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THE SORPTION OF NON-FERROUS METAL-IONS BY CHELATING RESINS

Abstract

Conditions of sorption equilibrium of copper, zinc, cadmium and lead-ions by chelatforming resins Amberlite IRC-748 and Duolite C 467 depending on the degree of neutralization of their ionogenic groups, the acidity of the medium and concentration of solutions were studied. Sorption isotherms were established, Langmuir and Freundlich models were proposed. In all cases, the selectivity is governed by the enthalpy factor with heat release and entropy reduction. Changing the experimental conditions (without interruption and with interruption) significantly affects the rate of ion sorption by the studied ion exchangers. This allows us to conclude that internal diffusion plays a significant role in the processes under study. Thermodynamic of these processes is considered at ideal ionite phase - the activity coefficients of absorbed ions in a solid phase haven't been taken into account. The calculated values of the diffusion coefficient, activation energy, activation entropy, enthalpy, free energy and entropy multiplier of all studied processes are given.

Keywords: *ion exchangers, sorption isotherms, isotherm equations, Langmuir and Freundlich models, kinetic and thermodynamic quantities*

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Əlvan metal ionlarının xelatəmələgətirici ionitlərlə sorbsiyası

Xülasə

Duolite C-467 və Amberlite IRC-748 ionitləri ilə Cu^{2+} , Zn^{2+} , Cd^{2+} və Pb^{2+} ionlarının sorbsiya tarazlığının şəraitləri, onların inogen qruplarının neytrallaşma dərəcəsi, mühitin

turşuluğundan və məhlulların konsentrasiyasından asılı olaraq öyrənilmişdir. Sorbsiya izotermələri qurulmuş, Lenqmyür və Freyndlix modelləri təklif olunmuşdur. Bütün hallarda seçicilik, istilik ayrılması və entropiyanın azalması ilə entalpiya amili tərəfindən idarə olunur. Təcrübə şərtlərinin dəyişdirilməsi (fasiləsiz və fasilə ilə) öyrənilən ionitlər tərəfindən ionların sorbsiya sürətinə əhəmiyyətli dərəcədə təsir göstərir. Bu, öyrənilən proseslərdə daxili diffuziyanın əhəmiyyətli rol oynadığı qənaətinə gəlməyə imkan verir. Bu proseslərin termodinamikası ideal ionit fazada nəzərə alınır - bərk fazada udulmuş ionların aktivlik əmsalları nəzərə alınmamışdır. Tədqiq olunan bütün proseslərin diffuziya əmsalı, aktivləşmə enerjisi, aktivləşmə entropiyası, entalpiya, sərbəst enerji və entropiya çarpanının hesablanmış qiymətləri verilmişdir.

Açar sözlər: *iondəyişdiricilər, sorbsiya izotermələri, izoterm tənlikləri, Lenqmyür, və Freyndlix modelləri, kinetik və termodinamik kəmiyyətlər*

Introduction

The availability of data on the equilibrium of ion exchange is necessary for selection and optimization of the conditions of ion concentration, ejection of a concrete ion from a complex system and for its separation from the other ions, as well as for the calculation and designing of technological equipment. As a result the investigation of equilibrium conditions of ion exchange brings to deriving of isotherm equations and to determination of the exchange constant and coefficient of selectivity. For this reason, the study of model solutions in the way of increase of sorption selectivity is regarded as an actual problem (Lin, Juang, 2007: 337-343; Nouredine, Lekhmici, Mubarak, 2008:1316-1319).

The aim of the presented research work is to study the mutual influence of ion exchangers macroporous Duolite C 467 and macroreticular Amberlite IRC-748 under consideration and ions of non-ferrous metals for the comparative evaluation of their sorption capacity.

Experimental Section. As the deprotonated form for the chelatforming resins (Yu, Zolotov, Tsizin, Morosanova, Dmitrienko, 2005:41-66) is coordinating- active their industrial form (Amberlite IRC- 748 and Duolite C 467 -Na⁺) was used; processes were carried out at the static conditions, in the ratio of resin: solution = 1:100. Concentration of the residual after sorption of the studied ions from the solution is determined by complexometric method using pyridile-azophthol PAN (Cu²⁺), eriochrome black T (Zn²⁺ and Cd²⁺) and xylenole orange (Pb²⁺) (Shvartsenbakh, Flashka, 1970: 562). At the joint presence of studied ions their content in the solution was determined by AAS method on the spectrometer Thermo Scientific iCE 3500 AA. The experiments with Amberlite IRC- 748 was practiced in the interval of 7,5-7,75 of pH and Duolite C 467 in the interval of 4,5-5,5. pH of solutions were measured by the pH meter OR-204/1. The quantity of ions absorbed by the resins is found on the basis of difference between the beginning and after sorption concentration (Eq.1).

$$A = (C_0 - C_e)V/m \quad (\text{Eq. 1})$$

Here A is the Zn²⁺, Cu²⁺, Cd²⁺ and Pb²⁺ ions, -ions adsorbed onto the ionites (mg·g⁻¹) at equilibrium, C₀ is the initial Zn²⁺ Cu²⁺, Cd²⁺ and Pb²⁺ ions concentration (mg·L⁻¹), C_e is the final Zn²⁺ Cu²⁺, Cd²⁺ and Pb²⁺ ions concentration in the solution (mg/L⁻¹) is the volume (L) of the solution and m is the amount of ionites (g) used.

Kinetics of these processes is studied by the method of “limited capacity” with solutions of initial concentration 1.0 g Me/l; the values of effective diffusion coefficients are calculated from the equation offered by G.Boyd and colleagues (Boyd, Adamson, Myers, 1947: 2836–48).

$$F = \frac{Q_t}{Q_\infty} = 1 - \frac{6}{\pi^2} \sum \frac{1}{n^2} \exp\left(-\frac{D\pi^2 n^2 t}{r_0^2}\right) \quad (\text{Eq. 2})$$

In Equation 2, Bt is defined as follows:

$$Bt = D_i \pi^2 \frac{t}{r_0^2} \quad (\text{Eq. 3})$$

B_t is called an intangible parameter or Fourier homochronous criterion. The value of effective diffusion coefficient has been calculated according to the formula:

$$D = B_t \cdot r_0^2 / t \cdot \pi^2 \quad (\text{Eq. 4})$$

The value of activation entropy has been calculated according to the equation offered by R.M.Barrer and colleagues (Barrer, Bartholomew, Rees, 1963: 51–62) (Eq.5):

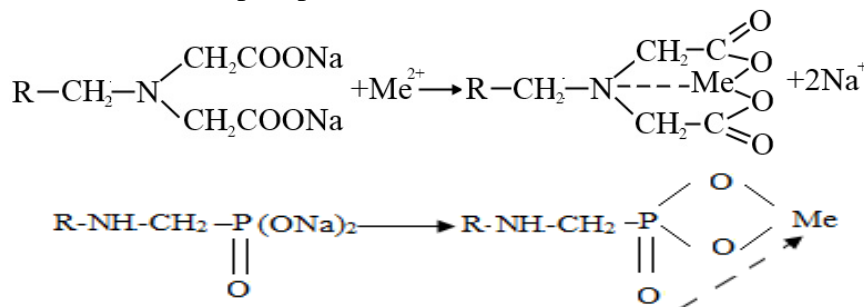
$$D_0 = D^2 \exp\left(\frac{kT}{h}\right) \cdot \exp\left(\frac{S}{R}\right) \quad (\text{Eq.5}),$$

the value of entropy multiplier $\lambda^2 \exp(S/R)$ – according to the formula offered by S.Glasstone (Glasstone, Laidler, Eyring, 1941: 501):

$$D = \lambda^2 \cdot \exp\left(\frac{S}{R}\right) \cdot \exp\left(\frac{kT}{h}\right) \exp\left(\frac{E_{akt}}{RT}\right) \quad (\text{Eq.6}).$$

Results and Discussion.

Amberlite IRC-748 and Duolite C 467 are characterized by the functional groups of $-N(\text{CH}_2\text{COONa})_2$ and $-\text{NH}-\text{CH}_2-\text{PO}(\text{ONa})_2$ (Jafarli, Abbasov, 2017: 449-462; Jafarli, 2022: 26-28) respectively; the sorption by the first 2 polyampholytes is realized at the expense of replacement of Na^+ ions with Me^{2+} ions and coordinating bond between the N atoms (Amberlite IRC-748) and Duolite C-467 is formed due to the formation of a coordination bond between the free electron pair of the oxygen atom bonded to the phosphorus atom and the metal ion (10).



Production of chelate acids in the resin phase, in other words, the selectivity of ion exchangers depends basically on the chemical nature of their functional groups and conditions of the sorption process conducting; kinetic parameters of sorbents, regeneration liability, swelling rates, mechanical and thermal stability depends on the properties of a polymer matrix (Khering, 1971: 279), in this connection these factors are also evaluated. Because of the fact that the groups of polyampholytes with the base nature depending on the medium acidity are subjected to partially or completely dissociation they are responsible for the sorption of metal ions at the expense of coordination bond. The sorption capacity of polyampholytes determines the quantity of acid groups, and the selectivity of sorption processes – basicity of amine groups and stereochemistry of ligand groups. Under small values of pH the acid groups of resins are weakly dissociated, that is why occurs the competitive sorption for functional groups between hydrogen and metal ions. In addition, effective mutual influence between ions and functional groups of the resins cannot realize because of protonation of amine groups.

Sorption isotherms for all studied systems are made (figure 1); parameters included in the considered models (Langmuir and Freundlich) are calculated on the basis of values get during the experiment. Analysis of the experimental data confirms with certain deviations the possibility of expression of the studied processes by the Langmuir equation:

$$A = A_{max} \cdot K \cdot C / 1 + K \cdot C \quad A = A_{max} \cdot K \cdot C_e / 1 + K \cdot C_e \quad (\text{Eq. 2})$$

with sufficient precision. This fact shows that there is a layer of monomolecular sorption in these systems and all sorption centers are characterized by equal energy. Freundlich equation can describe only beginning parts of the sorption curves: (0,25-1,50 gMe/l).

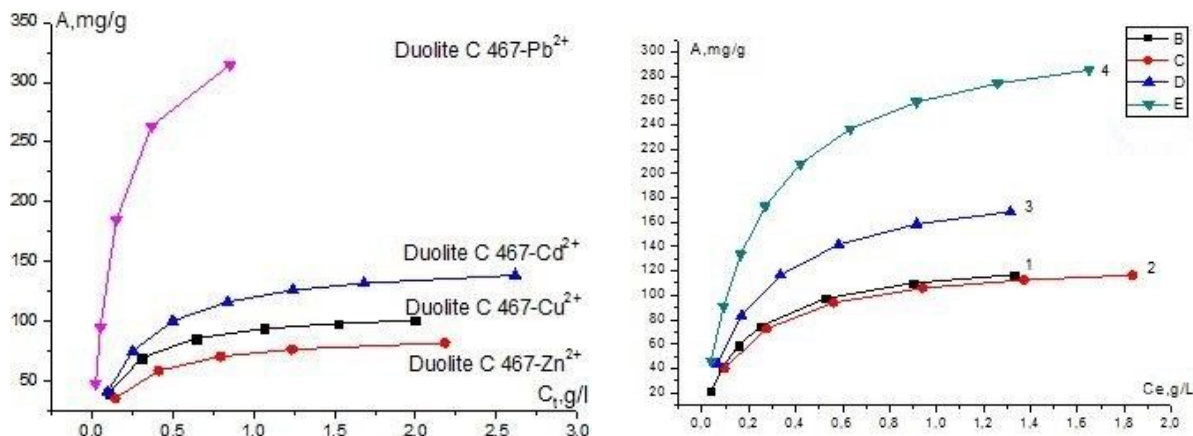


Fig.1. Isotherms of sorption of Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} -ions by studied resins.

The deviations in saturation regions of the curves between values theoretically calculated and the experimental results are so great that it becomes meaningless to compare. For Duolite C467: $\text{Pb} > \text{Cu} > \text{Zn} > \text{Cd}$, and for Amberlite IRC-748 $\text{Cu} > \text{Pb} > \text{Zn} > \text{Cd}$ selectivity sequences are determined; it is revealed that the polyampholyte with aminophosphon group is the most effective sorbent for the studied ions. We know from the literature that in comparison with the other bivalent metal ions the Cu^{2+} ions are susceptible to the oxygen atoms of the phosphorous sorbents. According to N. Sijvic classification the Cu^{2+} ions have a great avidity against azot atoms, so the reason of effective sorption of this ion with complex-forming sorbents keeping azot in its content is understood. All isotherms made by the method of changing concentrations are noted for the relief depending on the selectivity of the resin against the concrete ion. Absence of curves in the isotherms allows to suppose that absorption occurs mainly at the expense of functional groups. a and n included in the Freundlich equation are found from the graphic $-\lg(1-F) = a \cdot C_e^n$. At the specified graphic dependence the length of the segment cut from the ordinate axes gives the value of a, tangent of the angle formed by a straight line with the abscissa axis gives the value of n. In the foregoing sequence the forms of isotherms corresponding to Langmuir and Freundlich equations are the follows:

$$\begin{aligned} \text{Duolite C 467 - Pb}^{2+}: & A = 370,6 \cdot (6,65 \pm 0,06) \cdot C_e / 1 + (6,65 \pm 0,06) \cdot C_e; & A = 660,7 \cdot C_e^{0,7} \\ \text{Cu}^{2+}: & A = 109,6 \cdot (5,60 \pm 0,05) \cdot C_e / 1 + (5,60 \pm 0,05) \cdot C_e; & A = 95,5 \cdot C_e^{0,27} \\ \text{Zn}^{2+}: & A = 90,2 \cdot (4,51 \pm 0,04) \cdot C_e / 1 + (4,51 \pm 0,04) \cdot C_e; & A = 81,3 \cdot C_e^{0,62} \\ \text{Cd}^{2+}: & A = 152 \cdot (3,87 \pm 0,04) \cdot C_e / 1 + (3,87 \pm 0,04) \cdot C_e; & A = 125,9 \cdot C_e^{0,37} \end{aligned}$$

$$\begin{aligned} \text{Amberlite IRC-748- Cu}^{2+}: & A = 135,0 (425) (4,92 \pm 0,03) \cdot C_e / 1 + (4,92 \pm 0,03) \cdot C_e; & A = 195 \cdot C_e^{0,77} \\ \text{Zn}^{2+}: & A = 130,70 (4,0) (4,55 \pm 0,04) \cdot C_e / 1 + (4,55 \pm 0,04) \cdot C_e; & A = 109,6 \cdot C_e^{0,325} \\ \text{Cd}^{2+}: & A = 199,5 (3,15) (4,21 \pm 0,04) \cdot C_e / 1 + (4,21 \pm 0,04) \cdot C_e; & A = 276,8 \cdot C_e^{0,81} \\ \text{Pb}^{2+}: & A = 326,35 (3,15) (9,53 \pm 0,04) \cdot C_e / 1 + (9,53 \pm 0,04) \cdot C_e; & A = 276,80 \cdot C_e^{0,81} \end{aligned}$$

The study of kinetics of these processes shows in all cases that the sorption equilibrium arises in 2.5-3 hours. Simple and reliable method of “kinetic memory”, in other words, the partition method, is used for the experimental determination of demarcation stage. The increase in sorption rate in all cases after partitioning in comparison with the initial rate confirms that processes under the control of pore diffusion. The dependence of $-\lg(1-F)$ on time isn't expressed by a straight line under low saturation degrees, under higher saturation values ($F > 0.5-0.6$) dependence are expressed by a

straight line. The expression of saturation degree up to the values of dependence F -in $t^{1/2}$ equal to 0.4-0.5 by the straight line going from the beginning of origin of coordinates and quantities calculated for the prices charged for absolute values of the Bio criterion ($Bi > 50$) confirm once again that the processes are under control of the pore diffusion. The sorption rates of ions by the polyampholytes at the different way with increase in temperature. The positive effect of the temperature on the rate of processes is observed more clearly during the sorption of cadmium and lead ions: no matter how great are the values calculated for the activation energy, more intensive changes simultaneously with the change of the temperature the sorption rate. This is also evident in the 2nd figure. The values received by us for the activation energies are characteristic for sorption processes realized in the region of the pore diffusion.

Thermodynamical parameters of sorption of the studied ions by the polyampholytes are calculated on assumption of ideal conditions for the ionite phase, in other words, without taking into account the factor of activity of sorbed ions at the ionite phase. One of the most important energetic parameters of any chemical process, especially, sorption processes is considered to be thermal effect (Valdman, Panfilov, 1979:479). In all cases, the sorption of ions is accompanied with calorification ($\Delta H < 0$). The connection between the increase in sorption selectivity and decrease in entropy determined by us is justified in all investigated systems. A case of more rapidly establishment of the sorption equilibrium is specific for small values of the entropy factor. The values of the entropy factor are calculated in compliance with (Glasstone, Laidler, Eyring, 1941: 501). Characterization of the entropy factor of Duolite C467 by smaller values, the rapid establishment of sorption equilibrium is connected with the fact that its matrix is macroporous and it has to a certain extent relatively large sorption capacity. According to calorification and decrease in entropy it is possible to suppose that in all systems investigated by us the selectivity is controlled by the enthalpy factor. The values of half-time of exchange calculated for all system confirm these comments. The values of time of half-exchange for copper ion by the ionites Duolite C 467 and Amberlite IRC -748 are respectively the following: 23,96 min and 30,49 min.

Table.
Kinetic and thermodynamic parameters of studied systems.

$D_i \cdot 10^{-7} \text{ sm}^2/\text{sec}$	$D_0 \cdot 10^{-3} \text{ sm}^2/\text{sec}$	$E_{\text{akt.}}, \text{ kC/mol}$	$-\Delta S^*, \text{ C/mol}\cdot\text{K}$	$-\Delta H^0, \text{ kC/mol}$	$-\Delta G^0, \text{ kC/mol}$	K	$\lambda^2 e^{(\Delta S/R)} \cdot 10^{-17} \text{ sm}^2$
Duolite C-467-Pb ²⁺							
0,85	0,197	13,50	44,64	17,86	4,55	6,29	1,169
Duolite C-467-Cu ²⁺							
0,70	0,616	16,80	73,44	25,24	3,36	3,88	0,365
Duolite C-467-Zn ²⁺							
0,64	0,012	18,50	68,48	22,82	2,41	2,65	0,006
Duolite C-467-Cd ²⁺							
0,45	0,0275	21,60	61,00	20,81	2,64	2,90	0,0246
Amberlite IRC-748-Cu ²⁺							
5,50	2,245	20,60	43,54	16,21	3,23	3,69	1,33
Amberlite IRC-748-Zn ²⁺							
0,26	0,578	24,8	35,69	15,76	5,12	7,91	3,42
Amberlite IRC-748-Pb ²⁺							
0,21	0,727	31,6	14,64	9,84	5,47	9,12	0,43
Amberlite IRC-748- Cd ²⁺							
4,90	6,194	23,40	35,11	15,34	4,88	3,42	3,66

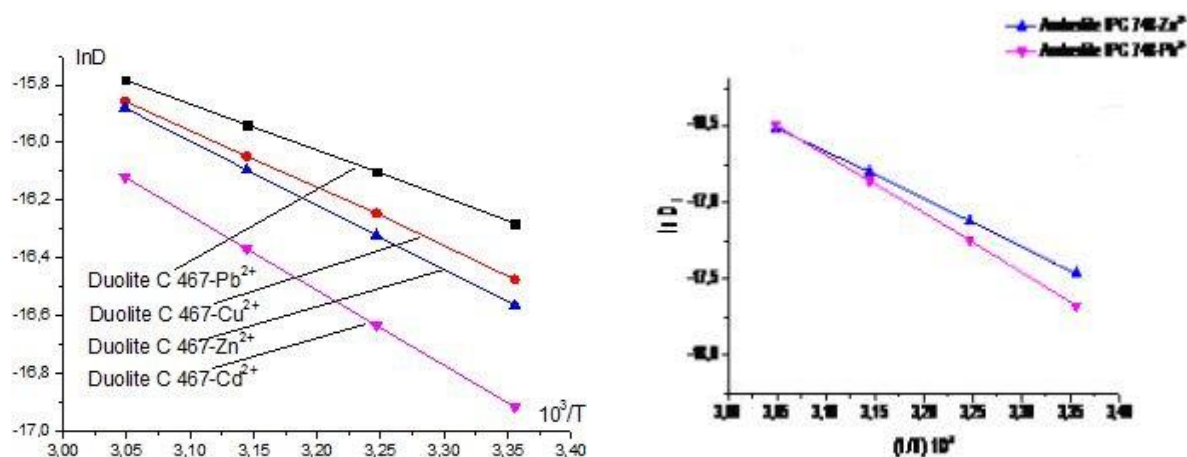


Fig.2. The dependence of the sorption of the studied ions ion exchangers Duolite C 467 and Amberlite IRC 748 on the temperature

Conclusion

The maximum degree of extraction of copper ions studied sorbents is about 90-95% of the injected amount (0,5-1,0g/l). As can be seen, with the joint presence of these ions corresponding ion exchangers division proceeds efficiently. The results obtained confirm the fact that the thermodynamic parameters of sorption processes carried out at high speed and selectivity are characterized by minimum values. The absorption rate of Cu^{2+} ion with Duolite C 467 and Amberlite IRC 748 sorbents is 3.77; 4.80. The data show that of industrial wastewater and other similar objects with a concentration of 0.5 g/l of copper and lead, they can be cleaned studied ion exchangers.

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