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Removal of lead, cadmium and copper ions from aqueous solutions by using ion exchange resin C 160

Introduction

At the present time, the pollution of the environment by toxic metals is a major environmental problem. Among the metals, lead, cadmium, mercury and copper are particularly dangerous for living organisms. Frequently, these metal ions get into natural waters with wastes from metallurgical, chemical and electronic industries, as well as leachates from industrial and municipal wastes. The sewage from the metallurgical industry constitutes a special type of waste. This is due to its toxicity. Apart from lead, cadmium and copper also contain such elements as cobalt, nickel, zinc, chromium, silver, gold, as well as complexing agents and cyanides. Therefore, their purification is extremely difficult and costly (Kolodynska 2009).

The ion exchange process plays a significant role in modern technologies concerning the removal of metal ions from waste water. It involves replacing ions included in ion exchange resin with an equal amount of other ions of the same sign, located in the purified aqueous solution (Winnicki 1978; Granops and Kaleta 2004; Bozecka 2013).

Synthetic ion exchangers (ion exchange resins) (Winnicki 1978) play a great practical role among the wide group of ion exchangers. This is due to their unique structure which allows for the selective exchange of ions present in their backbone to the ionic form in solu-

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tion. An important advantage of ion exchangers is also the possibility of regeneration and recovery of the removed metals. The technological usefulness of synthetic ion exchangers is identified by a number of factors, among them: particle size, bulk density, chemical resistance, selectivity, water content, exchange capacity (Bozecka et al. 2013).

Table 1.   Comparison of ion exchange capabilities of synthetic resins (Bozecka 2013)

Tabela 1.   Porównanie zdolności jonowymiennych syntetycznych jonitów (Bozecka 2013)

Metal ion	Ion exchange resin	Characteristics of the ion exchange resin	Dose [g/L]	The initial concentration of metal [mg/L]	pH	The maximum sorption capacity [mg/g]	Degree of purification [%]	Literature
Pb^{2+}	Purolite C100	Functional groups – sulfonic Ion form – H^+	25.0	2.7−265.0	n.d.	9.6	75.5 (for concentration 2.7 mg/L)	Abo-Farha et al. 2009
	Amberlite IR 120		5.0	5.0−100	5.0	9.8	98.6 (for concentration 20 mg/L)	Kocaoba 2007
Cd^{2+}	Duolite ES 467	Functional groups – aminophosphonic Ion form – Na^+	10.0	70.0−350.0	4.9	13.8	n.d.	Srinivasa et al. 2010
	Amberlite IR 120		2.0	20.0	5.5	n.d.	90.8	Kocaoba and Akcin 2005
	Amberlite IR 120	Functional groups – sulfonic Ion form – H^+	2.0	20.0	5.5	n.d.	81.1	
Cu^{2+}	Chelex 100 Amberlite IRC748	Macroporous chelating ion exchange resins containing iminodiacetic acid (IDA)	1.0	190–571	2–6.5	n.d.	n.d.	Lin and Juang 2007
	Lewatit TP207 Lewatit TP208	Chelating ion exchangers with the iminodiacetate functional groups (IDA)	20.0	6.35	1–7	n.d.	44.8 – pH = 1 99.0 – pH = 7	Rudnicki et al. 2014
	2.4-DHBEDF	Chelating copolymer resin	1.0	n.d.	4.5	n.d.	n.d.	Gurnule and Dhote 2012
	Lewatit TP207	Chelating ion exchanger resin with the iminodiacetate functional groups (IDA)	n.d.	0.5–14	7.3–7.6	n.d.	99	Korngold et al. 1996

n.d. – no data.

The use of ion exchange resins for the removal of toxic metals such as: lead, cadmium and copper from water and waste water is the subject of many scientific studies (Korngold et al. 1996; Rengaraj et al. 2001; Sanak-Rydlewska and Zięba 2001; Kocaoba and Akcin 2005; Kocaoba 2007; Lin and Juang 2007; Abo-Farha et al. 2009; Srinivasa et al. 2010; Gurnule and Dhote 2012; Rudnicki et al. 2014). The results of the studies of these teams are summarized in Table 1.

The aim of this study was to determine and compare the sorption properties of synthetic resin C 160 towards Pb^{2+}, Cd^{2+} and Cu^{2+} ions. The results obtained for Cd^{2+} and Cu^{2+} ions were compared with results obtained for Pb^{2+} ions which were published before (Bozecka et al. 2013; Bozecka et al. 2014).

1. Experimental methods

The subject of the research was C 160 ion-exchange resin produced by Purolite. It is a strongly acidic cation-exchange resin with sulfonic acid groups ($-SO_3H$). The applied synthetic ion exchange resin worked in a sodium cycle. A crucial step in the preparation of the resin for this research was swelling in deionized water for 24 hours.

For the purpose of the research test, a 0.5 g sample of the ion exchange resin was used. The range of the studied initial concentration of the Pb^{2+}, Cd^{2+} and Cu^{2+} ions in solutions was from 6.25 mg/L to 109.39 mg/L. The metal ions were introduced into the solution in the form of nitrates(V). All experiments were performed at a fixed pH value and at an ionic strength equal to 0.02 mol/L. Its value was adjusted using a KNO_3 solution at the concentration of 0.04 mol/L. The pH of the solution was equal to 4.0 (± 0.1). For pH adjustment 0.02 M HNO_3 was used. The applied experimental conditions were established according to the previous studies (Bozecka 2013).

The ion exchange processes were performed using a mechanical stirrer. For this purpose, 100 L of solutions with ion exchange resin were placed in a beaker which was then placed in a thermostatic bath at a constant temperature of 298 ± 0.5 K for 15 minutes. The contents of the beakers were continuously stirred for 60 minutes with the speed of 120 rpm. Samples used for analysis were collected after one hour of reaction, because after that time the system reached equilibrium. This was based on the experiments that were developed for natural sorbents (Bozecka 2013).

The final concentration of Pb^{2+} and Cd^{2+} ions in the solutions after the ion exchange process was determined by the flow-through coulometry using an EcaFlow 150 GLP device manufactured by POL-EKO. Before measurements, the solutions were filtered using filter paper to remove solid particles. Three measurements were performed for each sample. Equilibrium concentration values indicated in this paper are the arithmetic averages of three measurements.

In the case of Cu^{2+} ions, the final concentration in the solutions was determined using the kuprizon's method with UV-VIS spectroscopy. Assays were carried out in an ammonia-

-citrate medium at pH 8.0–9.5. The absorbance of the solution was measured at a wavelength of 600 nm.

The degree of purification of the solutions for Pb^{2+}, Cd^{2+} and Cu^{2+} ions, X (%), were calculated using formula (1):

$$X = \frac{c_o - c_{eq}}{c_o} \cdot 100\%$$

(1)

✤ c_o and c_{eq} –   are the initial and equilibrium concentrations of the studied ions in solutions [mg/L].

The sorption capacity, Q [mg/g], was determined as the amount of Pb^{2+}, Cd^{2+} and Cu^{2+} ions contained in the dry weight of ion-exchange resin according to the concentration in the aqueous solution, according to formula (2):

$$Q = \frac{V(c_o - c_{eq})}{m}$$

(2)

✤ V –   is the volume of the solution [L],
  c_o and c_{eq} –   are the initial and equilibrium concentrations of studied ions in the solution [mg/L],
  m –   is the quantity of dry mass of the ion-exchange resin [g].

2. Discussion of the results

2.1. Influence of the concentration of studied ions on their removal using ion-exchange resin C 160

The determined degree of purification of the solutions for Pb^{2+}, Cd^{2+} and Cu^{2+} ions using ion exchanger resin C 160 as a function of the initial concentration are shown graphically in Figs. 1–3 and summarized in Table 2.

The obtained results show that at the studied concentrations, the C 160 ion exchange resin effectively removes Pb^{2+}, Cd^{2+} and Cu^{2+} ions from aqueous solutions. The greatest degree of purification of the solutions was achieved for lead. They amounted to, respectively, 99.8% and 99.9% (Table 2).In the entire range of the studied concentrations of lead ions, the efficiency of the process is practically constant. For other solutions, the ion exchange process occurs with lower efficiency but also reaches more than 90%.
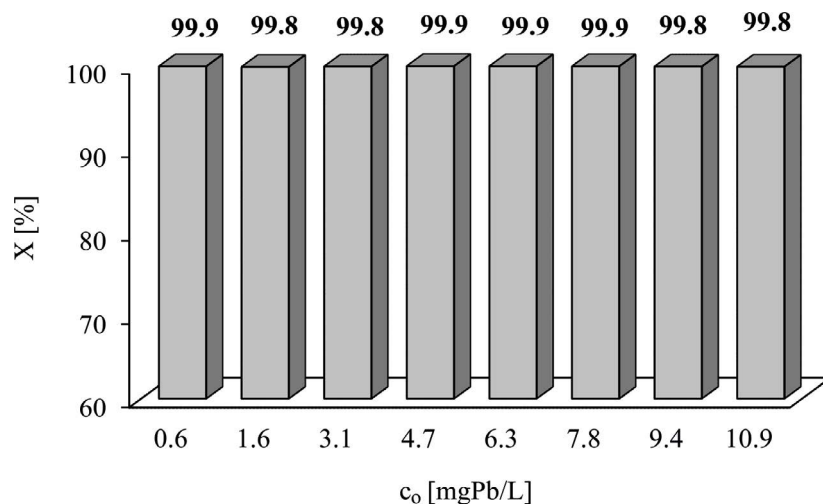
Fig. 1. Influence of the initial concentration of solutions on ion exchange of Pb^{2+} ions using ion exchange resin C 160 (weight of ion exchange resin 0.5 g; ionic strength 0.02 mol/L; pH 4.0±0.1; temperature (298±0.5) K; time of adsorption 1 h; mixing speed 120 rpm.)

Rys. 1. Wpływ stężenia wyjściowego roztworów na proces wymiany jonowej jonów Pb^{2+} na jonicie C 160 (masa jonitu 0,5 g; siła jonowa 0,02 mol/dm^3; pH 4.0±0.1; temp. (298±0,5) K; czas 1 h; szybkość mieszania 120 obrotów/min.)
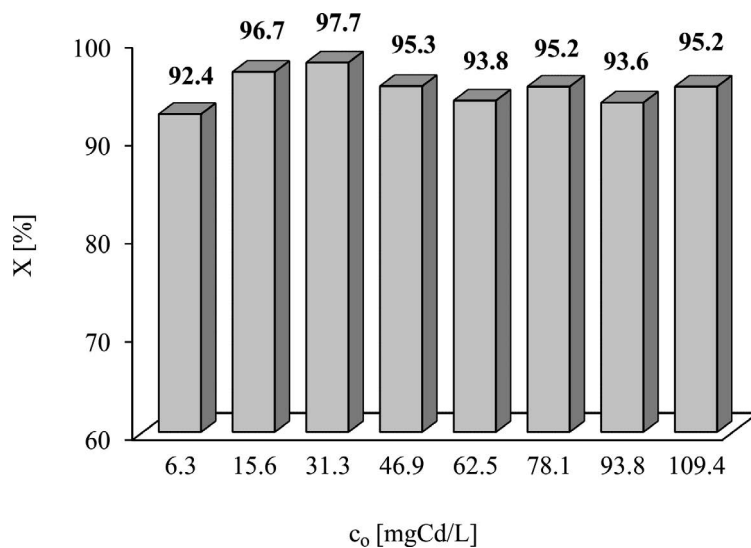

Fig. 2. Influence of the initial concentration of solutions on ion exchange of Cd^{2+} ions for ion exchange resin C 160 (weight of ion exchange resin 0.5 g; ionic strength of 0.02 mol/L; pH 4.0±0.1; temperature (298±0.5) K; time of adsorption 1 h; mixing speed 120 rpm.)

Rys. 2. Wpływ stężenia wyjściowego roztworów na proces wymiany jonowej jonów Cd^{2+} na jonicie C 160 (masa jonitu 0,5 g; siła jonowa 0,02 mol/dm^3; pH 4,0±0,1; temp. (298±0,5) K; czas 1 h; szybkość mieszania 120 obrotów/min.)
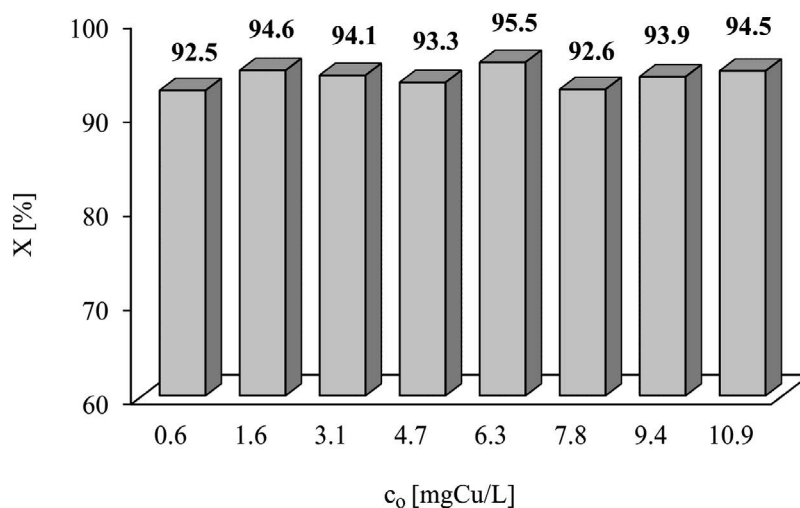
Fig. 3. Influence of the initial concentration of solutions on ion exchange of Cu^{2+} ions for ion exchange resin C 160 (weight of ion exchange resin 0.5 g; ionic strength of 0.02 mol/L; pH 4.0±0.1; temperature (298±0.5) K; time of adsorption 1 h; mixing speed 120 rpm.)

Rys. 3. Wpływ stężenia wyjściowego roztworów na proces wymiany jonowej jonów Cu^{2+} na jonicie C 160 (masa jonitu 0,5 g; siła jonowa 0,02 mol/dm^3; pH 4,0±0,1; temp. (298±0,5) K; czas 1 h; szybkość mieszania 120 obrotów/min.)

Table 2. Dependence of the degree of purification of the solutions as a function of the initial concentration of Pb^{2+}, Cd^{2+} and Cu^{2+} ions in the solution for studied ion exchange resin C 160

Tabela 2. Zależność stopnia oczyszczenia roztworów w funkcji stężenia wyjściowego jonów Pb^{2+}, Cd^{2+} i Cu^{2+} dla badanego jonitu C 160

Initial concentrations of metal c_o [mg/L]	Degree of purification [%]		
	Pb^{2+}	Cd^{2+}	Cu^{2+}
6.25	99.87	92.43	92.45
15.65	99.80	96.74	94.58
31.30	99.85	97.70	94.07
46.95	99.89	95.29	93.31
62.60	99.88	93.81	95.46
78.25	99.87	95.24	92.57
93.90	99.84	93.60	93.91
109.55	99.82	95.24	94.53

It was observed that with the increasing concentration of Cd^{2+} ions in the solution, the efficiency of the investigated process decreases. The Cu^{2+} ions behave similarly.

Interpretation of the results of sorption of studied ions based on the Langmuir adsorption model

The removal of Pb^{2+}, Cd^{2+} and Cu^{2+} ions using ion exchange resin C 160 was described using the Langmuir isotherm. The characteristics of this model are given in Table 3.

The results of the study approximated with the Langmuir equations were shown in Fig. 4.

Table 3. Characteristics of the Langmuir model (Bozecka 2013)

Tabela 3. Charakterystyka modelu Langmuira (Bozecka 2013)

The Langmuir isotherm		
Assumptions	• there is a specified number of adsorption centers on the adsorbent surface and each of them is able to adsorb only one molecule • energy state of each of the adsorbed individual is the same in all places on the surface of the adsorbent. • localized adsorption takes place which means that particles cannot move freely on the surface. Lateral interactions between the adsorbed molecules are irrelevant.	
Equation	$$Q = \frac{q_{\max} b \cdot c_{eq}}{(1 + b \cdot c_{eq})}$$	(3)
The linear form, where	$$\frac{1}{Q} = \frac{1}{q_{\max} b} \cdot \left(\frac{1}{c_{eq}} + b \right)$$ Q – amount of the metal ions adsorbed per weight unit of the ion exchanger [mg/g]; c_{eq} – the final concentrations of metal ions in solution [mg/L]; $q_{\max}$ [mg/g] and b [L/mg] are Langmuir constants	(4)

Table 4. The Langmuir isotherms coefficients with their uncertainty and correlation coefficient for Pb^{2+}, Cd^{2+} and Cu^{2+} ions adsorbed on ion exchange resin C 160

Tabela 4. Współczynniki izoterm Langmuira wraz z niepewnościami i współczynniki korelacji otrzymane dla jonów Pb^{2+}, Cd^{2+} i Cu^{2+} na jonicie C 160

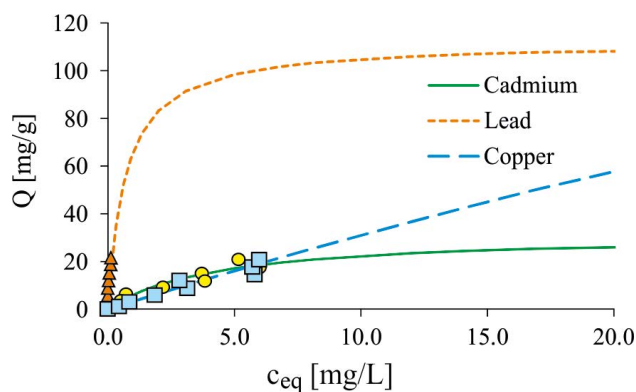| Studied ion	q_{max} [mg/g]	Δq_{max} [mg/g]	b [L/mg]	Δb [L/mg]	R
Pb^{2+}	112.17	2.19	1.4370	0.00200	0.9878
Cd^{2+}	31.76	0.69	0.2348	0.00020	0.8282
Cu^{2+}	468.42	9.35	0.0071	0.00001	0.9856

Fig. 4. A comparison of the Langmuir isotherms of Pb^{2+}, Cd^{2+} and Cu^{2+} ions for ion exchange resin C 160
(weight of ion exchange resin 0.5 g; ionic strength of 0.02 mol/L; pH 4.0±0.1; time of adsorption 1 h;
mixing speed 120 rpm.)

Rys. 4. Porównanie izoterm Langmuira jonów Pb^{2+} Cd^{2+} i Cu^{2+} na jonicie C 160
(masa jonitu 0,5 g; siła jonowa 0,02 mol/dm^3; pH 4,0±0,1; czas 1 h;
szybkość mieszania 120 obrotów/minutę)

The values of coefficient q_{max} and b in the Langmuir isotherms were determined on the basis of the linear form (Table 3). The values of these coefficients with uncertainties and the correlation coefficient R are presented in Table 4.

According to the data presented on Figure 4, for each of studied ions, sorption capacity increases until the saturation and equilibrium state is reached. The highest value of constant q_{max} was obtained in the case of Cu^{2+} ions. It was 468.42 mg/g. For other ions, respectively, the q_{max} parameter reached: Pb^{2+} 112.17 mg/g and Cd^{2+} 31.76 mg/g values (Table 4). Ion exchange resin C 160 shows the highest affinity for the Pb^{2+} ions. In this case, the value of coefficient b was 1.437 L/mg. For other ions, the obtained value were equal 0.2348 L/mg (for Cd^{2+} ions) and 0.0071 L/mg (for Cu^{2+} ions) (Table 4).

Conclusion

On the basis of this study the following conclusions can be drawn:
- C 160 is an effective ion exchange resin for the studied divalent metal ions such as: Cu, Pb and Cd;
- for the studied concentration range, the highest degree of purification of the solutions from the above-mentioned ions ranged from approximately 92% to over 99% (Table 2);
- the greatest degree of separation was observed for the lead ions, reaching over 99% in the range of the studied concentrations (Table 2 and Figure 1);

◆ based on the interpretation of the Langmuir equation coefficients, an indication can be made that the studied ion exchange resin has a major sorption capacities toward copper ions (q_{max} constant value was approximately 468.42 mg/g) (Table 4);

◆ the highest affinity (value of parameter b) ion exchange resin C 160 reached was for lead ions and it was approximately 1.44 L/mg (Table 4).

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USUWANIE JONÓW OŁOWIU, KADMU I MIEDZI Z ROZTWORÓW WODNYCH ZA POMOCĄ ŻYWICY JONOWYMIENNEJ C 160

Słowa kluczowe

jonity, wymiana jonowa, jony ołowiu, kadmu, miedzi

Streszczenie

Roztwory odpadowe zawierające m.in. jony metali Pb, Cu, Cd i inne powstają w przemyśle elektrochemicznej obróbki metali, w przemyśle przeróbki rud metali nieżelaznych, a także mogą być składnikiem odcieków ze składowisk odpadów tych rud. Toksyczność jonowych form tych metali jest znaczna, stąd w pracy podano wyniki badań jednego ze sposobów obniżenia ich koncentracji w roztworach wodnych.

W artykule podano wyniki badań dotyczących usuwania jonów Pb^{2+}, Cd^{2+} i Cu^{2+} z modelowych roztworów wodnych za pomocą syntetycznej żywicy jonowymiennej C 160 firmy Purolite. Badany jonit zawiera w swojej strukturze grupy sulfonowe ($-SO_3H$) i należy do silnie kwaśnych kationitów. Zakres badanych stężeń początkowych jonów Pb^{2+}, Cd^{2+} i Cu^{2+} w roztworach wynosił od 6,25 mg/dm^3 do 109,38 mg/dm^3. Otrzymane wyniki potwierdziły, że wykorzystana żywica jonowymienna C160 skutecznie usuwa wymienione jony z badanych roztworów. Dla przyjętego zakresu stężeń i warunków procesu wymiany jonowej, największy stopień oczyszczenia roztworów osiągnięto dla ołowiu. Wynosił on 99,9%. W przypadku pozostałych roztworów wymiana jonowa zachodzi z wydajnością niższą, ale wysoką i wynosi dla wszystkich jonów ponad 90%. Wyniki badań zinterpretowano opierając się na modelu adsorpcji Langmuira. Dla każdego badanego jonu pojemność sorpcyjna jonitu wzrasta, aż do osiągnięcia wysycenia i stanu równowagi. Z interpretacji współczynników równania Langmuira wynika, że badany jonit charakteryzuje się największymi zdolnościami sorpcyjnymi w stosunku do jonów miedzi. W ich przypadku otrzymano największą wartość stałej q_{max} izotermy Langmuira. Dla jonów Cu^{2+} wyniosła ona 468,42 mg/g. Dla jonów Pb^{2+} i Cd^{2+} parametr ten przyjął odpowiednio wartości 112,17 mg/g i 31,76 mg/g. Jonit C160 wykazuje największe powinowactwo w stosunku do jonów Pb^{2+}. W tym przypadku otrzymana wartość współczynnika b jest największa i równa 1,437 dm^3/mg.

REMOVAL OF LEAD, CADMIUM AND COPPER IONS FROM AQUEOUS SOLUTIONS BY USING ION EXCHANGE RESIN C 160

Keywords

ion exchange resins, ion exchange, lead, cadmium, copper ions

Abstract

Industrial waste solutions may contain toxic Pb, Cu, Cd and other metal ions. These ions may also be components of leachates in landfills of ores. The toxicity of the ionic forms of these metals is high.

For this reason the paper presents the results of studies on one of the methods to reduce their concentration in aqueous solutions. The article presents the results of studies on the removal of Pb^{2+}, Cd^{2+} and Cu^{2+} ions from model aqueous solutions with synthetic ion exchange resin C 160 produced by Purolite. The investigated ion exchanger contains sulfonic acid groups ($-SO_3H$) in its structure and is a strongly acidic cation-exchange resin. The range of the studied initial concentrations of the Pb^{2+}, Cd^{2+} and Cu^{2+} ions in the solutions was from 6.25 mg/L to 109.39 mg/L. The results confirmed that the used ion exchange resin C160 efficiently removes the above-mentioned ions from the studied solutions. The highest degree of purification was achieved in lead solutions for the assumed range of concentrations and conditions of the ion exchange process. It reached 99.9%. In the case of other solutions, the ion exchange process occurs with lower efficiency, however it remains high and amounts to over 90% for all the ions. The results of research were interpreted on the basis of the Langmuir adsorption model. For each studied ion, sorption capacity of the ion exchange resin increases until the saturation and equilibrium state is reached. Based on the interpretation of the Langmuir equation coefficients, an indication can be made that the studied ion exchange resin has a major sorption capacity towards the copper ions. In their case, the highest value of constant q_{max} was obtained in the Langmuir isotherm. For Cu^{2+} ions it was 468.42 mg/g. For Pb^{2+} and Cd^{2+} ions, this parameter reached the values of 112.17 mg/g and 31.76 mg/g, respectively. Ion exchange resin C 160 shows the highest affinity for the Pb^{2+} ions. In this case, the achieved value of coefficient b is highest and equals 1.437 L/mg.