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EQUILIBRIUM, KINETICS AND THERMODYNAMICS OF SORPTION OF Cu^{2+} , Zn^{2+} , Cd^{2+} AND Pb^{2+} IONS BY DOWEX MAC-3.

Abstract

In this study, equilibrium conditions and kinetics of sorption of Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} ions with Dowex MAC-3 (carboxyl group, H^+) cationite were studied, thermodynamic quantities were calculated based on kinetic parameters. It was noted that the kinetics of the processes at the selected concentrations are under internal diffusion control. 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. The variation of parameters such as activation energy of sorption, free energy, activation entropy and diffusion coefficients varies due to various factors. In the calculation of thermodynamic parameters, the ideality of the ionic phase was determined, in other words, the activity coefficients of the sorbed ions in the ionic phase were not taken into account.

Keywords: *ionite, ion exchange, Zn^{2+} , Cu^{2+} , Cd^{2+} and Pb^{2+} ions, sorption isotherms, Langmuir and Freundlich models, kinetic and thermodynamic parameters*

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Cu^{2+} , Zn^{2+} , Cd^{2+} VE Pb^{2+} ionlarının DOWEX MAC-3 kationiti ilə sorbsiyanın tarazlığı, kinetikasi və termodinamikası

Xülasə

Bu araşdırmada Cu^{2+} , Zn^{2+} , Cd^{2+} və Pb^{2+} ionlarının zəif turşu xassəli H^+ formalı Dowex MAC-3 (karboksil funksional qruplu) kationiti ilə sorbsiyanın tarazlıq şəraiti, kinetikasi öyrənilmiş, kinetik parametrlər əsasında termodinamik kəmiyyətləri hesablanmışdır. Seçilən konsentrasiyalarda proseslərin kinetikasi daxili diffuziyanın nəzarəti altında olması qeyd edilmişdir. Sorbsiya izotermələri qurulmuş, Lenqmyür və Freyndlix modelləri təklif olunmuşdur. Bütün hallarda seçicilik istilik ayrılması və entropiyanın azalması ilə entalpiya amili tərəfindən idarə olunur. Sorbsiyanın aktivləşmə enerjisi, sərbəst enerji, aktivləşmə entropiyası və diffuziya əmsalları kimi parametrlərin dəyişməsi müxtəlif amillərə görə dəyişir. Termodinamik parametrlərin hesablanmasında ionit fazasının ideallığı müəyyən edilmiş, başqa sözlə, sorbsiya olunmuş ionların ionit fazasında fəallıq əmsalları nəzərə alınmamışdır.

Açar sözlər: *ionit, iondəyişmə, Zn^{2+} , Cu^{2+} , Cd^{2+} və Pb^{2+} ionları, sorbsiya izotermələri, Lenqmyür və Freyndlix modelləri, kinetik və termodinamik parametrlər*

Introduction

Environmental pollution with toxic metals occurs globally through military, industrial, and agricultural processes and waste disposal (Duffus, 2002: 793-807). Metals that are released or transported into the environment can undergo transformation and affect the environment, public health, and the economy. Among the methods used for the removal of heavy metals in high concentrations, sediment-filtration, ion exchange, etc. should be considered.

The purpose of the presented research is to propose a cationite that meets the technological requirements by studying the sorption of Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} ions to Dowex MAC-3 cationiti and to calculate the parameters characterizing the processes (Abbasov, Jafarli, Heydarova, Memmedova, 2017: 42-47; Jafarli, Abbasov, 2017: 449-462; Pehlivan Erol, Altun Turkan, 2006: 149-156).

Experimental part. Sorption of studied ions from aqueous solutions with a concentration of $0.5\text{-}5.0 \text{ gMe}\cdot\text{L}^{-1}$ with H^+ -form cationite was carried out under static conditions, at room temperature, in the pH range of 5-6. The ratio between the mass of the sorbent and the volume of the solution was 1:100. The limiting sorption capacity of the cationite for the studied ions was determined by the method of saturation of the samples in H^+ form in solutions of varying concentrations. The acidity of the initial and equilibrium solutions was measured with a pH meter Acvilon pH-meter-pH 410.

Residual concentrations of studied ions in solution and after sorption were determined by complexonometric method using pyridyl-azo-naphthol-PAN (Cu^{2+}), eriochrome black T (Zn^{2+} and Cd^{2+}) and xylenol orange (Pb^{2+}) (Shvartsenbakh, Flashka, 1970: 562). Residual amounts of studied ions in equilibrium solutions were determined in a Thermo Scientific iCE 3500 atomic absorption spectrometer. The amount of absorbed Zn(II) , Cu(II) , Cd(II) and Pb(II) ions was calculated from the equation A (mg/g):

$$A = (C_0 - C_t)V / m \quad (1).$$

The kinetics of the processes was studied by the "limited volume" method with solutions with an initial concentration of $1.0 \text{ gMe}\cdot\text{L}^{-1}$, the values of the effective diffusion coefficients were calculated from the equation proposed by G. Boyd and colleagues (Boyd, Adamson, Myers, 1947).

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

There the rate of change of F-ions; Q_t and Q_∞ -show the amount of sorbed ion corresponding to the time t (when the sample is taken for analysis, sec.) and the time when the equilibrium is established:

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

Bt is called dimensionless parameter or Fourier measure of homochrony. The values of the effective diffusion coefficients were calculated by this formula:

$$D = B_t \cdot r_0^2 / t \cdot \pi^2 \quad (4)$$

r - indicates the average radius of the swollen ionite grain in cm. Values of the effective activation energy - E_{akt} were calculated from the Arrhenius equation:

$$D = D_0 \exp(-E_{akt} / RT) \quad (5)$$

based on the dependence of the values of the effective diffusion coefficients on temperature $\ln D - (1/T) \cdot 10^3$. Entropy of activation (ΔS^*) values was calculated from the equation proposed by R.M. Barrer et al (Barrer, Bartholomew, Rees, 1963: 51-62):

$$D_0 = d^2 (ekT/h) \cdot \exp(\Delta S^* / R) \quad (6).$$

In this equation, d is the jump distance of the ion in diffusion (this is assumed to be 0.5 nm), k is the Boltzman constant, h is the Plank constant, T is the absolute temperature, and R is the universal gas constant. The entropy multipliers is calculated by the formula $\lambda^2 \cdot \exp(\Delta S/R)$ – proposed by S.Gleston et al (Glasstone, Laidler, Eyring, 1941: 501):

$$D = e \lambda^2 kT/h \cdot \exp(\Delta S^*/R) \cdot \exp(-E_{akt}/RT) \quad (7).$$

Conclusion

Sorption with Dowex MAC-3 ionite occurs due to the replacement of functional groups of Me^{2+} ions by H^+ ions. The total sorption capacity of Dowex MAC-3 cationite (10.8 mg-eq/g) (9) and the maximum values of the sorption capacity for the studied ions are characterized depending on the acidity of the solution, the nature and concentration of the components. The high swelling capacity of cationite (swelling coefficient = 2.85) confirms the macroporous structure of the functional groups involved in the sorption process (Harju, Krook, 1995: 431-436). Maximum removal of metal ions is observed at pH 5.5-6.5.

The value of the change constant (especially in the sorption of copper and zinc ions) indicates the high selectivity of the sorption. Cu^{2+} isotherms have the greatest peak and convexity in the initial parts. The observed differences in the sorption selectivity of the studied ions can be related to the stability of their ionic and hydrate compounds. The absence of curves in the sorption isotherms indicates that the absorption of the studied ions occurs mainly due to their interaction with the functional groups of the cation exchanger.

Table 1.
Equilibrium parameters of adsorption of Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} - ions by Dowex MAC- 3 (H^+ form) ionite

C_0 , g.l ⁻¹	C_e , g.l ⁻¹	A , mg.g-1	P , ml.g ⁻¹	ω , %	K , Lang	K , Freund.	K_{exc}
Cu^{2+} - cation							
0,5	0,029	47,1	1624,14	94,20	8,64		
1,0	0,076	92,4	1215,79	92,40	8,52		12,85
1,5	0,157	134,3	855,41	89,53	8,48		
2,0	0,304	169,6	557,89	84,80	8,52		
2,5	0,558	194,2	348,03	77,68	8,51		
3,0	0,916	208,4	227,51	69,46	8,52	218,7	
4,0	1,792	220,8	123,21	55,20	8,62		
5,0	2,649	235,1	88,75	47,02	-		
Zn^{2+} cation							
0,5	0,05	45,0	900,00	90,0	5,37		
1,0	0,13	87,0	669,23	87,0	5,33		8,46
1,5	0,262	123,8	472,52	82,53	5,33	204,1	
2,0	0,475	152,5	321,05	76,25	5,35		
2,5	0,784	171,6	218,87	68,64	5,35		
3,0	1,17	183,0	156,41	61,0	5,30		
4,0	2,052	194,8	94,93	48,7	5,36		
5,0	2,87	212,5	73,91	42,5	-		
Cd^{2+}- cation							
0,5	0,06	44,0	733,33	88,0	3,61		
1,0	0,145	85,5	589,65	85,50	3,64		

1,5	0,272	122,8	451,47	81,87	3,62		
2,0	0,452	154,8	342,48	77,40	3,70		
2,5	0,712	178,8	251,12	71,52	3,66		
3,0	1,05	195,0	185,71	65,00	3,67		
4,0	1,847	215,3	116,56	53,82	3,64		
5,0	2,527	247,3	97,86	49,46	-		
Pb ²⁺ - cation							
0,50	0,042	45,8	1090,47	91,6	5,10		
1,00	0,102	89,8	880,39	89,8	5,17	45,71	2,59
1,50	0,195	130,5	669,23	87,0	5,17		
2,00	0,336	166,4	495,24	83,2	5,29		
2,50	0,575	192,5	334,78	77,0	4,96		
3,00	0,870	213,0	244,83	71,0	5,21		
4,00	1,663	233,7	140,53	58,42	5,34		
5,00	2,40	260,0	108,33	52,0	-		

Convex parts of sorption isotherms from the using of Langmuir equation (7): $A=A_{\max} \cdot K \cdot C_e / 1 + K \cdot C_e$ is converted to a linear form: $1/A = 1/A_{\max} + 1/A_{\max} \cdot K \cdot 1/C_e$ (7). Absorption of ion cations is expressed linearly with a high correlation coefficient in $C_e/A - C_e$ coordinates ($R^2 = 0.97-0.98$). This allows us to reliably calculate the maximum absorption value - $A_{\max}$ and the value of the change constant K from the dependence. From the obtained results, it is possible to compile the selectivity series for the sorption of studied ions by the studied sorbent at concentrations of 0.5-5.0 gMe·l⁻¹: $Cu^{2+} > Zn^{2+} > Cd^{2+} > Pb^{2+}$: 7,4; 6,5; 4,4 və 2,51 meq/g. The indicated range corresponds to the variation of the removal rate of metal ions in the range of 94.6-74.5%. Polyampholyte with carboxyl functional group was found to be the most effective sorbent for the studied ions. This is shown in the sorption isotherms and diagram (Figure 1-2).

Experimental materials show that the accuracy of the Langmuir equation, the source of processes, can be expressed with certain deviations. The Freundlich equation – $x/m = a \cdot C_e^n$ includes a and n $\lg x/m - \lg C_e$ also depends on the graph (Freundlich, 1906: 385-470). In graphical dependence, the length of the segment cut from the ordinate axis gives the value of a , and the tangent of the angle formed by the straight line with the abscissa axis gives the value of n . But the Freundlich equation can only satisfy the initial parts of the sorption curves: (0.15-0.9 g/l for Cu^{2+} , 0.05-0.3 g/l for Zn^{2+} , 0.05-0.3 g/l for Cd^{2+} and 0.04-0.6 g/l for Pb^{2+} ions). At the same time, the maximum sorption values of these ions are quite different in a wide concentration range and reach a maximum value of 2.51 (for Pb^{2+}) -7.40 (for Cu^{2+} ions) mg eq/g. The resulting isotherms are described by the following equations:

$$\begin{aligned}
 \text{Dowex MAC-3: } Cu^{2+} \quad A &= 235,1(8,54 \pm 0,05) \cdot Ct / 1 + (8,54 \pm 0,05)Ct & A &= 218,7 \cdot Ct^{0.23} \\
 Zn^{2+} \quad A &= 212,5(5,34 \pm 0,06) \cdot Ct / 1 + (5,34 \pm 0,06)Ct & A &= 204 \cdot Ct^{0.4} \\
 Cd^{2+} \quad A &= 247,3(3,65 \pm 0,06) \cdot Ct / 1 + (3,65 \pm 0,06)Ct & A &= 331,0 \cdot Ct^{0.7} \\
 Pb^{2+} \quad A &= 260,0(5,18 \pm 0,08) \cdot Ct / 1 + (5,18 \pm 0,08)Ct & A &= 457,1 \cdot Ct^{0.78}
 \end{aligned}$$

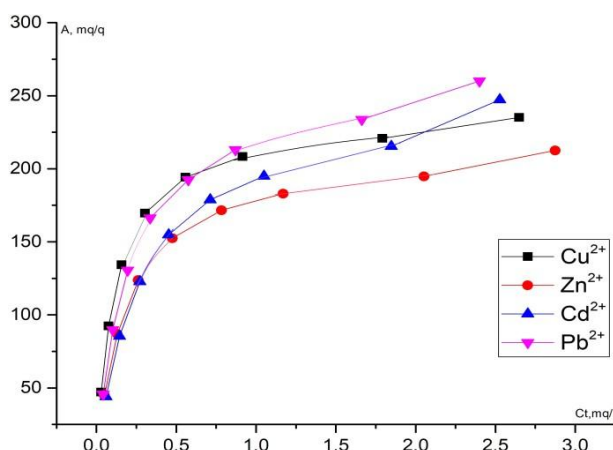


Fig.1. Sorption isotherms of Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} - ions by the studied Dowex MAC-3 ionite

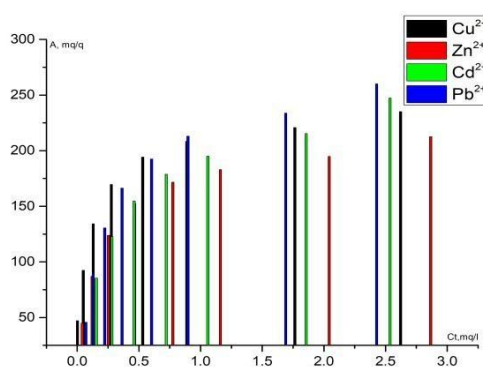


Fig. 2. Sorption diagram of Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} - ions by the studied Dowex MAC-3 ionite

The study of the kinetics of the processes shows that the sorption equilibrium is established within 2.5-3 hours in all cases. A simple and reliable "kinetic memory", in other words partition method, was used to determine the boundary phase in practice. The increase of the sorption rate compared to the initial rate in all cases after the partition confirms that the processes are under the control of internal diffusion. At low levels of saturation, the dependence of $-\log(1-F)$ on time is not expressed by a straight line, while at higher values of saturation ($F > 0.5-0.6$), the dependence obeys a straight line. The expression of the dependence of the degree of saturation F on $t^{1/2}$ up to values of 0.4-0.5 by a straight line from the coordinate origin and the quantities calculated for the absolute values of the Bio criterion ($\text{Bi} > 50$), (12) once again confirm that the studied processes are under the control of internal diffusion (Fig. 3). At optimal pH sorption of ions, the highest value of the internal diffusion coefficient is realized by Pb^{2+} ions. All results were statistically analyzed according to standard methods. The experimental error did not exceed 5% for three parallel experiments. As the temperature increases, the sorption rate increases sharply during the first minute of contact of the ion exchanger with the solution and then gradually decreases until an equilibrium state is reached.

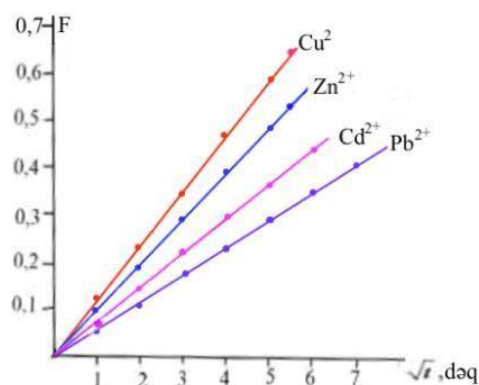


Fig. 3. Dependence of the degree of saturation of the studied ions with Dowex MAC-3 ionite on $t^{1/2}$

As the temperature increases from 25°C to 55°C, the speed of processes increases by about 1.5-2.5 times. During the sorption of lead and cadmium ions, the increase in temperature is more obvious. The higher the activation energy, the more intense the temperature change and sorption rate. The values we obtained for the activation energies are typical for the sorption processes occurring in the internal diffusion region (Fig. 4) (Chromatography, 2003-2004: 453).

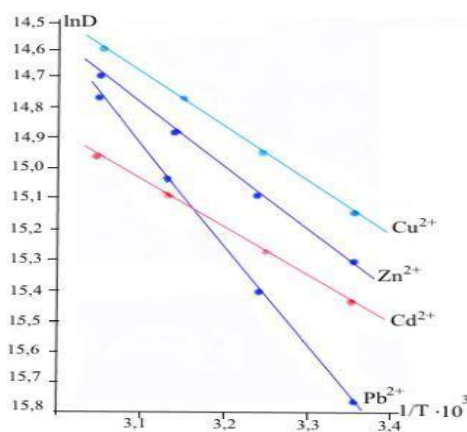


Fig. 4. Graphs of temperature dependence of absorption of studied ions by Dowex MAC-3 ionite

The thermodynamic parameters of ion sorption studied by polyampholyte were calculated assuming the ideality of the ionic phase, in other words, without taking into account the activity coefficients of the sorbed ions in the ionic phase. As it is known, one of the most important energy parameters of any chemical process, especially sorption processes, is the thermal effect of the reaction (Valdman, Panfilov, 1979: 479). The enthalpy change of the system was studied in all cases at 298 K, the obtained results were evaluated according to 1 mole. In all cases, the sorption of ions is accompanied by the release of heat ($\Delta H < 0$). The relationship we established between the increase in selectivity of sorption and the decrease in entropy holds true in all the systems we studied. For small values of the entropy product, the case of faster formation of sorption equilibrium is characteristic. Entropy product values were calculated according to (Glasstone, Laidler, Eyring, 1941: 501). The obtained results confirm the fact that thermodynamic quantities are characterized by minimal values for sorption processes that proceed at high speed and selectivity. It can be argued that the selectivity is controlled by the enthalpy factor in all the systems we have investigated with heat release and entropy reduction. The value of the entropy coefficient for copper ions is lower than for other ions. This indicates a faster establishment of sorption equilibrium, which is confirmed by experimental data. Since Dowex MAC-3 is characterized by a very high (10.4 mg-eq/g)

exchange capacity, its large number of functional groups makes sorption processes more efficient. The values of the diffusion coefficients and other kinetic and thermodynamic parameters calculated with it also confirm the claim (Table 2). Dowex MAC-3 ionite half-time period values are as follows: (21.78 min for Cu^{2+} ; 22.36 min for Zn^{2+} ; 23.46 min for Cd^{2+} and 24.30 min for Pb^{2+} ions) (Adsorption analysis: equilibria and kinetics, 1998: 913).

Table 2.

Kinetic and thermodynamic parameters of sorption of Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} - ions by Dowex MAC 3 ionite. ($r_0=0.063:2=0.0315$ cm)

$D_i \cdot 10^{-7}$ cm ² /sec	$D_0 \cdot 10^{-4}$ cm ² /sec	E_a , kJ/mol	ΔS^0 , C/mol.K	ΔH^0 , kJ/mol	ΔG^0 , kJ/mol	K	$\lambda_{2\exp\Delta S/R} \cdot 10^{-18}$ cm ²
Dowex MAC 3 - Cu^{2+}							
2,64	0,92	14,50	-50,98	-21,50	-6,32	12,85	5,44
Dowex MAC 3 - Zn^{2+}							
2,26	1,76	16,50	-45,56	-18,87	-5,29	8,46	10,43
Dowex MAC 3 - Cd^{2+}							
1,98	3,95	18,80	-38,85	-15,0	-3,42	3,98	23,37
Dowex MAC 3- Pb^{2+}							
1,44	74,76	26,90	-14,40	-14,40	-2,36	2,59	442,45

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