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Equilibrium, kinetic and thermodynamic of sorption of Zn^{2+} and Pb^{2+} -ions Amberlite IRP69 and Amberlite IRP64 with resin

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Abstract

This article presents the results of equilibrium, kinetics and thermodynamics of sorption Zn^{2+} and Pb^{2+} ions of strongly acidic Amberlite IRP-69 (sulpho-group, Na^+ -form) and Amberlite IRP-64 weakly acidic (carboxyl functional group, H^+ -form) cationites. The change of parameters, such as energy and entropy of activation, free energy of sorption and diffusion coefficients change on various factors. Analysis of the kinetic curves methods and interruption methods revealed that at a concentration of about of sorbates $1.0 \text{ g E}\cdot\text{L}^{-1}$ is controlled intradiffusion kinetics. The interaction between the selectivity of sorption and the kinetic properties of ionites has confirmed. Decrease in the numerical value of entropy and entropy is directly related to the increase in the selectivity of sorption in systems learned.

Key words: Resin, Zn^{2+} and Pb^{2+} ions, isotherms, sorption, equilibrium, kinetic and thermodynamic parameters.

Аннотация

В данной статье представлены результаты равновесия, кинетики и термодинамики сорбции ионов Zn^{2+} и Pb^{2+} сильнокислых катионов Амберлита ИРП -69 (сульфогруппа, Na^+ -форма) и слабокислотных Амберлита ИРП -64 (карбоксильная функциональная группа, H^+ -форма). Изменение параметров, таких как энергия и энтропия активации, коэффициенты свободной энергии сорбции и диффузии, происходит в зависимости от различных факторов. Анализ методов кинетические кривые и промежуточного разделения показывают, что кинетика сорбентов при концентрации $1,0 \text{ г Э}\cdot\text{л}^{-1}$ находится под контролем внутренней диффузии. Была подтверждена взаимосвязь между сорбционной селективностью и кинетическими свойствами ионотов. Уменьшение Энтропии и числового значения множителя энтропии является непосредственным условием селективности сорбции в исследуемых системах.

Ключевые слова: Смолы, ионы Zn^{2+} и Pb^{2+} , изотермы, сорбционных, равновесных, кинетических и термодинамических параметров.

Environmental pollution by toxic metals occurs globally through military, industrial, and agricultural processes and waste disposal [1]. Metals, discharged or transported into the environment, may undergo transformations and can have a large environmental, public health, and economic impact. Among various techniques, ion exchange technique on polymeric ion-exchangers is widely used for treatment of metal-contaminated wastewater [2], due to high efficiency; easy handling; cost effectiveness; reusability and ease of separation. The pollutants of concern include cadmium, lead, mercury, chromium, arsenic, zinc, cobalt and nickel as well as copper. When selecting ionite for practical purposes, the capacity, selectivity and kinetic characteristics of the sorbent have particular importance. It is also important to present a realistic view based on the calculation of thermodynamic parameters for substantiating the

amount of sorption processes. Extraction of non-ferrous metals from a variety of different facilities and their delivery in the form of sales products is a very important problem of chemical technology. The aim of the study was to investigate the sorption of Zn^{2+} and Pb^{2+} ions by Amberlite cations and to propose cationite that meets the technological requirements and calculate the parameters that describe processes.

Experimental results and discussion

The processes under investigations has been studied in static conditions, at the room temperature, at the ion exchanger-solution ratio of 1:100, at the concentration of metal ions $0,5-5,0 \text{ gMe}\cdot\text{L}^{-1}$. The experiments were conducted in the range of 3.5-5.5 PH. pH of solutions have been measured by Acvilon pH-meter pH-430.

Amberlite IRP64 (Polacrilex Resin) makroreutical, carboxyl weakly acidic functional structure resin is an insoluble, hydrogen form, cation exchange resin supplied as a dry, exchange capacity 10.0 meq/g , on dried basis fine powder. Amberlite IRP64 resin is derived from a porous copolymer of methacrylic

Fig 1. acid and divinylbenzene.

Amberlite IRP69 (Sodium Polystyrene Sulfonate USP) resin is an insoluble, strongly acidic, sodium form cation exchange resin supplied as a dry, fine powder. Amberlite IRP69 resin is derived from a sulfonated copolymer of styrene and divinylbenzene. The total cation exchange capacity ($\sim 5 \text{ meq/g}$) represents the maximum achievable capacity for exchanging cations. The chemical structure for Amberlite IRP64 (in Figure 1) and for Amberlite IRP69 is shown in Figure 2 [3].

Figure 2

The residual concentrations of the studied ions after sorption in the solution were determined by using complexonometric method, eriochrome black T (Zn^{2+}) and xylenol orange (Pb^{2+})[4]. In a series of experiments, the accuracy of the results was controlled by determining the concentration of Zn^{2+} and Pb^{2+} ions at atomic absorption spectrometer Thermo Scientific iCE 3500 AA. Quantity of Zn^{2+} and Pb^{2+} ions passing to the ionite phase at equilibrium condition has been calculated according to the formula: $A = (C_0 - C_e)V / m$ (Eq. 1).

Here A is the Zn^{2+} and Pb^{2+} -ions sorbed onto the ionites ($\text{mg}\cdot\text{g}^{-1}$) at equilibrium, C_0 is the initial Zn^{2+} and Pb^{2+} ions concentration ($\text{mg}\cdot\text{L}^{-1}$), C_e is the final Zn^{2+} and Pb^{2+} ions concentration in the solution ($\text{mg}\cdot\text{L}^{-1}$) V is the volume (L) of the solution and m is the amount of ionites (g) used.

Prevalence of isotherms suggests that the ionites are selective to the ions studied, claiming that K is greater than 1. Although the selectivity of cationites to the studied ions is high at the beginning of the processes, the in subsequent stages of absorption considerably decrease in the mol share of ions in the solid phase. This, is on the one hand in the beginning of the processes, of the equilibrium concentrations of ions in the solution have very small, on the other hand it can be explained by the down of capacity in parallel and the high price increase of the equilibrium concentration. Although Amberlite IRP-69 combines at the same time of 3 sulphogroups as a single active center to the matrix, it seems that, the number of such groups is not quite very. The data on the interaction of d - and f - order metals with

ionized carboxyl cationites not only in ion can be found but also in coordination bond, the character of both potentiometric curves and as well as the frequency slopes of ionized ionogenic groups.

The isotherms are risen follow the Langmuir equation: $A = A_{\max} \cdot K \cdot C_e / 1 + K \cdot C_e$ (figure 3). This is confirmed by a constant value characteristic in the wide concentration range of K which is included in the equation. From the dependence of $\log A - \log C_t$, the parameters included in the Freundlich equation: $x/m = K \cdot C_e^n$ were calculated and corresponding equations were proposed. $A = 426,6 \cdot C_t^{0,67}$ equation for the Amberlite IRP-64-Pb²⁺ system, $A = 169,83 \cdot C_t^{0,28}$ equation for the Amberlite IRP-64-Zn²⁺ system, $A = 200 \cdot C_t^{0,34}$ equation for the Amberlite IRP-69-Pb²⁺ system, $A = 81,28 \cdot C_t^{0,45}$ equation for the Amberlite IRP-69-Zn²⁺ system is in the form of. However, it should be noted that the equations shown are valid only in the beginning and in the middle of the isotherms. The end points of isotherms are not follow to the Freyndlix equation. The sorption capacity of the ionites is also different for the learned element ions. Since the last d-orbital completes in the Zn atom, its interaction with the ionite's counterion ion and complexforming groups is very weak. This also shows itself in studied elements of the sorption capacity for specific cationite. The maximum sorption capacity was obtained during the sorption of Pb²⁺ ion with Amberlite IRP-64 cationite: 3,85 meq/g. As amberlite IRP-64 cationite is characterized by sorption capacity of 10 meq/g, it can be considered more effective than other cationites. The presence of N atoms in the functional group makes the situation more complicated. The existence of a diazo-group that combines naphthaline rings in the composition of Amberlite IRP-69 cationite indicates that coordination bond may occur in more challenging conditions and at very low pH values.

Fig. 3. Sorption isotherms

Kinetics of the processes has been studied by the “limited volume” method in ion solutions with the concentration 1.0 g Me²⁺ L⁻¹. Values of effective diffusion coefficients in kinetic experiments have been calculated according to the equation of G. Boyd and colleagues

$$[5]: F = Q_t / Q_\infty = 1 - \left(\frac{6}{\pi^2} \right) \sum_{n=1}^{\infty} (1/n^2) \exp(-D_i \pi^2 n^2 t / r_0^2) \quad (\text{Eq. 2})$$

In this equation F- is the exchange ratio of ions, Q_t and Q_∞ are the relevant amount of sorbent ion according to time - t (time in which sample is taken for analysis, sec.).

In this equation: $Bt = D_i \pi^2 t / r_0^2$ (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 $D = B_t \cdot r_0^2 / t \cdot \pi^2$ (Eq. 4). r₀ - is the average radius of swollen sorbent granule in sm. The values of effective activation energy have been calculated by Arrenius equation: $D = D_0 \exp(-E_{akt} / RT)$ (Eq. 5) due to the temperature dependence of E_{akt}. effective diffusion coefficients. The temperature dependence of the sorption parameters studied at the U-10 branded thermostat at 25-55°C. The values of entropy of activation (ΔS*) are calculated by substituting D₀ in the equation proposed by R.M. Barrer and his colleagues' [6]: $D_0 = d^2 (ekT / h) \cdot \exp(\Delta S^* / R)$ (Eq. 6). Where k is the Boltzmann constant, d is the ionic

jump distance (the distance between two successive positions of ion in the process of diffusion) and is equal to 0,5 nm, h is Planck's constant, and R is the gas constant. The value of entropy multiplier $\lambda^2 \cdot \exp(\Delta S/R)$ – according to the formula offered by S. Glasstone [7]:
 $D = e \lambda^2 kT / h \cdot \exp(\Delta S^* / R) \cdot \exp(-E_{akt} / RT)$ (Eq. 7).

The diminution of radius of ionite granule, with increasing the speed of sorption shows that the sorption of metal ions is diffusion character. In all cases, decrease of half-change period $\tau_{1/2} = 0,03 \cdot r_0^2 / D_i$ is observed. The linear dependence of F from $\sqrt{t}$ and $\ln(1-F)$ to t for the beginning of sorption processes indicates that the speed of the processes under study is under the control of internal diffusion.

Table

Kinetic and thermodynamic parameters of sorption of Zn^{2+} and Pb^{2+} -ions with Amberlite IRP-64 and Amberlite IRP-69 resin ($r_0=0,0275$ sm)

Di sm ² /sec	D ₀ sm ² /sec	E _{akt} kJ/mol	-ΔS*, J/mol·K	-ΔH ⁰ , kJ/mol	-ΔG, kJ/mol	K	$\lambda^2 e^{\Delta S/R}$, sm ²
Zn²⁺ - Amberlite IRP-64							
56,5·10 ⁻⁷	2,05·10 ⁻³	14,60	44,30	17,62	4,42	5,95	12,1· 10 ⁻¹⁸
Pb²⁺ - Amberlite IRP-64							
1,16·10 ⁻⁸	3,29·10 ⁻⁴	25,40	40,36	15,75	3,72	4,5	19,5· 10 ⁻¹⁸
Zn²⁺ - Amberlite IRP-69							
5,3·10 ⁻⁷	0,062·10 ⁻³	17,50	54,25	20,25	4,08	5,2	3,66· 10 ⁻¹⁷
Pb²⁺ - Amberlite IRP-69							
3,2·10 ⁻⁸	17,3·10 ⁻⁴	27	26,73	12,3	4,33	5,75	10,3· 10 ⁻¹⁸

Zn^{2+} ion is close to Pb^{2+} ion according to its essential characteristics. Unsatisfactory kinetic indicators with Amberlite IRP-69 cationite should be explained by the spatial condition of cationite functional groups. Sulfogroups at a certain distance from each other may possible to create a sterile effect and the N-atoms of the diazogroup may also have a significant negative impact on the steric effect. For these reasons, the values of the internal diffusion coefficients of the learned ions with Amberlite IRP-64 are 10 times higher than the average value of the Amberlite IRP-69. Low values of activation energy indicates that the sorption process is controlled by cation exchange.

Increasing the kinetic capacity of the ionites promotes the process to be more effective by raising the selectivity of the sorption. Decrease in the numerical value of entropy factor and entropy is conditioned by increased selectivity of sorption in the studied systems. The high sorption capacity of iodine, characterized by relatively good kinetic performance, can be successfully used for their purification of hydrometallurgical or complex facilities where these ions are involved in some manufacturing processes.

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