of this functionality: cationic exchange resins (with  $-\text{SO}_3\text{H}$  and  $-\text{COOH}$  active groups), anionic exchange resins (with  $-\text{N}^+(\text{CH}_3)_3-$ ;  $-\text{N-R}_2$ ;  $-\text{N-RH}$  active groups), or chelating resins (with active iminodiacetate, carboxylate, aminophosphonate groups). The aim of this article is to select an ion exchange resin to remove toxic heavy metals (Cd and Zn ions) from inorganic industrial waste leachate. A study was carried out into the behavior of several ion exchangers (Amberlite 200, 252-C, IR-120, IRC 718, Duolite C-464 and XAD-2) in the removal of the Cd and Zn present in leachate from COGERSA's security landfill for inorganic industrial waste. Once the resin that obtained the best removal results had been selected, column trials were carried out.

Table 3  
Physical and chemical properties of exchange materials employed in the selection trials

	Bulk density (g/l)	Moisture content (%)	Swelling (%)	Total exchange capacity (meq/ml)	Particle size (mm)
Amberlite 200	800	46–51	3	1.75	0.35–1.2
Amberlite 252-C	800	50–54	4	1.65	0.43–0.51
Amberlite IR 120	850	44–48	4–7	2	0.3–1.2
Duolite C-464	650–800	50–60	40	3	0.315–1.25
Amberlite IRC 718	750	60–65	30	1.35	0.50–0.65
XAD 2	640–700	–	–	–	0.30–0.45

nitrite selective-electrode with an Orion Mod. 90-02 reference electrode. Metals were determined by atomic absorption and emission spectrophotometry using a Perkin Elmer Mod. 3110 spectrophotometer equipped with a FIAS system [20].

### 2.3. Selection of the exchange materials

In the selection of the most appropriate exchange materials for treating this type of leachate, batch ion exchange experiments were carried out using a SELECTA “vibromatic” oscillating stirrer equipped with 14 stirring positions for 500 ml capacity Erlenmeyer flasks. Different types of exchange materials were used (Table 3): Amberlite 200 and 252-C (strongly acidic macroporous cationic exchangers with sulphonic active groups), IR-120 (a strongly acidic gel-type cationic exchanger with sulphonic active groups), Duolite C-464 (a weakly acidic macroporous cationic exchanger with carboxyl active groups), IRC 718 (a weakly acidic macroporous cationic exchanger with chelate-forming iminodiacetate active groups) and XAD-2 (a polymeric adsorbent). Experiments were carried out mixing 100 ml of real leachate with 2 g of exchange material (resin, adsorbent or zeolite) in 500 ml Erlenmeyer flasks. The mixture was continuously stirred for 3 h. This time was employed on the basis of prior experiments with the same resins, though with aqueous solutions containing 100 mg/l of Cd or Zn. Total removal of both metals was achieved in this period of time [21]. At the end of each experiment, the solid and liquid phases were separated by filtration. The Cd and Zn concentration was determined before and after the exchange process; in the latter case, this process was carried out on the filtered solution.

### 2.4. Cd and Zn removal in packed beds

The column experiments were carried out with the chelating resin Amberlite IRC 718, the exchange material with which the best results were obtained in the selection trials. Glass columns were employed measuring 30 cm in length and 1.5 cm internal diameter and equipped with two porous plates, one at the bottom (which served as a support for the bed of resin) and another at the top that impeded the bed from exiting during the regeneration step. The loading and regeneration steps were carried out counterflow, due to the improvement in operational performance, hence resulting in a decrease in consumption of reagents under similar conditions. The qual-

ity of the treated effluent also improves the ability to see that the treated layers are regenerated with a strong excess of reagent [22,23]. The volume of resin used was 16.4 ml in the Na-form; the loading step was carried out from top to bottom with 11 BV/h ( $1.02 \text{ m}^3/\text{m}^2 \text{ h}$ ) and the regeneration step was carried out with 2 M HCl (the concentration recommended by the chelating resins with iminodiacetate group manufacturers: Bayer and Rohm and Haas Company [24,25]) from bottom to top and at a flow rate of 18 BV/h ( $1.7 \text{ m}^3/\text{m}^2 \text{ h}$ ). During all the steps, the flow rate was controlled by means of a Reglo-Digital pulse multichannel pump (ISMATEC) [21]. Samples of 30 and 15 ml were taken, respectively during the loading and regeneration steps, determining the concentration of Cd and Zn in accordance with the aforementioned analytical techniques.

## 3. Results and discussion

### 3.1. Selection of the exchange materials

Cationic exchange resins, chelating resins and adsorbents were used. The results obtained are given in Fig. 1. As can be seen, the cationic resins did not achieve high removal percentages for either Cd or Zn. This may be due to the interference of other cations present in the leachate at higher concentrations than the metals under study (mainly Na, K,  $\text{NH}_4^+$ , Ca and Mg). Poor results (20% removal) were obtained either with the adsorbent resin XAD-2, although the removal obtained with this resin was greater for Zn than for Cd, which might indicate the greater tendency of Zn to form neutral complexes in the leachate. The highest removal percentages were obtained with the chelating resin IRC 718.

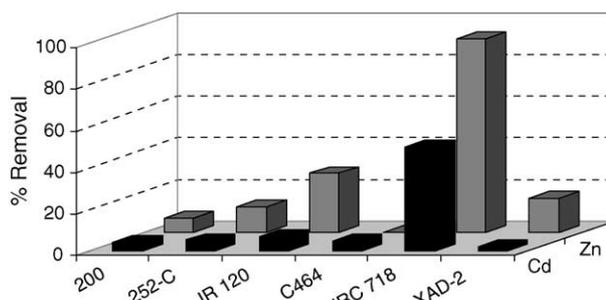


Fig. 1. Removal of the Cd and Zn present in the leachate using different resins.

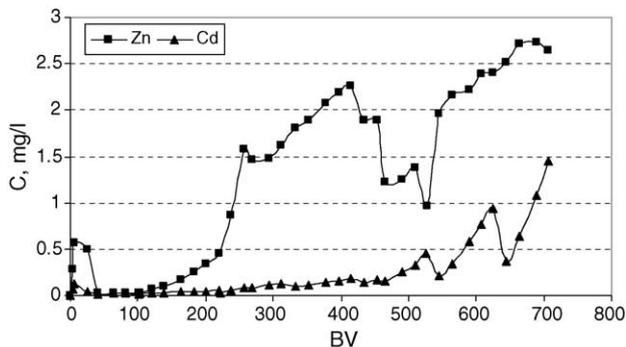


Fig. 2. Results of the removal of Zn and Cd from “L1” using Amberlite IRC 718.

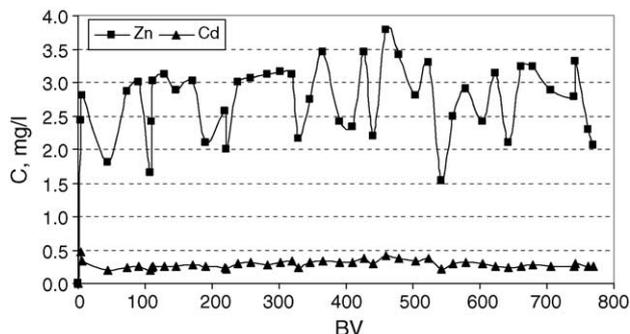


Fig. 4. Results of the removal of Zn and Cd from “L3” with Amberlite IRC 718.

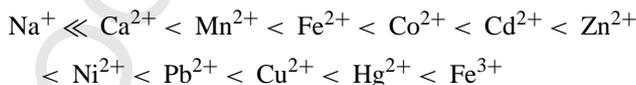
Zn removal percentages of 93% were achieved with this resin, although this percentage was lower for Cd (50%). This type of resin, based on the iminodiacetate group, is of the weak cationic type and presents a high selectivity for heavy metals such as Cd and Zn versus sodium, calcium and magnesium ions when working at pH values of between 4 and 8 [26,27]. According to the results obtained, the resin shows higher selectivity for Zn than for Cd.

3.2. Cd and Zn removal in packed beds

In light of the results obtained, the chelating resin Amberlite IRC 718 was chosen for the removal of the metals Cd and Zn. The aim of the undertaken study was to ascertain up to which volume of leachate might be treated while generating an effluent whose concentration of Cd and Zn allow it to be directly discharged into a watercourse, or into a public sewage system. On the basis of the discharge limits established by law, more restrictive values were considered to define the breakthrough point in the loading step of the ion exchange process, accordingly establishing this point at a concentration of 0.1 mg/l Cd in the effluent.

The results of the treatment of the three types of leachate with the chelating resin Amberlite IRC 718 are shown in Figs. 2–4. The main difference with respect to the results obtained in the selection trials (batch experiments) was that the chelating resin presented a greater selectivity for Cd than

for Zn, the opposite of what occurred in the batch experiments. This may be due to the concentration of Zn being higher than that of Cd in the batch experiments and to the possibility of the existence of different complexes in the leachates (since the leachate employed in the batch and column experiments did not have the same composition). For divalent cations, selectivity of the complexes formed with the iminodiacetate active group of the resin increases as follow:



This order applies in the case of metals not forming complexes with the anions in the solution. If, on the other hand, they do, then the order changes slightly [24,25].

It was also observed that there existed a fraction of both Cd and Zn that the chelating resin was not able to remove, which had already appeared from the commencement of the loading step of the ion exchange process. If we compare the results obtained with respect to the removal of Cd by the resin, very marked differences are not observed in the treatment of the three leachates under study, obtaining treated effluents with a residual concentration of Cd ranging between 0.1 and 0.3 mg/l. The leachates studied presented important concentrations of chloride, sulphate and carbonate ions, above all in the case of leachates 2 and 3 (Table 2). According to the consulted sources, Cd may be found forming both organic as well as inorganic species [28–40]. Holm et al. [30] studied the speciation of Cd presents in an industrial leachate with very similar characteristics to the leachate treated in this study. The main components of said leachate were Cd (71 μg/l), organic matter (79 mg/l), chloride ions (2900 mg/l) and sulphate ions (15 mg/l). In the aforementioned leachate, 64% of the dissolved Cd was found forming inorganic complexes (mainly with chloride ions, which are the ones that were found at the highest concentration), 19% as free ions (Cd<sup>2+</sup>) and 17% associated with organic matter. As regards the tendency of Cd to form chlorinated complexes, Petrangeli et al. [37] observed that the Cd present in the leachate from municipal waste was found mainly forming complexes with acetate, chloride and carbonate ions. Gómez-Serrano et al.

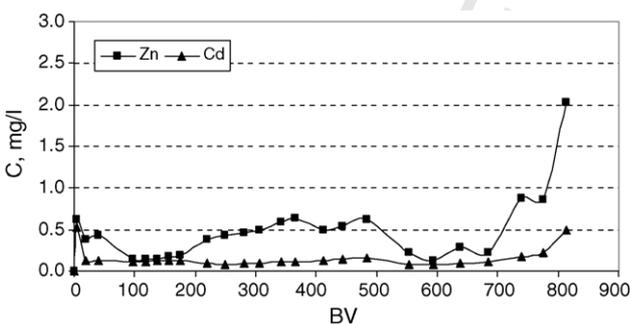


Fig. 3. Results of the removal of Zn and Cd from “L2” with Amberlite IRC 718.

[31] found that in cadmium chloride solutions (concentration ranged between  $3.8 \times 10^{-2}$  and 7.3 mol/l and pH 6.2), the predominant Cd species are:  $\text{Cd}^{2+}$ ,  $\text{CdCl}_2$  and  $[\text{CdCl}_3]^-$ . It was also observed that in the presence of humic and fulvic acids, Cd forms fairly stable complexes at neutral pH values [38,39]. On the basis of these findings, it is possible that the majority of the Cd present in the leachates under study are found in the form of chlorinated complexes or as free Cd. In the bibliographical sources consulted, the following values of the formation constants of these chlorinated complexes were found:  $\log \beta[\text{CdCl}^+]$ : 2.00;  $\log \beta[\text{CdCl}_2]$ : 2.60;  $\log \beta[\text{CdCl}_3^-]$ : 2.40 and  $\log \beta[\text{CdCl}_4^{2-}]$ : 1.70 [36]. As can be observed, these constants are not very high, which would explain the high removal percentage obtained from this metal with the chelating resin employed. The nonretained fraction may be due to the presence of stable complexes that the Cd would form with other components in the leachate, such as the organic matter.

As regards Zn, the differences found in the treatment of the three leachates were more marked. In the bibliographical sources consulted, it was found that Zn does not present as strong a tendency as Cd to form complexes with organic matter, although it may be found bound to humic substances in aquatic media [29,41,42]. Furthermore, studies carried out using the program MINTEQA2 for inorganic species show that approximately 50% of the heavy metals (among these Zn) present in surface water polluted with leachate from municipal solid waste landfills are found complexed to carbonates and bicarbonates, whereas between 29 and 59% are found as free cations [35]. In the presence of carbonate ions, Zn may appear in solution as  $\text{ZnCO}_3$ , a species for which a value of  $\log K$  equal to 4.52 was found in the bibliographical sources. Moreover, in the presence of chloride and sulphate ions, it may form complex species, though of lower stability, as can be seen from the value of the formation constants [43] ( $\log \beta[\text{ZnSO}_4]$ : 1.84;  $\log \beta[\text{ZnCl}^+]$ : 0.40;  $\log \beta[\text{ZnCl}_2]$ : 0.60;  $\log \beta[\text{ZnCl}_3^-]$ : 0.50;  $\log \beta[\text{ZnCl}_4^{2-}]$ : 0.20). Hence, the major residual concentration found for Zn in the different leachates treated with the resin may be due to the greater tendency that this cation has to form complexes with carbonates, which are possibly more stable than those that Zn would form with the iminodiacetate group of the resin employed. This assertion does not hold, however, in the case of leachate 2. When treating leachate 2, 12.7 l of treated leachate were obtained containing 0.14 mg/l of Cd and 0.50 mg/l of Zn, whereas when leachate 3 was treated, 12.5 l of treated leachate were obtained with a concentration of Cd and Zn of 0.30 and 2.80 mg/l, respectively. In light of these results, the ion exchange process was found to be better in the case of leachate "L2", which presents a higher concentration of ammonium. Leinonen and Koivula et al. carried out experiments with chelating resins that contained different active groups (among these, iminodiacetate and aminophosphonate groups), studying the influence of the presence of ligands such as ammonium and cyanide on the capacity of the active groups in the resins to retain heavy metals. They observed

Table 4

Experimental results obtained in the trials carried out with the chelating resin Amberlite IRC 718 for the different leachates

	L1	L2	L3
Volume treated (ml)	11600	12750	12500
Volume treated (BV)	706	776	761
Capacity			
meq Cd/ml resin	0.23	0.21	0.13
meq Zn/ml resin	0.37	0.20	0.10
Concentration of the treated effluent			
mg Cd/l	0.2	0.1	0.30
mg Zn/l	1.3	0.5	2.80
Volume treated up to breakthrough capacity (BV <sup>a</sup> )	510	639	0
Breakthrough capacity			
meq Cd/ml resin	0.17	0.18	–
meq Zn/ml resin	0.28	0.17	–
Concentration of the treated effluent up to breakthrough capacity			
mg Cd/l	0.1	0.1	(0.3)
mg Zn/l	1.0	0.4	(1.5–3.5)
Regeneration volume (ml)	180	180	180
Regeneration volume (BV)	11	11	11
Regeneration capacity			
meq Cd/ml resin	0.17	0.17	0.11
meq Zn/ml resin	0.23	0.15	0.07
% Regeneration			
Cd	75.5	82.1	83.8
Zn	61.2	74.7	70.4
Concentration factor up to breakthrough capacity	46	58	–

<sup>a</sup> Calculated for a concentration of Cd in the treated effluent of 0.1 mg N/l.

that the presence of ammonium significantly increased the uptake of Zn by the aminophosphonate resin, and especially, of cadmium by the aminophosphonate and iminodiacetate resin in comparison with the original  $\text{ZnCl}_2$  or  $\text{CdCl}_2$  solutions. The reason for this unexpected enhancement is not yet known [44,45].

As can be seen in Table 4, if we establish the breakthrough point in the loading step at a concentration of Cd in the treated effluent equal to 0.1 mg/l, 510 BV of Leachate 1 may be treated and up to 640 BV of Leachate 2. With Leachate 3, the ion exchange process would allow us to obtain a treated effluent with a concentration in Cd of 0.3 mg/l. In this case, in compliance with current legislation, it would not be possible to discharge the obtained effluent into a public watercourse, although it would be possible to do so into a public sewage system.

As regards the regeneration of the resin (Fig. 5), significant changes were not observed in the treatment of the different leachates, achieving regeneration percentages of between 75 and 84% with respect to Cd and between 61 and 75%, with respect to Zn, with only 11BV of 2 M HCl. Thus, by applying this process to this type of leachate, concentration factors of 58 may be achieved (Table 4), obtaining a treated effluent with a concentration in Cd and Zn lower than 0.1 and 3.0 mg/l, respectively.

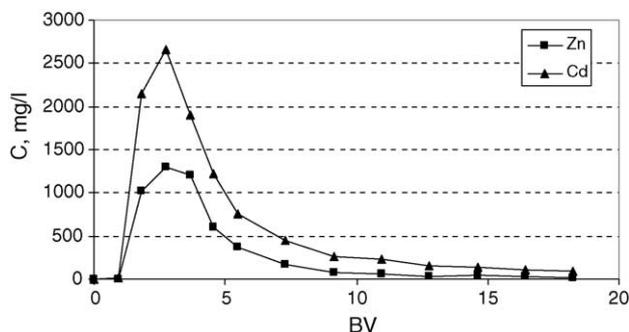


Fig. 5. Regeneration curves for the resin Amberlite IRC 718 after the treatment of "L2".

#### 4. Conclusions

Of the different exchange resins studied (Amberlite 200, 252-C, IR-120, Duolite C-464, Amberlite IRC 718 and XAD-2), the chelating resin Amberlite IRC 718, with an active iminodiacetate group, was the most efficient in removing the Cd and Zn present in the leachate from an inorganic industrial waste landfill.

The species that Zn may form with compounds such as carbonates, bicarbonates and organic matter reduce the affinity of the iminodiacetate group, the resin showing higher selectivity for Cd in the column experiments carried out.

The use of the chelating resin Amberlite IRC 718 to treat leachate from inorganic industrial waste landfills with low alkalinity and Cd and Zn concentrations of around 20 mg/l allows around 500 BV of treated effluent to be obtained with concentrations of Cd and Zn lower than 0.1 and 3.0 mg/l, respectively. For high alkalinity leachates, the results depend on the ammonium content. Regeneration of the resin is carried out employing 11 BV of 2 M HCl.

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