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SORPTION OF Zn^{2+} AND Pb^{2+} IONS BY RESINS WITH DIFFERENT FUNCTIONAL GROUPS**M.M.Jafarli A.D.Abbasov**

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Conditions of sorption equilibrium of Zn^{2+} and Pb^{2+} ions by resins of Diaion CR 11 and Dowex M 4195 have been analyzed depending on the degree of neutralization of their ionogenic groups, acidity of the medium and concentration of sorbate solutions. Equations expressing the isotherms of sorption are offered; equilibrium and kinetic parameters typical for these processes have been established; thermodynamic quantities calculated. It revealed that under selected conditions the selectivity is controlled by enthalpy factor with calorification and a decrease in entropy.

Key words: *resins of Diaion CR 11 and Dowex equilibrium, kinetics, thermodynamical parameters, isotherms, Langmuir and Freundlich equations*

INTRODUCTION

At present, the reagent technology is commonly used for sewage treatment from metal cations. Besides, there are other purification methods, such as electro-coagulation, electro-dialysis, reverse osmosis, ultra-filtration, membrane technologies and biological treatment. But they are not widely used due to low profitability of related processes. Less costly but effective are

sorption methods which make it possible to remove the greatest variety of contaminations up to any residual contamination regardless of their chemical stability. The paper analyzes ionites *Diaion CR 11* and *Dowex M 4195* for extraction of $Zn(II)$ and $Pb(II)$ ions out of solutions through the study of kinetic and thermodynamic characteristics.

RESULTS AND DISCUSSIONS

As the deprotonated form of chelating resins is coordinating-active they have been involved into research in a salt form, in the ratio of resin: solution = 1:100; concentration of Zn^{2+} ions is determined by complexometric method [1] with eriochrome black T, concentration of Pb^{2+} ions—by xylenole orange; quantity of Zn^{2+} and Pb^{2+} ions absorbed by resins is calculated using the formula $A = V(C-Ct)/m$, the distribution of ions to solid and liquid phases is calculated according to the formula $P=V(C-Ct)/m \cdot Ct$.

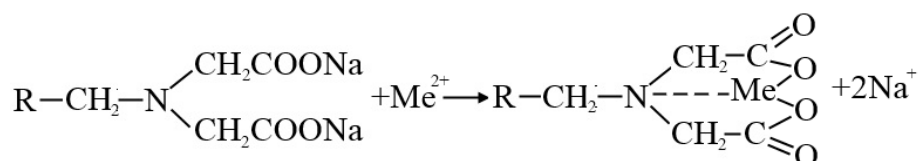
Quantitative determination of ions in mixed solutions is carried out by the spectrometer Thermo Scientific iCE 3500 AA. Kinetics of these processes is studied by the method of

"limited capacity" [2] with solutions of initial concentration 1.00 g Me/l; the temperature dependence of these processes is examined through the use of the model U-2 thermostat.

The role of nitrogen atoms is of interest as the sorption process by Dowex M 4195 with bis-picolilamine functional group of $-C_5H_4N-CH_2-N-(matrix)-CH_2-C_5H_4N$ is realized at the expense of 3 nitrogen atoms. Thus, the assumption that triple nitrogen combined with the matrix forms a complex with metal ion seems to be unconvincing. In our opinion, the resin-metal complex is carried out mainly at the expense of nitrogen atoms of pyridine molecules. Creation of chelate by triple nitrogen combined with the matrix seems unconvincing from energetic standpoint. It is

greater activity of pyridine nitrogen and its reactivity characteristics that make it possible to assume that coordination bond occurs just at their expense. Sorption process was carried out

in the sulphate form of the resin. Note that the sorption of analyzed ions by Diaion CR 11 proceeds according to



mechanism, that's why formation of chelate occurs on the basis of vacant orbitals of a nitrogen atom. This is confirmed by the absence of valence vibration fluctuations concerning non-ionized carboxyl groups (-COOH) at 1702 cm^{-1} in the IR-spectrum after sorption of zinc and lead ions and also by the formation of asymmetric (1390 cm^{-1}) and symmetric (1530 cm^{-1}) valence-vibration fluctuations concerning ionized carboxyl groups (-COO-). That, in turn, can be explained by the formation of Me-O bond with different ionization degree in the sorbent phase. Reduction of the absorption band intensity in the spectral wavelength range between $1165\text{--}1170\text{ cm}^{-1}$ is, in our opinion, related to the formation of N-Me bond. Both resins have been characterized by a small total sorption capacity, that's why their maximum capacity against studied ions is not so large. Although Dowex M 4195 is able to operate in low (pH = 0-7) and Diaion CR 11 - in the relatively wide range of acidity (pH = 4-10), their optimal sorption regions are identified as pH= 4-6. Interesting fact was established by Dowex M 4195- Pb^{2+} . Thus, high selectivity of the resin against Pb^{2+} ion is identified at the density of $C_0 = 0,1\text{--}1,0\text{ gPb}^{2+}/\text{l}$ and value of distribution coefficients $2,3 \cdot 10^3\text{ ml/g}$. This quantity for Zn^{2+} is 30 times smaller than for Pb^{2+} . This type of resins forms coordination bond with groups of basic nature in the region of pH = 1.5-2. Depending on the pH values acid groups are partially or completely subjected to dissociation and realize sorption according to the mechanism of ion exchange of metal ions. So, it can be assumed that the sorption parameters of ampholytes depend on

the amount of acid groups, selectivity of the sorption process depends on basicity of amino groups and stereochemistry of ligand groups [4]. As carboxyl groups of Diaion CR 11 are weakly dissociated at lower pH values, occurs the competition for these groups of hydrogen and metal ions and effective interaction with metal ions don't arise because of amino groups protonation. Currently accepted for separation of ions of two elements by the method of selective sorption provides the condition of $P_1 > 100\text{--}300$ and $P_2 < 3\text{--}10$ for values of distribution coefficients of less or more absorbed ions, value of 30 is to be implemented for the separation coefficient for effective realization of the separation [5]. As the proper condition is hold at the sorption of Zn^{2+} and Pb^{2+} ions by Dowex M 4195 these two ions can be effectively separated from the mixed solutions of density of $0.5\text{--}1.0\text{ g/l}$.

Sorption isotherms for all studied systems are made (figure 1); parameters included in the considered models (Langmuir, Freundlich, Sips and Redlich-Peterson) are calculated on the basis of values get during the experiment. In spite of certain errors experiment materials are expressed by Langmuir equation with sufficient accuracy. So, 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: ($0,25\text{--}1,50\text{ gMe/l}$). 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. Three unknown parameters are included to the

equations of Sips ($A = K_s \cdot C_t^{1/n} / (1 + \alpha_s C_t^{1/n})$) and Redlich-Peterson ($A = K_{RP} \cdot C_t / (1 + \alpha_{RP} \cdot C_t^\beta)$) [6]; therefore the minimization procedure (OriginPro 7.5) is used [7], results adequately satisfying theoretical and practical data aren't

obtained. In our opinion, the cause of it is concerned with the fact that last two models have been simulated on the basis of the hybrid mechanism.

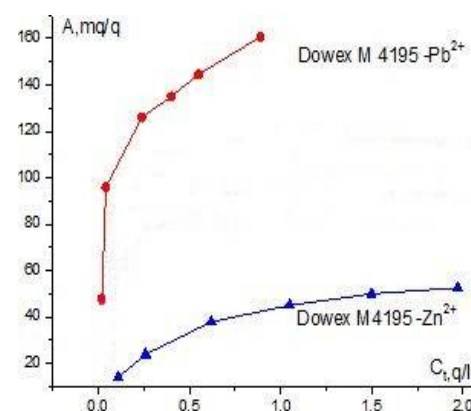
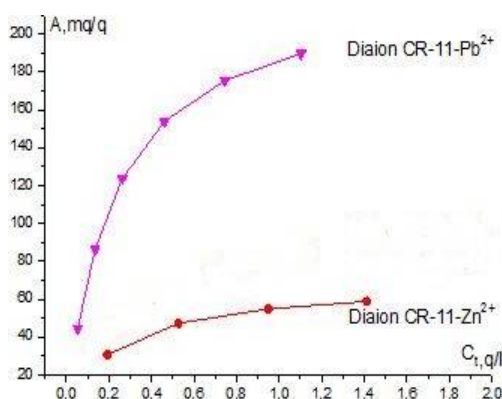


Fig.1. Isotherms of sorption of Zn^{2+} and Pb^{2+} -ions with analyzed resins

All isotherms made by the method of changing densities are noted for the relief depending on the selectivity of the resin against the concrete ion. Initial domains of the isotherms are close to the linear dependence (Henry distribution), then, in practice, amount of absorbed ions is proportional to the concentrations of metal ions. 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 $-x/m = a \cdot C_t^{1/n}$ are found from the graphic $\lg x/m = \lg C_t$. 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 [7].

Diaion CR 11 - Pb^{2+} : $A = 227.9 (4.50 \pm 0.04) C_t / 1 + (4.50 \pm 0.04) C_t$	$A = 234.4 C_t^{0.55}$
Zn^{2+} : $A = 68.7 (4.19 \pm 0.04) C_t / 1 + (4.19 \pm 0.04) C_t$	$A = 57.74 C_t^{0.36}$
Dowex M 4195- Zn^{2+} : $A = 52.55 (3.95 \pm 0.06) C_t / 1 + (3.95 \pm 0.06) C_t$	$A = 50.12 C_t^{0.59}$
Pb^{2+} : $A = 160.65 (21.1 \pm 0.5) C_t / 1 + (21.1 \pm 0.5) C_t$	$A = 245.5 C_t^{0.70}$

Cation sorption by both resins is expressed in coordinates of $C_t/A - C_t$ by linear dependence with a high correlation coefficient ($R^2 = 0.97-0.98$). That, in turn, gives the possibility to calculate authentically from the shown dependence the values of the change constant and maximum value of absorption - A_{\max} . 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 internal diffusion. The dependence of $-\lg(1-F)$ on time factor is not 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 temperature increase effects the rate of sorption of ions by polyampholites in a different way: 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. As the temperature rises from 25°C to 55°C, the rate of processes increases in 1.5-2.5 times. This is also apparent in the 2nd figure. The values received by us for the activation energies are typical for sorption processes occurring in the region of the pore diffusion.

Proper values of kinetic and thermodynamic parameters (effective diffusion coefficients, front-exponential factors, activation energy and entropy, enthalpy, free energy, change constant and entropy factor [8]) characterizing the sorption of Zn^{2+} və Pb^{2+} ions by Dowex M 4195 and Diaion CR 11 are the follows:

Table. Equilibriumal, kinetic and thermodynamic parameters of the reviewed processes

$D_i \cdot 10^{-7}$. 10^{-17} sm^2	$D_0 \cdot 10^{-3}$ sm^2/san	$E_{akt.}$ sm^2/san	$-\Delta S^{\ddagger}$, kC/ mol	$-\Delta H^0$, C/ mol.K	$-\Delta G^0$, kC/mol	K kC/mol	$\lambda^2 e^{\Delta S/R}$
Dowex M 4195- Zn^{2+}							
0.16	0.7068	26.50	34.00	11.25	1.12	1.57	4.18
Dowex M 4195- Pb^{2+}							
0.145	0.959	27.50	31.47	18.13	8.75	34.26	5.68
Diaion CR-11- Pb^{2+}							
0.55	0.2156	20.50	43.88	16.43	3.36	3.88	1.276
Diaion CR-11- Zn^{2+}							
0.40	0.35	22.5	39.86	13.57	1.69	1.98	0.078

Yelovich equation – $q_t = \frac{1}{\beta} \ln(1 + \alpha\beta t)$ offered for chemical reactions of the second order is used to determine the role of chemical reactions in the studied processes [9]. If the product $\alpha\beta t$ is much greater than the above, this equation takes the form of $q_t = \frac{1}{\beta} \ln(\alpha\beta t)$. The equation is used mainly in the linear form: $q_t = \frac{1}{\beta} \ln(\alpha + \beta) + \frac{1}{\beta} \ln t$. Resin surface is expected to be homogeneous from energetic point of view in the processing of the kinetic data according to the model of second order reactions by this equation during the ion exchange. When parameter α in the equation (the degree of saturation of sorbent surface) is equal to zero it characterizes the rate of chemical reaction, parameter β shows the dependence of the sorbent surface on the degree of saturation and activation energy of chemisorption. $q_t - \ln t$ shows the concentration of metal ions (amount of absorbed ions) falling for mass unit of proper sorbent at any instant of time. The value of α is found from the value of ordinate axes segment, β is found from the straight line dependence of $q_t - \ln t$.

The period during which the equilibrium of the analyzed ions is formed on both ionites changes in the range of 180-270 minutes. Acceptable values of correlation coefficients ($R^2 > 0.95-0.96$) shows that there is an important role of complexing in the kinetics of the sorption processes. Kinetic curves marks the start of the second part of the experience drawn from the responses to the proposed equation for the coordination of communications has emerged from the combination of the results might prove very closely.

Resin phase thermodynamic calculation parameters adopted in other words, the ions sorption ratios resin considered active phase [10]. In all cases, the change in viscosity varies significantly depending on the degree of saturation constant prices. According to the same concentration of ions in solutions sorption during sorption no matter how high, is rising in parallel to speed the process. Proceeding from values of diffusion factor of velocity constant and entropy, it is

possible make a well-grounded estimation of process rates. Thus, the thermodynamic quantities at high speed processes are characterized by minimal quantities. For processes that run with relatively low velocity, the activation energy is characterized by high

values; therefore the rise in temperature has a positive effect on velocity of these reactions. It is clearly apparent in the diagram of dependence $\ln D - \frac{1}{T} \cdot 10^3$.

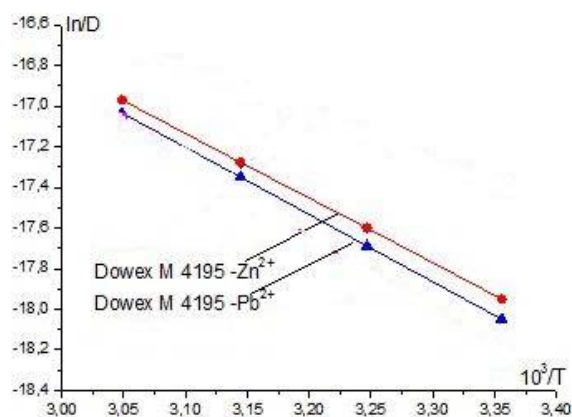
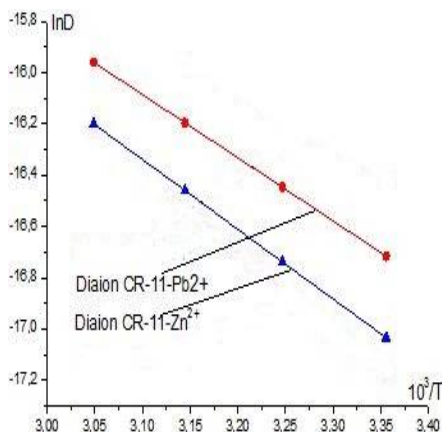


Fig.2. Temperature depending sorption Zn^{2+} and Pb^{2+} -ions with studied resins

Decrease in the intensity of thermal flow which is parallel to saturation of ionite with ions is possibly attributable to additional energy consumption needed for diffusion of ions into ionite granules. In all the cases, negative values of free energy $\Delta G < 0$ contribute to spontaneous processes development at room temperature. Calculations allow making a main conclusion: the reduction of entropy value with growth of selectivity and aspiration of the system toward more adjusted state.

In all cases, the separation of temperature and enthalpy selectivity factor in the decline is driven by entropy. Dowex M-4195 was proposed as Cu^{2+} ion resin voters, under the same conditions, together with its Zn^{2+} sorption of about 15.6 against resin the first time, the pH of 2.8 to 2.7 and 7 times more than the price of selectivity. After the study of desorption and regeneration regimes of resins used for both ions it is determined that 96-98% desorption degree can be achieved of the use of solutions of different concentrations of nitrate acid, acid optimal concentrations (0.4-0.5 N) with minimal acid consumption can be of the desorption rate. For

95-96% desorption of Zn^{2+} ions is required in 1.5 times less acid in comparison with desorption of Pb^{2+} ions. That manifests itself in the graphic dependence of processes. So, at the desorption curve of Zn^{2+} ion from Diaion CR-11 the left side of the curve is more distinct, that's why the amount of spent desorbent is significantly small. Per contra, in of Pb^{2+} ion both the left and right sides are noted for especially large diffuseness. It shows that overconsumption of sorbent is unavoidable [11]. During sorption of the mixture of Cu^{2+} - Pb^{2+} by Dowex M 4195 the picture is changing, although partially. So, Pb^{2+} ions are absorbed at the level comparable with Cu^{2+} ions. Sorption capacity and the distribution coefficients of both ions confirm that. During the sorption both ions are absorbed by the resin in the range of 80-85% from solution with initial density of 0.50 gMe/l (0.5q Cu^{2+} /l + 0.5q Pb^{2+} /l). Dowex M 4195 can be effectively used in the refinement of lead containing waters and other objects up to the concentration of this ion of 1.0 g/l. However, both ionites can be successfully applied in cases when the density of analyzed ions is not higher than 0.5 qMe/l.

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Zn²⁺ və Pb²⁺ İONLARININ MÜXTƏLİF FUNKSIONAL QRUPLU İONİTLƏRLƏ SORBSİYASI

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Zn²⁺ və Pb²⁺ ionlarının Diaion CR 11 və Dowex M 4195 ionitləri ilə sorbsiyasının tarazlıq şəraiti ionitlərin ionogen qruplarının neytrallaşma dərəcəsi, mühitin turşuluğu və sorbat məhlullarının qatılığından asılı olaraq öyrənilmişdir. Sorbsiya izotermələrini ifadə edən hesablama tənlikləri təklif edilmiş, prosesləri xarakterizə edən tarazlıq və kinetik parametrlər təyin edilmiş, termodinamik kəmiyyətlər hesablanmışdır. İstiliyin ayrılması və entropiyanın azalması ilə seçiciliyin entalpiya amili ilə idarə olunduğu müəyyənləşdirilmişdir.

Açar sözlər: *Diaion CR 11 və Dowex ionitləri, tarazlıq, kinetik parametrlər, termodinamik kəmiyyətlər, Lenqmür və Freyndlix tənlikləri*

СОРБЦИЯ ИОНОВ Zn²⁺ и Pb²⁺ ИОНТАМИ С РАЗЛИЧНЫМИ ФУНКЦИОНАЛЬНЫМИ ГРУППАМИ

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Изучены условия равновесия сорбции ионов цинка и свинца ионитами Diaion CR 11 и Dowex M 4195 в зависимости от степени нейтрализации их ионогенных групп, кислотности среды и концентрации растворов. Предложены соответствующие уравнения, описывающие изотермы сорбции. Изучена кинетика процессов, на основе равновесных и кинетических параметров вычислены термодинамические величины. Показано, что в выбранных условиях с выделением тепла и уменьшением энтропии системы, избирательность управляется энтальпийным фактором.

Ключевые слова: иониты Diaion CR 11 и Dowex, равновесие, изотермы сорбции, уравнения изотермы, кинетические параметры, термодинамические величины, уравнения Ленгмюра и Фрейндлиха.

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