

Ion-exchange of Pb^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Ni^{2+} ions from aqueous solution by Lewatit CNP 80

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Abstract

Removal of trace amounts of heavy metals can be achieved by means of selective ion-exchange processes. The newly developed resins offered a high resin capacity and faster sorption kinetics for the metal ions such as Pb^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Ni^{2+} ions. In the present study, the removal of Pb^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Ni^{2+} ions from aqueous solutions was investigated. Experimental investigations were undertaken using the ion-exchange resin Lewatit CNP 80 (weakly acidic) and were compared with Lewatit TP 207 (weakly acidic and chelating). The optimum pH range for the ion-exchange of the above mentioned metal ions on Lewatit CNP 80 and Lewatit TP 207 were 7.0–9.0 and 4.5–5.5, respectively. The influence of pH, contact time, metal concentration and amount of ion-exchanger on the removal process was investigated. For investigations of the exchange equilibrium, different amounts of resin were contacted with a fixed volume of Pb^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Ni^{2+} ion containing solution. The obtained sorption affinity sequence in the presented work was $\text{Ni}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Pb}^{2+}$. The metal ion concentrations were measured by AAS methods. The distribution coefficient values for metal ions of 10^{-3} M initial concentration at 0.1 mol/L ionic strength show that the Lewatit CNP 80 was more selective for Ni^{2+} , Cu^{2+} than it was for Cd^{2+} , Zn^{2+} and Pb^{2+} . Langmuir isotherm was applicable to the ion-exchange process and its contents were calculated. The uptake of metal ions by the ion-exchange resins was reversible and thus has good potential for the removal of Pb^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Ni^{2+} from aqueous solutions. The amount of sorbed metal ion per gram dry were calculated as 4.1, 4.6, 4.7, 4.8, and 4.7 mequiv./g dry resin for Pb^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Ni^{2+} , respectively. Selectivity increased in the series: $\text{Cd}^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+}$. The results obtained showed that Lewatit CNP 80 weakly acidic resin had shown better performance than Lewatit TP 207 resin for the removal of metals. The change of the ionic strength of the solution exerts a slight influence on the removal of Pb^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Ni^{2+} . The presence of low ionic strength or low concentration of NaNO_3 does not have a significant effect on the ion-exchange of these metals by the resins. We conclude that Lewatit CNP 80 can be used for the efficient removal of Pb^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Ni^{2+} from aqueous solutions.

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1. Introduction

People have used metals for many centuries and in our day the mass usage of metals is accepted as an inalienable fact. The hydrometallurgical industry produces many types of waste streams. The toxic nature of heavy metal ions, even at trace levels in natural waters, has been a public health problem [1]. To solve this problem, industrial waters must be treated to remove the toxic metal ions before they can be discharged into the sewerage. The increasing accumulation of Pb^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} ,

and Ni^{2+} in the environment from industrial outputs has caused great concern [1–3]. Pb^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Ni^{2+} ions are a common pollutant introduced into natural waters from a variety of industrial wastewaters including those from the textile, leather tanning, electroplating and metal finishing industries [2–7].

The most important technologies for toxic ion removal or to reduce the concentration of metal ion in aqueous water are chemical precipitation, ion-exchange, phytoextraction, ultra filtration, reverse osmosis, and electro dialysis and sorption [7–15]. Nevertheless, many of these approaches can be marginally cost effective or difficult to implement in developing countries. Therefore, there exists a need for a treatment strategy that is simple, and compatible with local resources and constraints. The effective

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recovery of these metals is possible only if the separation process is selective enough. Selective ion-exchangers can be used for reducing the amount of metal wastes; they can be used for purification of process liquids for re-use and for the treatment of final wastewaters [11–15].

A weak acid cation (WAC) resin with weakly ionized carboxylic acid groups is prepared by the suspension copolymerization of acrylic or methacrylic acid with divinylbenzene. WAC resins have very high selectivity for divalent cations, particularly Pb^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Ni^{2+} ions. This makes them ideal candidates for the removal of various metals from wastewater streams. WAC resins offer extremely high capacity than strong cation resins, higher selectivity for divalent cations than chelating resins, especially at neutral to alkaline pH, have relatively low cost, and have lower kinetics, compared to chelating resins.

The most common resins used in formulations are cross-linked polystyrene and polymethacrylate polymers. Lewatit CNP 80 is made from acrylic polymers, cross-linked with divinylbenzene (DVB) and functionalized with carboxylic exchange groups and can be economically used for the removal of Pb^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Ni^{2+} from wastewaters at a pH-value >5 . Any counter ion associated with the ion-exchange resin is physically separated from the surrounding fluid and it is bound to the polymer matrix. The interaction is ionic, rather than covalent. Its principal characteristics are excellent physical, chemical and thermal stability, good ion-exchange kinetics and high exchange capacity [10,15–19].

A number of investigators have studied the removal of inorganic metal ions Pb^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Ni^{2+} from aqueous solution using different resins. Gode and Demirbas reported on the removal of Pb^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Ni^{2+} and Cr^{3+} from aqueous solution using ion-exchange resins [18,19]. Ion-exchange resins such as IRN-77 [20], Ionac SR-5 [21], Amberlite [22–24], Purolite S-930 [25], Lewatit [26] and others are also often employed for extraction of heavy metal ions. The cation exchanger Dowex-I-A is used for selective extraction of heavy metal ions from considerably concentrated solutions of salts of alkaline and alkaline earth metals [27].

The main objective of this study was to investigate the equilibrium and kinetic parameters of Lewatit CNP 80 and compare it with Lewatit TP 207. In addition, parameters that influence adsorption, such as initial Pb^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Ni^{2+} concentration, pH, isotherm and kinetic studies were investigated.

2. Material and methods

2.1. Materials

All chemicals were of an analytical grade. Solutions of certain molarities of test metals were prepared by dilution of sulphate, chloride and nitrate salts of metals ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, ZnCl_2 , $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ and $\text{Pb}(\text{NO}_3)_2$ from Sigma Co.) with double distilled water. The pH buffer solutions were obtained from Aldrich Company. Synthetic Lewatit CNP 80 and Lewatit TP 207 in hydrogen form (0.315–1.6 mm) were obtained from Fluka Co. The properties of the resins are given in Table 1.

2.2. Apparatus

Unicam 929 Model Atomic Absorption Spectrometer (AAS) operating with an air-acetylene flame was used to analyze the concentration of metals in solutions. The pH measurements were performed with Jenway 3010 Model pH meter. A thermo stated shaker (Gallenkamp Incubator) of Orbital model was used for ion-exchange experiments.

2.3. Procedures

2.3.1. Water washing of ion-exchangers

The resins were washed with diluted HCl and, then, the hydrogen form of the resin was washed with double distilled water to remove all the excess acid. The dried material at 378 K was used for further experimental work.

2.3.2. Equilibrium studies

The initial pH of the solutions was adjusted with 0.05 mol/L HNO_3 and 0.05 mol/L NaOH, respectively. The addition of different sodium nitrate quantities into the solution changed the ionic strength. Samples of the resin (0.1 g by dry weight) were equilibrated with 30 mL aqueous solution of metal ions at varying concentrations, pH values, and ionic strengths in vessels. In batch operation, resins and solution dumped into the vessel and after mixing, the solution and the resin allowed for equilibrium for 4 h in the shaker. The Lewatit CNP 80 and solution were separated by filtration through a membrane filter (0.45 mm). Sorption of the metal by the filter medium was controlled by washing it twice with diluted HCl and the filtrate was analyzed for the remaining metal ion concentration. The metal ion concentration in the original solution and the metal ions left in bulk solution

Table 1
Characteristic data of tested Lewatit CNP 80 and Lewatit PT 207

Resin type	Weak acid cation exchange resin Lewatit CNP 80	Weak acid cation exchange resin Lewatit TP 207
Active group	–COOH	Iminodiacetic acid
Matrix	Cross-linked polyacrylate	Cross-linked polystyrene
Ionic forms as shipped	H^+	H^+
Physical form	Spherical beads	Macro-porous
Mean particle size (mm) (90%)	0.315–1.60	0.4–1.25
pH range	0–14	0–14
Total exchange capacity	4.3 equiv./L	2.4 mmol/(g of resin)

were determined by the AAS technique. The same measurements were repeated three times and average values have been taken as the remaining metal amount in the solution phase. The maximum deviation was 3%.

Equilibrium data for Pb^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Ni^{2+} ions were determined by contacting different amount of resin with equal volumes of a solution containing 10^{-3} M of the metal at constant temperature. Preliminary runs showed that about 2 h were needed to reach equilibrium. After equilibrium, the resin and solution were separated by filtration and the metal content of the solution was determined by AAS. The metal concentration in resin was obtained by a material balance.

3. Results and discussion

3.1. Effect of pH

WAC resins are all made from acrylic polymers, cross-linked with divinyl benzene (DVB) and functionalized with carboxylic exchange groups. WAC resins have higher selectivity for hydrogen ions than for any other ion. This property is what differentiates WAC resins from strong acid resins. WAC resins love hydrogen so much that when in the hydrogen form, they are practically non-ionized. This means they are poor ion-exchangers when in acidic form. The internal concentration for carboxylic groups is so high, that some groups can share hydrogen ions, thus leading to a small amount of apparent strong acid cation capacity. WAC resin cannot operate for long below a pH of 4.0.

Hydronium ion concentration (pH effect) is an important parameter affecting the ion-exchange process. The dependence of equilibrium concentration of metal ions on the sorption capacity at pH 3.0–9.0, created and maintained by buffer solutions of potassium hydrogen phthalate–NaOH and potassium dihydrogen phosphate–HCl, was investigated. The final pH of buffered solution after contact with the Lewatit CNP 80 and Lewatit TP 207 remained close to the initial pH of the metal solution. The maximum recoveries for strong electric field are present and electrostatic effects may become the dominant factor, such that small ions, which have a higher charge density, are bound more strongly [19]. The maximum recoveries (about 98–99%) for Cu^{2+} , Zn^{2+} , Ni^{2+} , Cd^{2+} and (about 95%) for Pb^{2+} were found at pH ranges 7–9, as shown in Fig. 1. It is clear that all the metals were poorly adsorbed at $\text{pH} < 4$ for Lewatit CNP 80 and for $\text{pH} < 3$ Lewatit TP 207 [18]. It was assumed that during the first 30 min, H^+ ions transport would compete with the exchange of Me^{2+} ions from solution. Because of this process, hydrolysis of functional groups would occur. This hydrolysis was accompanied by the replacement of Me^{2+} ions by H^+ ions and by the release of OH^- ions into the solution, causing the pH of the solution to change from 5.0 to 7.0.

Equilibrium distribution coefficient values (K_d) for the investigated metal ions at various initial solution concentrations were calculated using bath experiment data as follows:

$$K_d = \frac{q_e}{C_e} \quad (1)$$

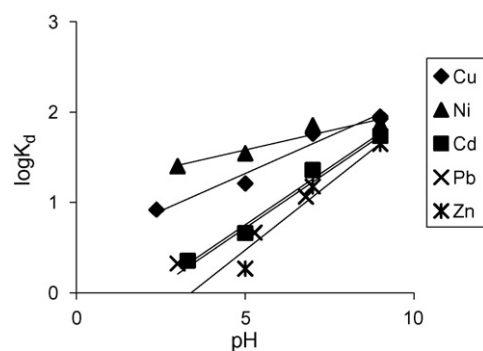


Fig. 1. The equilibrium distribution coefficients of Pb^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Ni^{2+} ions on the Lewatit CNP 80 as a function of pH. (Initial concentration of metals, 10^{-3} M; amount of resin, 0.1 g; volume of sorption medium, 20 mL; temperature, 25 ± 1 °C; stirring rate 180 rpm.)

where q_e is the amount of metal ion sorbed at equilibrium (mol/g), and C_e is the equilibrium concentration of metal ion in solution (mol/mL). Although, in general, the experimental conditions, such as metal concentration and pH, have a strong effect on K_d and it can be used as a comparative measure of the efficiencies of various exchangers. The (K_d) values for the investigated heavy metal ions at 10^{-3} M initial solution concentration at 0.1 mol/L ionic strength were calculated and the results are shown in Fig. 1. The distribution coefficients show that the Lewatit CNP 80 was more selective for Ni^{2+} , Cu^{2+} than it was for Cd^{2+} , Zn^{2+} and Pb^{2+} .

The results show that pH value is very significant for the performance of the Lewatit CNP 80 and Lewatit TP 207, thus pH adjustment may be a feasible alternative to prepare effluent for ion-exchange. The pH regions in which a rapid increase in metal ion sorption at an initial concentration of 10^{-3} mol/L of the metal ions were found were 3.0–9.0 for Pb^{2+} , Cd^{2+} , Zn^{2+} ions and 5.0–9.0 for Ni^{2+} , Cu^{2+} ions. Because the functional groups of ion-exchanger contain carboxylic groups, the recovery of metal ions with free orbital from water solutions could be carried out by forming ionic, coordination, or a simultaneous realization of both kinds of bonds.

Every dissolved metal has a distinct pH between 7.9 and 11.0 at which the optimum hydroxide precipitation will occur. Metal hydroxides are amphoteric, i.e., they are increasingly soluble at both low and high pH, and the point of minimum solubility (optimum pH for precipitation) occurs at a different pH value for every metal. At a pH at which the solubility of one metal hydroxide may be minimized, the solubility of another may be relatively high. Lead adsorption on Lewatit CNP 80 beads was found to be strongly pH-dependent and displayed a maximum uptake capacity at pH around 7 and a minimum at pH about 5.0. Sorption occurred even though the interaction between lead and Lewatit CNP 80 was electrostatically repulsive at $\text{pH} < 6.3$. Complexation, ion exchange, and electrostatic interaction are all believed to play a role in lead adsorption on Lewatit CNP 80, but the relative importance of each of mechanism varies with solution pH values.

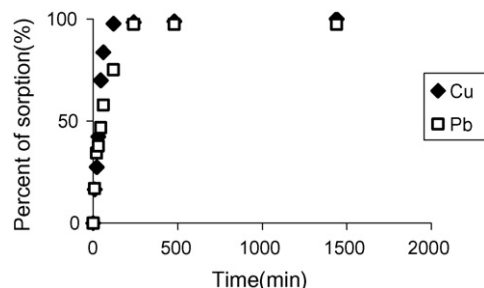


Fig. 2. Effect of contact time on the sorption of Cu^{2+} and Pb^{2+} by Lewatit CNP 80. (Initial concentration of metals, 10^{-3} M; amount of resin, 0.1 g; volume of sorption medium, 100 mL, temperature, 25 ± 1 °C; stirring rate 180 rpm; pH 8.)

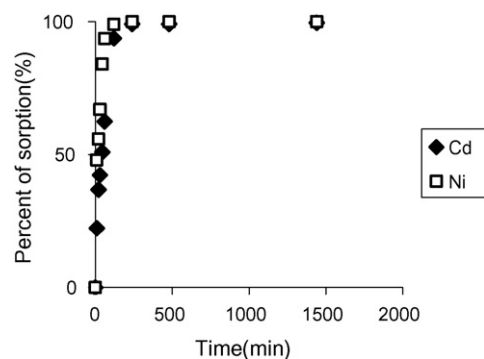


Fig. 3. Effect of contact time on the sorption of Ni^{2+} , Cd^{2+} by Lewatit CNP 80. (Initial concentration of metals, 10^{-3} M; amount of resin, 0.1 g; volume of sorption medium, 100 mL, temperature, 25 ± 1 °C; stirring rate 180 rpm; pH 8.)

3.2. Effect of contact time

The actual rates of ion exchange can vary over a wide range, requiring a few seconds to several months to reach equilibrium. Ion exchange is an equilibrium reaction that is dependent on the ionic concentrations of various ions both inside and outside the resin bead. The effect of contact time on the ion exchange of metal ions by the Lewatit CNP 80 resin was studied by taking 0.1 g resin with 100 mL of a metal solution in different stoppered flasks. The flasks were shaken for different time intervals in a temperature-controlled shaker. Fig. 2 shows the effect of contact time on ion-exchange of Cu^{2+} and Pb^{2+} using Lewatit CNP 80. Fig. 3 shows the effect of contact time on ion-exchange of Cd^{2+} and Ni^{2+} using Lewatit CNP 80. Fig. 4 shows the effect of contact time on ion-exchange of Zn^{2+} using Lewatit CNP 80

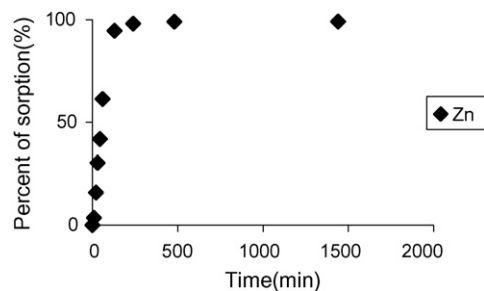


Fig. 4. Effect of contact time on the sorption of Zn^{2+} by Lewatit CNP 80. (Initial concentration of metals, 10^{-3} M; amount of resin, 0.1 g; volume of sorption medium, 100 mL, temperature, 25 ± 1 °C; stirring rate 180 rpm; initial pH 8.)

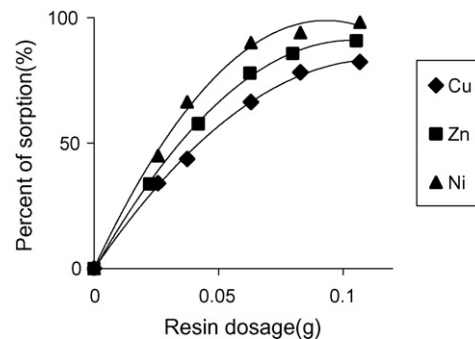


Fig. 5. Effect of resin dosage on the ion-exchange of Ni^{2+} , Zn^{2+} and Cu^{2+} on Lewatit CNP 80 resin. (Initial concentration of metals, 5×10^{-3} M; amount of resin, 0.02–0.1 g; volume of sorption medium, 20 mL, temperature, 25 ± 1 °C; stirring rate 180 rpm; pH 8.)

resin. The results show that the percentage of metal ion adsorbed increased with increasing time of equilibration and it reached the plateau value at 120 min for Cu^{2+} and Ni^{2+} and 200 min for Zn^{2+} , Pb^{2+} and Cd^{2+} .

When considering Lewatit TP 207 involving, it is accepted that a coordinate bond is formed between metal ions and the carboxyl group on the surface during the exchange process. Chelation-exchange invariably involves an ion-exchange process in conjunction with the formation of a coordinate bond. The batch ion-exchange process was relatively faster for Lewatit TP 207 than Lewatit CNP 80 but the cation exchange capacity of Lewatit CNP 80 is higher than Lewatit TP 207. The maximum recoveries of metals about 95–99% for Lewatit CNP 80 at pH 9.0 were found as shown in Figs. 2–4 and about 95% for Lewatit TP 207 at pH 5.0 [18].

3.3. Effect of resin amount

The resin amount is also important parameters to obtain the quantitative uptake of metal ion. The retention of the metals was examined in the relation to the amount of the resin. For this reason, amount of the resin were tested in the range of 0.02–0.1 g and equilibrated for 2 h at an initial $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, ZnCl_2 , $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ and $\text{Pb}(\text{NO}_3)_2$ concentration of 5×10^{-3} M, 20 mL solution. All experiments were carried out at the same stirring speed, 180 rpm. The results are given in Figs. 5 and 6. It is apparent that by increasing the resin amount, the sorption density, and the amount adsorbed metal ion per unit mass increases. It was found that the retention of metals increased with increasing amount of the resin up to 0.10 g. This value was taken as the optimum amount for other trials. Since the fraction of metal removed from the aqueous phase increases as the resin dosage is increased in the batch vessel with a fixed initial metal concentration, the curves in Figs. 5 and 6 approach asymptotic values from 0.08 to 0.1 g of the resin.

Sorption of metal ion was increased as the resin amount rises. This result was expected because for a fixed initial metal concentration, increasing adsorbent amount provides greater surface area or ion exchange sites and sorption sites [27–29]. It is readily understood that the number of available sorption sites increases by increasing the resin amount. It may be concluded

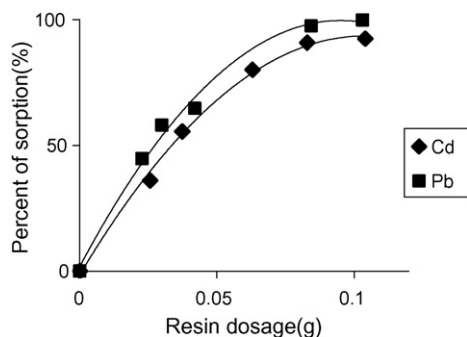


Fig. 6. Effect of resin dosage on the ion-exchange of Cd^{2+} and Pb^{2+} on Lewatit CNP 80 resin. (Initial concentration of metals, 5×10^{-3} M; amount of resin, 0.02–0.1 g; volume of sorption medium, 20 mL, temperature, 25 ± 1 °C; stirring rate 180 rpm; pH 8.)

that by increasing the adsorbent dose the removal efficiency increases but ion-exchange density decreases. The decrease in ion-exchange density can be attributed to the fact that some of the ion-exchange remains unsaturated during the sorption process; whereas the number of available ion-exchange sites increases by an increase in sorbent and this results in an increase in removal efficiency [30].

3.4. Ion-exchange studies

3.4.1. Batch sorption

The ion-exchange isotherms were plotted between the amount of metal ion adsorbed per gram of resin (mmol/g) and the amount of metal ions left in equilibrium solution, C_e , mmol/L. Sorption isotherms (Figs. 7–9) reveal that metal uptake increased with increased metal concentration. The curves for Pb^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Ni^{2+} ions reflect a gradual increase in the amount sorbed and show ion saturation at higher solution concentrations. The amount of sorbed metal ion per gram dry resin was calculated as 4.1, 4.6, 4.7, 4.8, and 4.7 mequiv./g dry resin for Pb^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Ni^{2+} , respectively. The precision of the method was examined at under optimum conditions. The mean recovery was $99.0 \pm 0.06\%$ ($n=8$, $p=0.96$) and the R.S.D. was $\sim 3.6\%$. These results show that the sorption amount of Cd^{2+} , Ni^{2+} and Zn^{2+} was higher than Cu^{2+} and Pb^{2+} for Lewatit CNP 80.

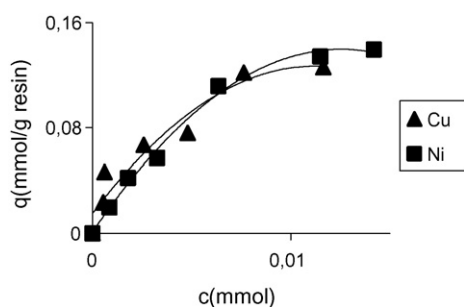


Fig. 7. Ion-exchange isotherms of Cu^{2+} and Ni^{2+} ions on Lewatit CNP 80. (Initial concentration of metals, 1×10^{-4} , 2×10^{-4} , 4×10^{-4} , 6×10^{-4} , 8×10^{-4} , 10^{-3} ; amount of resin, 0.1 g; volume of sorption medium, 20 mL, temperature, 25 ± 1 °C; stirring rate 180 rpm; initial pH 8.)

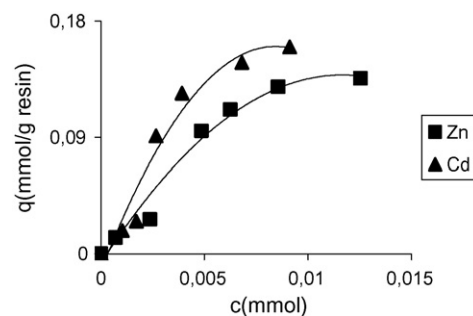


Fig. 8. Ion-exchange isotherms of Zn^{2+} and Cd^{2+} ions on Lewatit CNP 80. (Initial concentration of metals, 1×10^{-4} , 2×10^{-4} , 4×10^{-4} , 6×10^{-4} , 8×10^{-4} , 10^{-3} ; amount of resin, 0.1 g; volume of sorption medium, 20 mL, temperature, 25 ± 1 °C; stirring rate 180 rpm; initial pH 8.)

The sorption capacity of the Amberlite IR-120 for Cu, Zn, Cd, Ni, and Pb was also evaluated in our previous work at the same experimental conditions [19]. Adsorption analysis results obtained at various concentrations showed that the adsorption pattern on the Amberlite IR-120 followed Freundlich isotherms and the adsorption of Ni(II) and Zn(II) was higher than that of the other metal ions studied. This study does not claim any kinetic evaluation of the adsorption process, but it has shown that the equilibrium was attained in about 200 min. It has been observed that the maximum adsorption capacity of the Amberlite IR-120 was 50.9 mg/g for Cu, 765.1 mg/g for Zn, 235.3 mg/g for Ni, 201.1 mg/g for Cd, and 19.6 mg/g for Pb. The mean recovery was $99.2 \pm 0.07\%$. As can be seen, the cationic resin did not achieve high removal percentages as much as weak cation exchanger. The weak cationic type and presents a high selectivity but reached equilibrium slowly than strong cation exchanger for heavy metals.

It is natural that a high degree of swelling, as well as a cross-linking agent concentration, leads to the polymer chain extension that makes the functional groups of resin efficiently involved in the exchange process. The metal sorption capacity of the resin could be explained by the easy access of carboxylic functional groups for ion exchanging. Ion-exchange of the $-\text{COOH}$ groups increases with atomic number, valence and degree of ionization of the exchange metal ion. The ionic radius changes of these ions are $\text{Ni}^{2+} < \text{Cu}^{2+} < \text{Zn}^{2+} < \text{Cd}^{2+} < \text{Pb}^{2+}$ [19,31]. Small ions, which have a higher charge density are bound more strongly

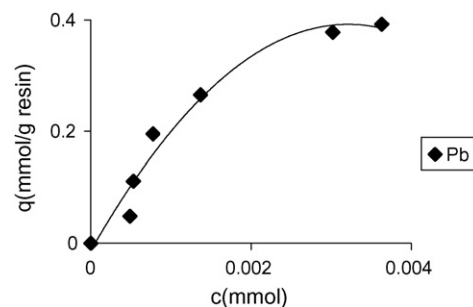


Fig. 9. Ion-exchange isotherms of Pb^{2+} ions on Lewatit CNP 80. (Initial concentration of metals, 1×10^{-4} , 2×10^{-4} , 4×10^{-4} , 6×10^{-4} , 8×10^{-4} , 10^{-3} ; amount of resin, 0.1 g; volume of sorption medium, 20 mL, temperature, 25 ± 1 °C; stirring rate 180 rpm; initial pH 8.)

[26]. As ionic radius increases due to charge density decreases, the ion-exchange capacity of the Lewatit CNP 80 resin increases, as for Ni^{2+} and Cd^{2+} .

The heavy metal sorption from industrial wastewater is usually carried out in the presence of various ingredients. The acid–base and electron-donor properties of the resin, the flexibility of the polymer chains and the degree of polymer swelling in water depends on the ionic strength of the solution. The effect of changed electrolyte concentration of 0.1 and 0.5 M (in this case NaNO_3) on the sorption behavior toward metal ion removal was studied in a model solution of metal concentration of 10^{-3} mol/L at pH 7.0. The nitrate was the only anion in the system. Nitrate is an extremely poor ligand; therefore, any significant complexation between divalent cations and nitrate ions can be ruled out. The ionic strength of the solution affects the ion sorption capacity of the resin. However, if a charged functional group is able to form a surface complex with the metal ions, the effect of ionic strength will be much less. Nevertheless, chelation exchange is not totally insensitive to ionic strength. The presence ionic strength (NaNO_3) slightly lowered the metal ion removal. At pH 7.0, the removal efficiency for the initial concentration of 10^{-3} M metal ion was almost 99% in the absence of ionic strength, while it was decreased to 94% at an ionic strength of 0.5 M.

The concentration of background electrolyte must have in effect on the activities of the ions and, therefore on the stability constants. The change in retention time with increased salt concentration on chelating surfaces will be expected to be more complex, particularly if residual ion exchange is present. For the carboxylic acid chelating resin the total sorption or distribution coefficients (K_d) of metal ions decreased with increasing ionic strength. The relatively large change in the (K_d) curves in Fig. 1 for metal ions at lower ionic strengths is due to ion exchange effects. Increasing ionic strength will increase the ratio of chelation-to-ion-exchange and, at very high salt concentrations; ion exchange will become very small. A further increase in the salt concentration may significantly lead to a decrease in the efficiency of removal.

3.4.2. Isotherm models

Sorption equilibrium is normally represented by ‘sorption isotherm’ curves. In general, a sorption process could be preceded by the following mechanisms:

- Physical sorption.* There is no exchange of electrons in physical sorption, rather intermolecular attractions occur between ‘valence happy’ sites and are therefore independent of the electronic properties of the molecules involved.
- Chemical sorption.* Chemisorption, involves an exchange of electrons between specific surface sites and solute molecules, which results in the formation of a chemical bond. Chemisorption is defined by much stronger adsorption energy than physical adsorption.
- Electrostatic sorption (ion-exchange).* This is a term reserved for coulombic attractive forces between ions and charged functional groups and is more commonly classified as ion-exchange.

- Complex formation* between the counter ion and the functional group.
- Hydrate formation* at the surface or in the pores of the ion-exchanger [16,19,36].

The obtained sorption affinity sequence in the presented work was $\text{Ni}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Pb}^{2+}$. The sorption (binding) constant for nickel ions was bigger than other metal ions. This phenomenon is not rare for the binding of metal ions in carboxyl sites. The lead ions have the lowest sorption capacity.

The most common shape of the graph of amount adsorbed for unit weight of adsorbent versus the concentration in the fluid in equilibrium is Langmuir sorption isotherms. The Langmuir sorption isotherm was used to analyze the results as these isotherms have been shown to be useful in describing ion-exchange behavior of metals on resins [31–34]. The shape of the resulting curve indicated the feasibility of the separation media. Equilibrium isotherms for metals $q=f(C)$ were plotted in Figs. 7–9. These isotherms relate metal uptake per unit weight of resin q_e to the equilibrium metal concentration in the bulk fluid phase C_e . The sorption data were fitted with the Langmuir adsorption equation.

Langmuir equation:

$$\frac{C_e}{q_e} = \frac{1}{K_b A_s} + \frac{C_e}{A_s} \quad (2)$$

where A_s and K_b are coefficients, q_e the weight adsorbed per unit weight of adsorbent and C_e is the metal concentration in bulk solution at equilibrium. Since the correlation coefficients were high for each metal–sorbent equilibrium condition as seen from Table 2, the Langmuir-type sorption isotherm was suitable for equilibrium studies. The data for the uptake of metal ion by the resin has been processed in accordance with a linear form of the Langmuir isotherm equation. The linear model, which describes the accumulation of solute by sorbent was directly proportional to the solution concentration. The Langmuir isotherm applies to ion-exchange on a completely homogenous surface with negligible interaction between adsorbed molecules.

The ion-exchange process is not a surface phenomenon; more exchange can be found in the interior of the bead. Comparison of the changes in the rate and isotherms of exchange, associated with the change in the concentration of the solution, showed that there is a definite relation between them. Reaction rates are variable as the size range of metal that may diffuse into and out of the resin structure. The rate of exchange, or kinetics, of

Table 2
Parameters of Langmuir isotherm for sorption of metals on Lewatit CNP 80

Metal	Langmuir isotherm method		
	A_s^a	K_b (l/mol)	Correlation coefficient
Cu^{2+}	0.1610	453.370	0.996
Zn^{2+}	0.3089	90.935	0.998
Ni^{2+}	0.3229	81.070	0.993
Cd^{2+}	0.0439	225.67	0.872
Pb^{2+}	0.3541	209.09	0.926

^a mmol/g dry resin.

Table 3

Selectivity of Lewatit CNP 80 resin relative to its affinity for Cu^{2+} , Zn^{2+} , Ni^{2+} and Cd^{2+}

$K_{\text{Zn}}^{\text{Cu}}$	1.192
$K_{\text{Cd}}^{\text{Cu}}$	2×10^{-5}
$K_{\text{Ni}}^{\text{Cu}}$	1.439
$K_{\text{Pb}}^{\text{Cu}}$	0.705
$K_{\text{Cd}}^{\text{Zn}}$	0.933
$K_{\text{Ni}}^{\text{Zn}}$	1.452
$K_{\text{Pb}}^{\text{Zn}}$	0.472
$K_{\text{Cd}}^{\text{Ni}}$	0.384
$K_{\text{Pb}}^{\text{Ni}}$	0.275
$K_{\text{Pb}}^{\text{Cd}}$	0.671

ion-exchange reactions depends on several factors. The solution being treated, the size of the ions being exchanged and the ionic mobility influence the kinetic rate. The comparison of the rate and isotherms of exchange, associated with the change in the concentration of the solution showed that there is a definite relation between them.

The competitive effect of metal ions was interpreted using the selectivity coefficient. This coefficient is a measure of the relative selectivity between two competing solutes and is equal to the ratio of their distribution ratio between the exchanger phase and the aqueous phase [35]:

$$D_{A/B} = \frac{K_{d(A)}}{K_{d(B)}} \quad (3)$$

At the same concentration, the rate of exchange is higher the greater the selectivity of the ion-exchange resin with respect to the entering ion. Table 3 shows the selectivity coefficients, which are the measure of the affinity of Lewatit CNP 80 for a particular metal ion as compared to that for Cu^{2+} , Zn^{2+} , Ni^{2+} , Cd^{2+} and Pb^{2+} . We immersed the exchanger in a solution containing two metals ions, which their relative concentration in the exchanger equal. If the Lewatit CNP 80 favors one of the ions, then the isotherm for its uptake appeared above the others. The deviation from the other indicated the relative affinity of the exchanger for the ion. The actual selectivity value depends on the pH, the ionic strength, and the presence of other complex-forming agents. Selectivity increased in the series: $\text{Cd}^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+}$. Due to electrostatic effects, the metal binding strength increases with decrease of the radius of hydrated metal ion and increase of charge of the metal ion. If a strong electric field is present, electrostatic effects may become the dominant factor, such that from the isotherm of metal ions it could be assumed that the stronger binding sites are occupied first; and then the binding strengths are decreased with increasing degree of site occupation [37]. Since the selectivity changes in the conformity with the change in the concentration, the rate of mass exchange is influenced simultaneously.

3.4.3. Ion-exchange kinetics

Experiments were also performed in order to understand the kinetics of metal removal by Lewatit CNP 80. For the equilibrium rate study, to determine the time required for the separation

to reach equilibrium, 10^{-3} M solution of metals was treated with the resin and mixed. With time, small aliquots of the solution are periodically removed and the solution separated from the media was analyzed with AAS. It is a well-established fact that the ion-exchange of ions in aqueous system follows reversible first-order kinetics, when a single species is considered on a heterogeneous surface. It must be remembered that the two important physico-chemical aspects for parameter evaluation of the ion-exchange process as a unit operation are the kinetics and the equilibrium. Kinetics of sorption describing the solute uptake rate, which in turn governs the residence time of ion-exchange reaction, is one of the important characteristics defining the efficiency of ion-exchange. Hence, in the present study, the kinetics of metal removal has been carried out to understand the behavior of this resin.

The kinetics may be affected by a number of parameters, such as the nature of the exchanger, the nature of the counter ions, the extent of agitation and the concentration of the counter ions, etc. The ion-exchange reaction occurring between the resin particle and the solution will involve five distinct steps. (a) Diffusion of the ions through the bulk solution in order to reach the ion-exchanger particle, (b) diffusion of the ion through the hydrated film surrounding the particle, (c) diffusion of the ion across the film-particle interface, (d) diffusion of the ion through the particle and (e) the actual chemical reaction involving the exchange of ions. Providing that the concentration of ions in the solution is not extremely low steps (a), (c) and (e) are generally fast and do not determine the rate of the reaction. It is only step (b) diffusion through the hydration film (d) diffusion through the particle that controls the kinetics of the overall process, although sometimes both may determine the rate simultaneously. This is a simplified picture of the mechanism of an ion-exchange process and its kinetics [15–19,38,39].

Using the kinetic equations numbered (2)–(17) in our earlier previous work [18], the overall rate constant, the forward and backward rate constants were calculated. For instance, by plotting $\ln(1 - U_t)$ versus t (Figs. 10–14), the overall rate constant k for given concentration of metal was calculated by considering the slope of straight lines by using Eqs. (7) and (9) in Ref. [18], the equilibrium constant K_C , forward and backward

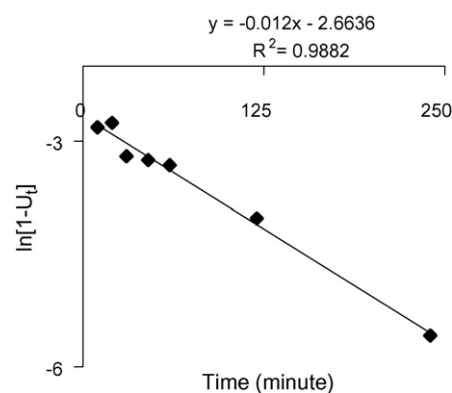


Fig. 10. Kinetic fits for the ion-exchange of Cu^{2+} on Lewatit CNP 80. (Initial concentration of metals, 10^{-3} M; amount of resin, 0.1 g; volume of sorption medium, 100 mL, temperature, 25 ± 1 °C; stirring rate 180 rpm; initial pH 8.)

Table 4
Rate constants for removal of Pb^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Ni^{2+} with Lewatit CNP 80 system

Metal	Metal amount (mmol)	Overall rate constant $k = k_1 + k_2$ (h^{-1})	Forward rate constant k_1 (h^{-1})	Backward rate constant k_2 (h^{-1})
Cu^{2+}	0.10	0.0120	0.0097	0.0023
Zn^{2+}	0.10	0.0203	0.0182	0.0021
Ni^{2+}	0.05	0.0066	0.0064	0.0002
Cd^{2+}	0.05	0.0340	0.0339	0.0001
Pb^{2+}	0.05	0.0116	0.0078	0.0038

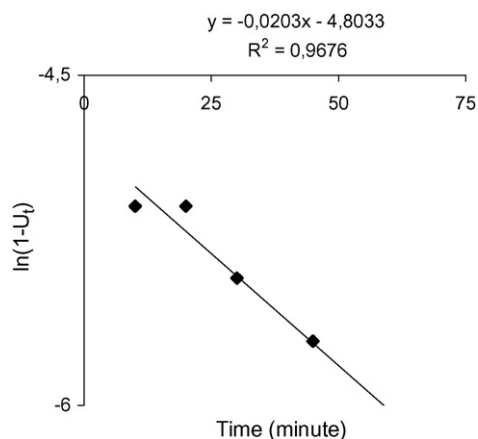


Fig. 11. Kinetic fits for the ion-exchange of Zn^{2+} on Lewatit CNP 80. (Initial concentration of metals, 10^{-3} M; amount of resin, 0.1 g; volume of sorption medium, 100 mL, temperature, 25 ± 1 °C; stirring rate 180 rpm; initial pH 8.)

rate constants k_1 and k_2 were calculated and shown in Table 4. From Table 4, it is seen that the forward rate constants for the removal of metal were much higher than the backward rate constants namely, the desorption process. This suggests that the rate of ion-exchange is clearly dominant. Both resins have about the same order of magnitude for the ion-exchange rates even if they are characterized where k_1 is the forward reaction rate constant, k_2 the backward reaction rate constant. The kinetics of the resin Lewatit CNP 80 was determined to be slightly slower than Lewatit TP 207.

The exchange reaction is diffusion so the rate of diffusion of ion has effect of the ion-exchange reaction. A characteristic future of the systems considered is that the rate of mass exchange

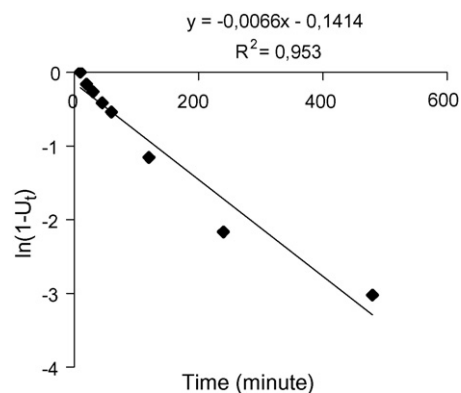


Fig. 12. Kinetic fits for the ion-exchange of Ni^{2+} on Lewatit CNP 80. (Initial concentration of metals, 10^{-3} M; amount of resin, 0.1 g; volume of sorption medium, 100 mL, temperature, 25 ± 1 °C; stirring rate 180 rpm; initial pH 8.)

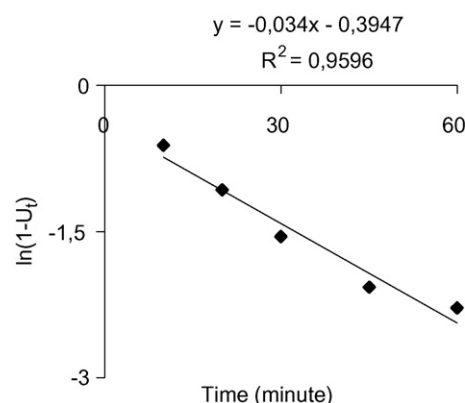


Fig. 13. Kinetic fits for the ion-exchange of Cd^{2+} on Lewatit CNP 80. (Initial concentration of metals, 10^{-3} M; amount of resin, 0.1 g; volume of sorption medium, 100 mL, temperature, 25 ± 1 °C; stirring rate 180 rpm; initial pH 8.)

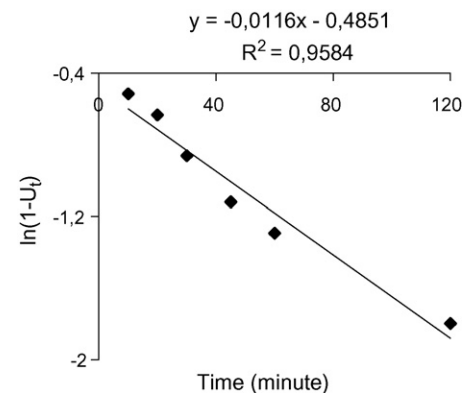


Fig. 14. Kinetic fits for the ion-exchange of Pb^{2+} on Lewatit CNP 80. (Initial concentration of metals, 10^{-3} M; amount of resin, 0.1 g; volume of sorption medium, 100 mL, temperature, 25 ± 1 °C; stirring rate 180 rpm; initial pH 8.)

in the case of external and internal diffusion kinetics depends on the concentration of the solution and the selectivity of the exchange and the separation of the regions where a particular mechanism operates is, therefore, extremely complex. The internal diffusion kinetics is favored by a convex sorption isotherm, a high concentration and a large resin grain diameter. Thus, sections through resin treated with metal solutions in Figs. 7–9 showed gradually rising curves, which is evidence in support of the internal diffusion transport mechanism.

4. Conclusion

The results show that the equilibrium between Lewatit CNP 80 and metals was reached in 120 min for Cu^{2+} and Ni^{2+} and

200 min for Zn^{2+} , Pb^{2+} and Cd^{2+} ions. The maximum recoveries (about 98–99%) for Cu^{2+} , Zn^{2+} , Ni^{2+} , Cd^{2+} and (about 95%) for Pb^{2+} were obtained at pH ranges 7–9. The equilibrium in the ion-exchanger–metal ion solution systems were described by the Langmuir adsorption isotherm. The sorption of metal ions on the resin was strongly dependent on the equilibrium pH value of the solution. The distribution coefficient values for metal ions at various initial concentrations at 0.1 mol/L ionic strength increased in the following order: $Ni^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} > Pb^{2+}$. The Lewatit CNP 80 has a high selectivity toward Ni^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} , Pb^{2+} ions at pH 6.0–9.0 and can be successfully used to remove different amounts of these elements from metal-bearing solutions and industrial wastewater.

The kinetics of metal ion-exchange by the Lewatit CNP 80 followed first-order reversible kinetics. A batch contactor requires about 100–120 min contact time to achieve 95–99% removal from aqueous solution. The resins have good thermal stability, and very good resistance to attrition and the action of solvents. WAC has very high selectivity for divalent cations. This makes them ideal candidates for the removal of various metals from wastewater streams. Under less drastic conditions, this resin has proved to cope with the presence of other ions and could be applied to the removal of metal ions in aqueous solution.

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