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The Equilibrium, Kinetics and Thermodynamics of Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} Sorption in Sorbents with Different Functional Groups

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Abstract: The equilibrium condition and kinetics of the sorption of Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} ions with Amberlite İRC 748 (with iminodiacetic group, Na$^+$), Duolite C 467 (with amino-fosfon group, Na$^+$), Dowex MAC-3 (with carboxyl group, H$^+$) and Amberlite İR 120 (with sulpho-group, H$^+$) cationites have been studied and thermodynamic parameters of the processes have been calculated on the basis of data gained from the equilibrium and kinetic studies. Sorption isotherms have been organized and relevant equations have been suggested. It has been defined that the kinetics of the processes in the selected concentrations under the control of the internal diffusion. Kinetic parameters have been calculated and it has been noted that heat release and entropy reduction are managed with enthalpy factor.

Keywords: Ion Exchangers, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}-ions, Sorption Isotherms, Langmuir and Freundlich Models, Kinetic and Thermodynamic Parameters

1. Introduction

The mechanism of combining the sorbent metal ions with the functional groups of sorbents depends on the nature of the communication, the acidity of the solution, the ratio of the ion sorbed with functional group, position character of the functional groups. This process is complicated by the presence of complex forming sorbents, which also contain both groups of ion exchange and donor-acceptor communications. The change of Hibbs energy in sorption processes depends on the electron structure of sorbent metal-ions, solvation capability of functional groups and saturation degree of sorbents. Even thermodynamic aspects of ion exchange of metal ions with mono functional sorbents are far from complete solution. Finding out the equilibrium quantities characterizing processes, constructing of sorption isotherms, proposing of computational equations for isotherms, studying the kinetics of sorption, evaluating of kinetic mechanisms, calculating of thermodynamic quantities between equilibrium and kinetic parameters, determining of thermodynamic parameters that governs the sorption process

are extremely important both theoretically and practically. For this reason, investigations on model solution for enhancing of the sorption selectivity are accepted as a topical problem. There is enough information on clarifying the equilibrium conditions, the kinetic properties, the calculating the thermodynamic parameters of the sorption of ferrous metal ions with the sorbents of various natures and functional groups. In these studies, the selection of sorption, the factors affecting to the selectivity, the nature of the environment, the analysis of sorption isotherms, suggesting the calculation equations of isotherms, the regeneration regimes of the done ionites were thoroughly investigated [1-6].

The aim of the presented research work was to study the interaction of the searched sorbents with non-ferrous metal ions to evaluate their sorption capability comparatively.

2. Method

2.1. Equilibrium Experiments

Since the deprotonated form was active-coordination for chelate formatting sorbents [7], they were involved to the

investigations as industrial (Amberlite IRC 748 and Duolite C 467-Na$^+$), Amberlite IR-120 but Dowex MAC-3 as in the H$^+$ form, and the processes were statistically sorbent: Solution = 1:100 ratio. Since the formation of complexes with investigated ionites in neutral and weak alkaline solutions was realized between the metal cations and the N-atom of the ion exchanger and between the metal cations and oxygen atoms of phosphonic groups of sorbent in the acid solutions, experiments with Amberlite IRC 748 was practiced in the interval of 7.5-7.75 of pH and Dowex MAC 3, Duolite C 467 and Amberlite IR 120 in the interval of 4.5-5.5. pH of solutions were measured by the pH meter OR-204/1

2.2. Definition of Metal-ions in Solutions

The residual concentrations of the studied ions after sorption in the solution were determined by using complexometric method, pyridyl-azo-naphthalene-PAN (Cu^{2+}), eriochrome black T (Zn^{2+} and Cd^{2+}) and xylenol orange (Pb^{2+})[8]. 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 amount of ions absorbed by sorbents has been calculated by using the formula

$$A=V (C_0-C_e)/m \qquad (1)$$

based on the difference between their initial and post sorption concentrates.

2.3. Kinetic Experiments

The kinetics of the processes were studied by the way of "limited volume" with 1g Me^{2+}. L^{-1} initial concentrated solution and the values of effective diffusion coefficients were calculated according to the Q. Boyd and colleagues' equation [9]. The equation proposed by G. Boyd and his colleagues has been used to calculate the values of effective diffusion coefficients in kinetic experiments:

$$F = Q_t/Q_\infty =1–6/\pi^2 \sum 1/n^2.\exp(-Bt.n^2), \qquad (2)$$

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.) and equilibrium time,

$$Bt=D\pi^2 t/r^2 \qquad (3)$$

is an indefinable parameter or Fourie's homochromia criterion. The values of the effective diffusion coefficients of ions have been calculated according to equation $D=Bt.r_0^2/t.\pi^2$: r- is the average radius of swollen sorbent granule in sm. The values of effective activation energy have been calculated by Arrenius equation:

$$D=D_0\exp(- E_{akt.}/RT) \qquad (4)$$

due to the temperature dependence of $E_{akt.}$ effective diffusion

coefficients. The dependence of the sorption elements on temperature was studied by the help of U-10 thermostat at 25-55°C.

2.4. Calculation of Thermodynamic Parameters

The values of entropy of activation (ΔS^*) are calculated by substituting D_0 in the equation proposed by R.M.Barrer and his collegaues [10]:

$$D_o=d^2 (ekT/h) \exp(\Delta S^*/R) \qquad (5)$$

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 enthalpy change has been selected as the energetic parameter of the studied processes and the experimental measurements have been carried out directly by a calorimetric method in differential heat transfer micro calorimeter MID 200. The change of enthalpy of the system has been studied at 298 K in all cases, and the results have been evaluated according to 1 mol. The entropy multipliers $-\lambda^2.\exp(\Delta S/R)$ have been calculated by the method suggested by S. Glasstone [11] – the equation of
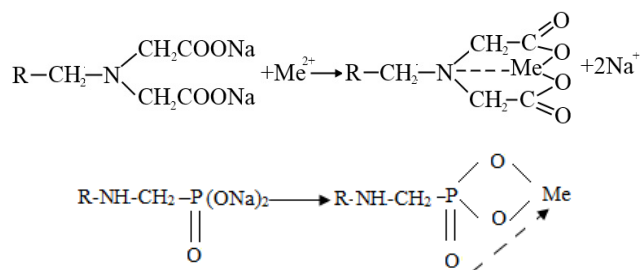
$$D=e\lambda^2 kT/h.\exp(\Delta S^*/R).\exp(-E_{акт.}/RT). \qquad (6)$$

3. Results and Discussion

3.1. The Discussion of Statics of the Sorption Processes

Since Amberlite IRC 748, Duolite C 467, Dowex MAC-3 and Amberlite IR-120 are consistently characterized by functional groups: -N(CH$_2$COONa)$_2$, -NH-CH$_2$-PO (ONa)$_2$, -COOH and -SO$_3$H [6], sorption with first two polyampholyte are realized due to substitution of Na$^+$ ions with Me^{2+} and formation of coordinate communication between Me^{2+} ions and N and **O** atoms, substitution of the sorbents of Me^{2+} ions with H$^+$ ions of functional groups [12].

The structure of the complexes formed by Amberlite IRC 748 and Duolite C 467:

Since the formation of complexes in neutral and weak alkaline solutions realizes mainly between metal cations and nitrogen groups but in acid solutions are between metal cations and oxygen atoms of phosphonic groups, these cases has been taken into consideration in the experiments with Amberlite IRC 748 and Duolite C467. The maximal sorption capacity of these sorbents is 4.40; 3,50; 10,80 and 4,40 meq/g according to

the above sequence, their matrices are in the form of macro-reticular, macroporous, macroporous and gel, their swelling rates are 3,52; 3,50; 2,84 and 2,316. There is also enough information in the literature about the guidance of complex formation beside ion exchange and sorption of metal ions with other carboxyl grouped cationites like Dowex MAC-3 [13]. The absorption zones in 1060,42 sm^{-1} of the phosphoryl groups in the IR-spectra of Duolite C 467 done by Cu^{2+} and Pb^{2+} ions slide to 1087.67 (Cu^{2+} -forma) and 1041.29 cm^{-1} (Pb^{2+} -forma), absorption zones in 1118,71 sm^{-1} are lost, new absorption zone arise in the 1002,58 and 971,50 sm^{-1} area of the Cu^{2+} and Pb^{2+} structured sorbent. These changes in the spectra approve the formulation of coordination communication between ionogenic groups of the sorbent and copper and lead ions. IR spectra were drawn on the IRR-10 spectrometry with the preparation of KBr pills. The similar situation is observed in the interaction of the same ions with Amberlite IRC 748 sorbent. It is impossible to observe the corresponding complexes of these ions in IQ spectra because zinc and cadmium ions have not vacant orbits [14].
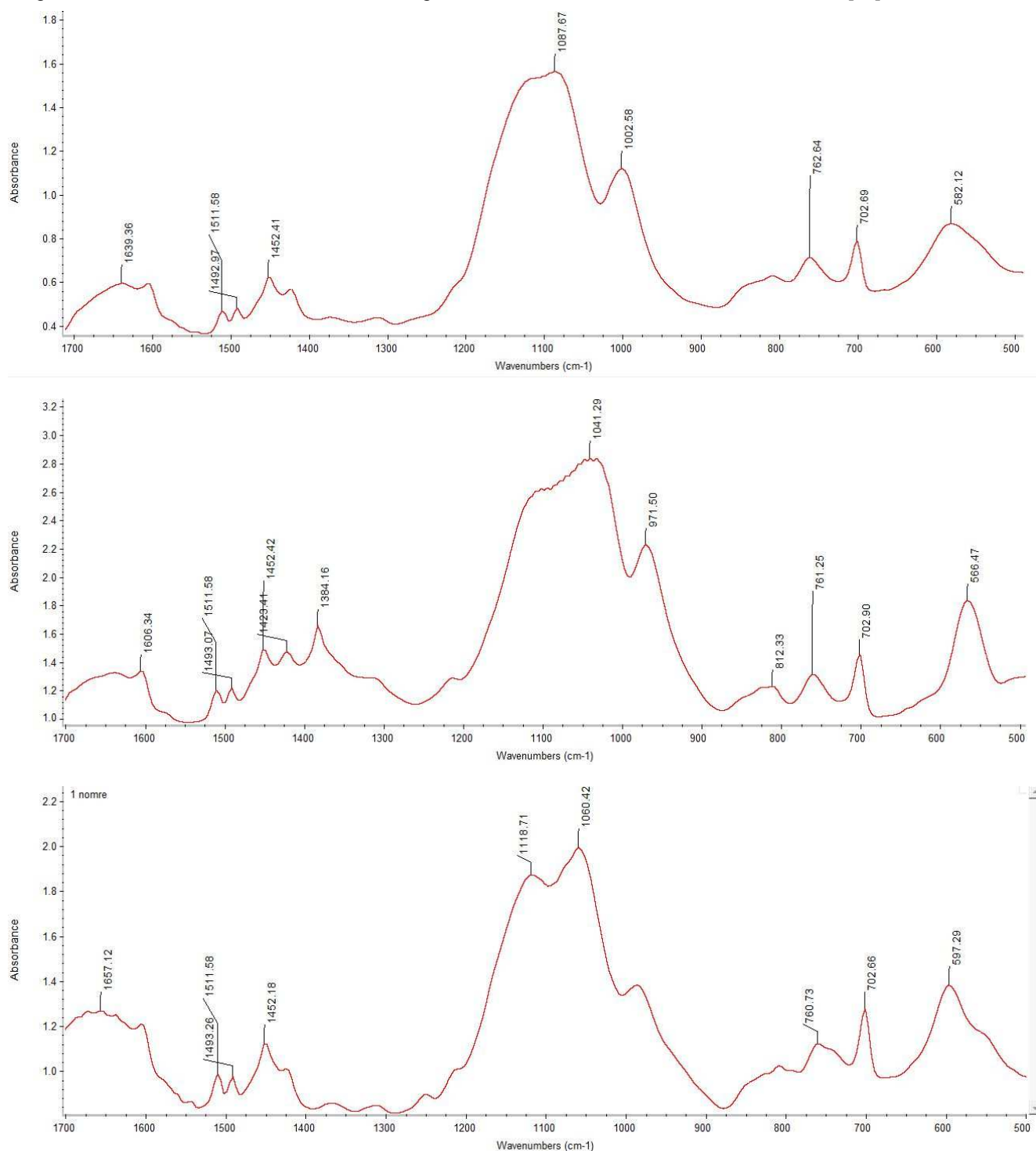

Figure 1. *IR-spectrums of Duolite C 467(1) and its forms done by Cu^{2+}(2) and Pb^{2+}(3) ions.*

The numbering is in Figure 1 descending order:(1-pure Duolite C 467; 2-Duolite C 467-Cu^{2+}, 3-Duolite C 467-Pb^{2+}).

These factors have been evaluated since the formation of chelate cycles in the sorbent phase, in other words, the selectivity of the sorbents mainly depends on the chemical nature of the functional groups and the conditions of the sorption process, the kinetic indicators of the sorbents, their regeneration tendencies, their swelling rates, and their mechanical and technical endurance depend on the nature of the polymer matrix. Main natured groups of polyampholythes are responsible for sorption of the ions due to ion exchange as they undergo the dissociation partially or totally depending on the acidity of the environment. The sorption capability of polyampholythes determined by the amount of acid groups but the selectivity of the sorption processes is determined by the baseline of the amine groups and the stereochemistry of the ligand groups. Because of the weak dissociation of ionic acid groups in smaller pH values, there is a competitive sorption between hydrogen ions and metal ions for functional groups. Furthermore, due to protonation of amine groups, effective interaction between metal ions and functional groups of sorbents cannot be realized.

Sorption isotherms have been organized for all systems (figure 2), convex parts of the isotherms have been turned into linear form by using Langmuir equation: the values of $1/SC=1/SC_{max}+1/SC_{max}\cdot K\cdot 1/C_e$, K and SC_{max} have been calculated. Saturation zones of the sorption isotherms turn to larger concentration of the cations. Perhaps this factor is related to the full saturation of functional groups of sorbents. Analysis of the experiment materials proves that it is possible to formulate the processes studied by certain deviations by the Langmuir equation. This shows that monomolecular sorption layer is formed in these systems and all sorption centres are characterized by equal energy. In all cases, the results submit the linear dependence of the $C_e/A-C_e$ with high correlation coefficient (R = 0,97-0,98). The Freundlich equation can only cover the star-ting parts of the sorption curves: (0.25-1.50 $gMe^{2+}.L^{-1}$). The differences between theoretically calculated values and experimental results in the saturation zones of the curves are so high that comparison is non-essential.
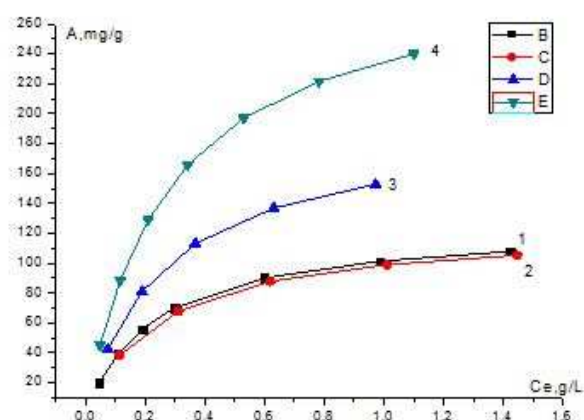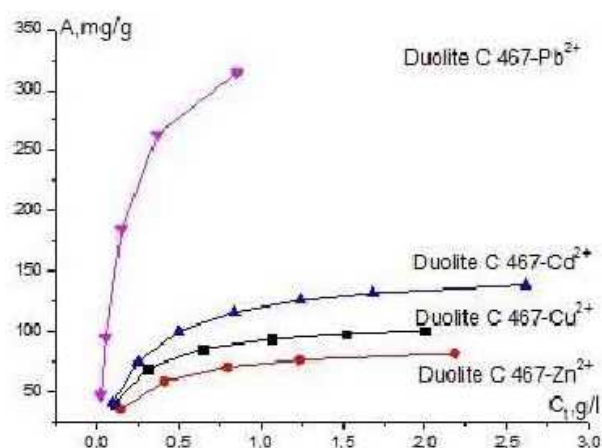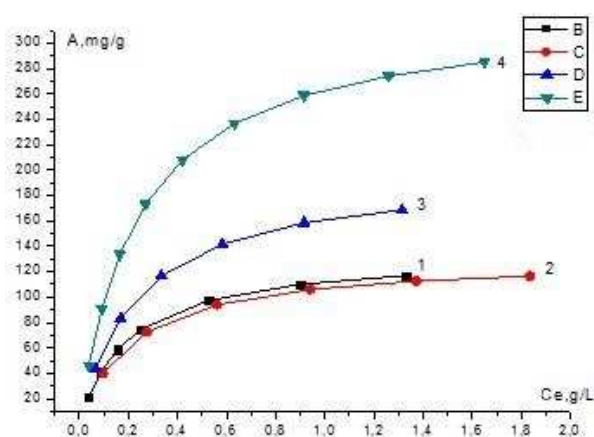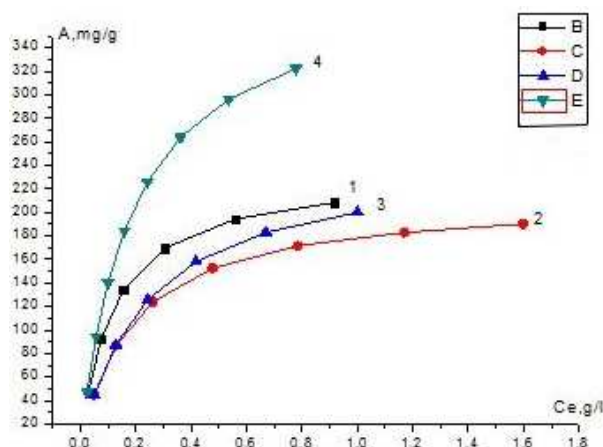

Figure 2. *İsotherms of sorption of Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}-ions by studied resins: a) Dowex MAC 3, b) Amberlite IRC 748, c) Amberlite IR 120, d) Duolite C 467.*

As three unknown parameters include to the equations of Sips

$$(A= K_s.C_t^{1/n}/1+\alpha_s.C_t^{1/n}) \qquad (7)$$

and Redlix-Peterson

$$(A= K_{RP}. C_t/1+\alpha_{RP}.C_t^{\beta}) \text{ [15]} \qquad (8)$$

minimizing procedure has been used [16], but adequately corresponding theoretical and experimental information

couldn't be resulted. According to our view, this is due to the modelling of the latter two models on the basis of hybrid mechanism. The selectivity lines Pb>Cu>Zn>Cd for Duolite C 467, Cu>Zn=Cd>Pb for other sorbents have been determined, it has been cleared that carboxyl grouped Dowex MAC 3 is much more effective sorbent for studied ions. Compared to other bivalent metal ions the high inclination of Cu^{2+} ions to oxygen atoms of sorbents containing the phosphorus is known in the references. On the other hand, according to N. Sedgwick's classification, the reason of effective sorption with complex forming sorbents containing nitrogen are clear

because of higher inclination of Cu^{2+} ions to nitrogen atoms. All the isotherms organized by the unstable concentrations method differ with their convexities for the selectivity of sorbents to concrete ion. The non-existence of clear refraction in isotherms sets ground for thinking on realisation of absorption especially through functional groups. The slightest refraction proves the existence of complexes slightly. a and n lg x/m-lgC_e in Freundlich equation ($x/m = a \bullet C_e^n$) have been found according to graphic dependence. In the above sequence, the form of the isotherms relevant to Langmuir and Freundlich equations are following:

Dowex MAC-3

Cu^{2+}: A= 235,1(7,400) (8,54 $\pm$ 0,05) C_e/1+(8,54 $\pm$ 005)·C_e ; b=218,7·$C_e^{0,23}$

Zn^{2+}: A= 212,51(6,50) (5,34 $\pm$ 0,06)·C_e/1+(6,50 $\pm$ 0,06) ·C_e; b=204,1·$C_e^{0,40}$

Cd^{2+}: A=247,3 (4,400) (4,25 $\pm$ 0,05)·C_e/1+(4,25 $\pm$ 0,05)·C_e; b=275,4·$C_e^{0,57}$

Pb^{2+}: A=398,85 (3,85)(5,76 $\pm$ 0,04)·C_e/1+(5,76 $\pm$ 0,04)·C_e; b=955·$C_e^{0,78}$

Amberlite İR 120

Cu^{2+}: A= 126,0(3,96) (4,21 $\pm$ 0,04)·C_e/1+(4,21 $\pm$ 0,04)· C_e ; b=154,88·$C_e^{0,675}$

Zn^{2+}: A=123,4(3,776) (4,01 $\pm$ 0,05)·C_e/1+(4,01 $\pm$ 0,05) ·C_e; b=112,2· $C_e^{0,36}$

Cd^{2+}: A= 193,90(3,45) (3,80 $\pm$ 0,06)·C_e/1(3,80 $\pm$ 0,06) ·C_e; b=169,8·$C_e^{0,445}$

Pb^{2+}: A= 336,70 (3,25) (4,57 $\pm$ 0,03)·C_e/1+(4,57 $\pm$ 0,03)·C_e b=537·$C_e^{0,74}$

Amberlite İRC 748

Cu^{2+}: 135,0 (425) (4,92 $\pm$ 0,03)·C_e/1+(4,92 $\pm$ 0,03)·C_e; b=195·$C_e^{0,77}$

Zn^{2+}: 130,70 (4,0) (4,55 $\pm$ 0,04)·C_e/1(4,55 $\pm$ 0,04)·C_e; b= 109,6· $C_e^{0,325}$

Cd^{2+}: 199,5 (3,55) (4,21 $\pm$ 0,04)·C_e/1+(4,21 $\pm$ 0,04) ·C_e; b= 229·$C_e^{0,65}$

Pb^{2+}: A= 326,35 (3,15) (9,53 $\pm$ 0.04)·C_e/1+ (9,53 $\pm$ 0,04) ·C_e; b= 276,8·$C_e^{0,81}$

Duolite C 467

Cu^{2+}: A=109,6(5,60 $\pm$ 0,05)C_e /1+(5,60 $\pm$ 0,05) C_e; b=95,5·$C_e^{0,27}$

Zn^{2+}: A=90,2(4,51 $\pm$ 0,04)C_e /1+(4,51 $\pm$ 0,04) C_e ; b=81,3·$C_e^{0,62}$

Cd^{2+}:A=152(3,87 $\pm$ 0,04)C_e/ 1+(3,87 $\pm$ 0,04) C_e; b=125,9·$C_e^{0,37}$

Pb^{2+}: A= 370,6(6,65 $\pm$ 0,06) C_e /1+ (6,65 $\pm$ 0,06) C_e; b=660,7·$C_e^{0,7}$

3.2. The Discussion of Kinetic Experiments

The kinetic experiments have revealed that the sorption equilibriums created in 1.5-2.5 hours in all cases. Simple and reliable "kinetic memory", in other words, partition method has been used for determination of delimiting period in the experiment. In all cases after partition increasing of the sorption speed in comparison with initial speed proves that processes are under the control of internal diffusion. In lower saturation rates the dependence of lg (1-F) from time is not expressed by straight line, but in higher rates of saturation (F>0,5-0,6) is straight line. Saturation rate, expressing of dependence of F on $t^{1/2}$ with straight line from the beginning of coordinate to 0,4-0,5

coordinates and calculated quantities of absolute values of bio criteria prove that the studied processes are under the control of internal diffusion. The results have been worked statistically according to standard methodology, error level of three parallel experiments have not been over 5%. As the temperature increase, the sorption speeds of the ions increases in differently. The positive effect of the temperature on the speed of processes is more apparent during the sorption of cadmium and lead ions: the higher calculated values for activation energy are, the more intensively sorption speed changes by the temperature change parallelly. These are clear in the figure 2. The final values for activation energies are characteristic for the sorption processes in

the internal diffusion area. In the cases of the activation energy is high (this case are mainly observed on sorption of studying metal ions with Amberlite IR120), the sorption speed changes considerably with increasing of temperature. A dependency graph of diffusion coefficients from temperature change with other sorbents has been created and similar graphs were obtained. Non-observation of clear refractions in isotherms, the weak formation of complexes indicates that sorption is mainly realized by ion exchange.
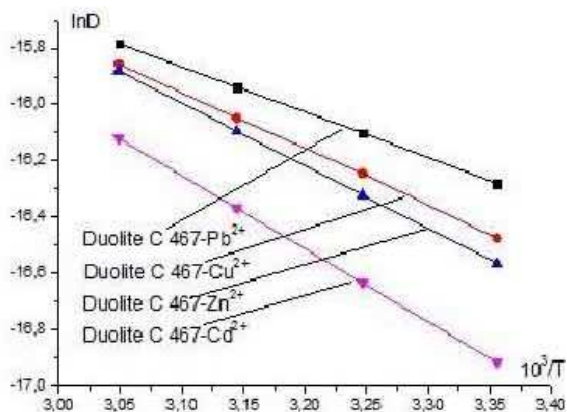

Figure 3. *The dependence of the sorption of the studied ions Duolite C 467 on the temperature.*

The thermodynamic parameters of the sorption of studied ions have been calculated by assuming conditional of the idealness of the ionic phase, in other words without considering the activity coefficients in the ionic phase of sorbated ions. It is known that one of the most important energetic parameters of any chemical process, especially sorption processes, is the thermal effect of the reaction [17]. In all cases, the sorption of ions is accompanied by the heat release ($\Delta H < 0$). Especially, it should be noted that the error between calorimetric experiments and theoretically calculated values for enthalpy does not exceed 5-7%.

The relationship between increasing of the selectivity of sorption and decreasing of the entropy proves itself in all the studied systems. The condition of quick formation of sorption equilibrium is characteristic for small values of entropy multiplier. Characterization of Duolite C 467 and entropy multiplayer with smaller values, quick formation of sorption equilibrium is related to the fact that its matrix has macroporous and larger sorption capacity. The results prove the fact that thermodynamic quantities are characterized by minimal values for sorption processes with high speed and selectivity. It is possible to assume that selectivity is managed by the enthalpy factor in all systems investigated with the heat realise and decreasing of entropy.

Table 1. *Kinetic and thermodynamic parameters of studied systems.*

D_i, $sm^2 \cdot s^{-1}$	D_o, $sm^2 \cdot s^{-1}$	E_a KC/mole^{-1}	$-\Delta S^*$, C/(mole·K)	$-\Delta H^0$, KC·mole^{-1}	$-\Delta G^0$, KC·mole^{-1}	K	$t_{1/2}$, min	Entropy multipliers· 10^{-17}, sm^2
Dowex MAC 3-Cu^{2+} $7,70 \cdot 10^{-8}$	$0,577 \cdot 10^{-4}$	16,40	54,84	16,96	0,62	1,285	21,78	0,34
Dowex MAC3- Pb^{2+} $6.90 \cdot 10^{-8}$	0,836	17,60	51,76	16,07	0,65	1,30	24,30	0,495
Dowex MAC 3-Zn^{2+} 7,50	0,66	16,80	53,72	17,46	1.45	1,794	22,36	0,39
Dowex MAC 3-Cd^{2+} 7.15	0,77	17,30	52,44	16,24	0,61	1,28	23,46	0,456
Amberlite İR120-Cu^{2+} 4,40	14,07	25,70	28,29	10,0	1.58	1,89	39,12	3,49
Amberlite İR 120-Pb^{2+} 3,55	24,45	27,60	23,69	7,63	0,57	1,26	47,24	14,47
Amberlite İR 120-Zn^{2+} 4,0	16,97	26,40	26,73	9,50	1,53	1,8567	41,93	10,04
Amberlite İR 120-Cd^{2+} 3,80	20,54	27,0	25,14	8,48	0,98	1,49	44,14	12,15
Amberlite İRC 748-Cu^{2+} 5,50	2,245	20,60	43,54	16,21	3,23	3,69	30,49	1,33
Amberlite İRC 748-Pb^{2+} 4,20	13,98	25,80	28,34	13,92	5,48	9,11	39,93	8,28
Amberlite İRC 748- Zn^{2+} 5,20	3,31	21,70	40,32	15,12	3,10	3,50	32,25	1,96
Amberlite İRC 748-Cd $^{2+}$ 4,90	6,194	23,40	35,11	15,34	4,88	3,42	34,23	3,66
Duolite C 467-Cu^{2+} 7,0	6,16	16,80	73,44	25,24	3,36	3,88	23,96	0,3646
Duolite C 467-Pb^{2+} 8,50	1,97	13,50	44,64	17,86	4,55	6,29	19,73	0,117
Duolite C 467-Zn^{2+} 6,40	0,12	18,50	68,48	22,82	2,41	2,41	26,20	0,665
Duolite C 467-Cd^{2+} 4,50	0,275	21,60	61,0	20,81	2,64	2,90	37,26	1,63

As it is seen from the table, according to its kinetic features the sorbents can be lined up by the Dowex MAC-3>Duolite C467>Amberlite IRC748>Amberlite IR-120 sequence. The K values calculated from the

$$K = C^{1/2}_{sorbent} \cdot C_{H(Na)solution} / C_{H(Na)sorbent} \cdot C^{1/2}_{solution} \qquad (9)$$

equation used for the change of the monovalent to bivalent ion and mono carboxyl and sulpho grouped functional cations are extremely little from the values calculated from the

$$K = A^2 / (C_0.V-A).(A_{max}.m-A) \qquad (10)$$

equation used for the change of the same valent ions and amino phosphorus and iminodiacetate functional group cations. In our opinion, this is because of the nature of the first equation. In experiments with relatively high concentrations of ($>2,00$ g $Me^{2+}.L^{-1}$), high values are obtained from the calculations with the first equation.

4. Conclusions

The equilibrium conditions of copper (II), zinc, cadmium and lead ions have been studied, sorption isotherms have been constructed and calculating formulas that meet isotherms respective to the Langmuir and Freundlich equations has been suggested. The submission of isotherms to the Langmuir equation indicates that the monomolecular layer was formed on the sorbent surface. Being the kinetic mechanism of the processes under the control of internal diffusion is determined by known methods, and the values of diffusion coefficients and substitution period are calculated. It was noted that thermodynamic parameters for rapidly occurring sorption processes are characterized by minimal values, a significant change of the sorption speed has been occurred in cases where the activation energy is high with the temperature change. Enthalpy values from direct calorimetric measurements and theoretical calculations can be normal with 5-7% error. The studied sorbents are lined up according to their sorption capability and kinetic indicator. Since Dowex MAC-3 is characterized by a very high (10,4 mg-ekv/g) exchange capacity, its large number of functional groups make the sorption processes more effective in comparison with other sorbents. The values of the diffusion coefficients and other kinetic and thermodynamic parameters calculated with it also prove the statement. The sorption speed of Cu^{2+} ion with this sorbents 3,77; 4,80; 6,0 times higher than the sorption speed of the same sorbent with Duolite C 467, Amberlite IRC 748 and Amberlite IR 120 ions. The values of semi-exchange period calculated for all systems also prove the mentioned statements.

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