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EQUILIBRIUM CONDITIONS, ADSORPTION KINETICS OF THE GeO₂-Cu(II)-NaCl SYSTEM ON DIAION CRBO₂ ANIONITE AND DESORPTION MODE FROM SPENT COLUMNS

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Abstract. The IR spectrum of DIAION CRBO₂ anionite synthesized on the basis of a chelating agent, a styrene macromolecule with a glucamine functional group, has been studied. Sorption properties of anionite with respect to the germanium(IV)-copper(II)-Cl-system have been studied.. It is shown that the interaction of hydroxyl and amino groups of anionite with germanate and copper(II) ions is based on the formation of corresponding complexes. Various variants of sorption isotherms are constructed, calculation equations are proposed, which are followed by isotherms, the role of external, mixed and internal diffusion on the basis of the kinetic mechanism of processes is clarified. The desorption mode of the studied components from the treated anionite column was determined.

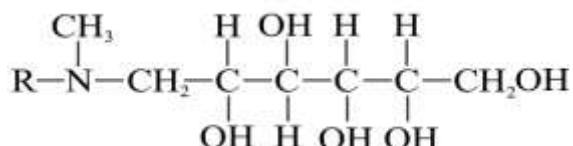
Key words: ionite, germanate-, Cu²⁺-, Cl⁻ ions, sorption, sorption isotherms, isotherm equations, kinetic parameters, Bio criteria, desorption of treated columns

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Introduction

Although highly porous Diaion CRBO₂, synthesized on the basis of styrene macromolecule with glucamine functional group, is shown in the literature as an anionite with high selectivity against borate ions [1], our research also established its selectivity against germanate ions. During sorption even from a concentrated solution GeO₂, the saturation of the isotherm cannot be observed. We established that 1.00 g of anionite absorbed 440-

450 mg of Ge from solid solutions. Since it is debatable which anion form of germanium in the solution depending on the concentration, the measurement unit mgGe/g was used to characterize its absorption. The study presented by us is the first time it has been submitted to the opinion of experts. Anionite, containing hydroxyl and amine groups can be represented as follows:



The total sorption capacity of anionite is 2.7 mg-eq/ml 0-14 mg-eq/g and it belongs to the group of weakly basic anionites of polyamine type [1].

Anionite shows high selectivity against

borate and germanate ions (formation of compatible complexes with both anions) [2,3], as well as cations of d-elements due to amino and hydroxyl groups in its content. In considering that these ions (Ge(IV) and Cu²⁺)

occur side by side in technological solutions, and the (Cl⁻) ion is one of the integral components of such systems, we set ourselves the goal of investigating the proposed system. This complicates the subsequent regeneration scheme of ions sorbed by ionite separately and the conversion of regenerates products into sales products. On the other hand, it allows searching for other ways of using sorbates saturated with different ions. Rejection of existing standard technological schemes is due to the use of copper-germanium ionites as catalysts in low-temperature processes. In this regard, first of all, clarifying the mechanism of stabilization of the studied ions in the ionic phase during their co-sorption determines the relevance of the study. The relevance of the research is specified by the search for new sorbents with higher sorption capacity and selectivity.

The sorption of a number of metal ions (Cu²⁺, Zn²⁺, Cd²⁺, Co²⁺, Pb²⁺, etc.) from chloride solutions with this type of anionites is explained as the formation of complex compounds with the unpaired electrons of

nitrogen atoms of the mentioned ions [4]. As the the concentration of Cl⁻ ions in the solution increases, the formation of complexes increases as well which leads to the increase in their concentration in the sorbent phase. On the other hand, the opposite situation is observed in diluted solutions of chloride. Since there are not enough studies in this direction, it is necessary to calculate the sorption regularities of both germanate and copper(II) ions with Diaion CRBO₂ anionite, as well as the physicochemical parameters of their joint sorption from chloride solutions. The kinetic mechanism of the processes and the study of the desorption mode of the anionite column treated with investigated sorbates will be of interest both from a theoretical and a practical point of view.

The purpose of the proposed research was to clarify the features of co-sorption of germanate and copper (II) ions from chloride solutions, as well as to determine the stabilization conditions of Cu(II) ions in the ionic phase.

Experimental part

The sorption of germanate and Cu²⁺ ions by OH⁻ anionite was studied separately due to their joint solutions in the ratio of ionite-solution=1:100 under static conditions. The concentration of germanium in the solution was determined by titration with a standard solution of NaOH in the presence of mannitol and by the photometric method [4] using phenylfluorane up to $\lambda=500-560$ nm, and the amount of Cu²⁺ ions was established by the complexometric method with pyridyl-azo-naphthalene (PAN) [5]. The amount of ions in a few samples was established by the atomic-absorption spectroscopy method (ThermoScientific AA3500) and values close or sometimes overlapped with the results obtained by classical methods.

Under static conditions, the sorption of germanium was studied from GeO₂ with a concentration of 0.05-10.0 gGe/l, and the sorption of Cu²⁺ ions from CuCl₂ (chemically clean) solutions with a concentration of 0.05-5.0 gCu²⁺/l. A 10.00 gGe/l GeO₂ solution was prepared by dissolving 14.4083g of special purity GeO₂ in a 1 l flask by creating a weak alkaline environment, and low concentration

solutions were used by diluting that solution. There is sufficient information in the literature that germanium (IV) is in metagermanate, pentagermanate, and polygermanate forms, depending on its concentration in the solution [6]. The amount of ions absorbed by anionite was calculated from the difference between their initial and post-sorption concentrations. Based on preliminary experiments, it was determined that equilibrium had been formed within 2.5-3.5 hours, depending upon the initial concentrations. At the same time, it was established that both ions are normally sorbed by anionite in a wide pH range (pH-3.5-11.5).

According to the accepted methodology, a pill of powdered anionite with KBr was prepared and its spectrum recorded in a Nicolet 10 IR-spectrometer. As can be seen from the structure of the functional group, amine and hydroxyl groups attached to the carbon atom are the main fragments of the skeleton, so these groups have an advantage in the spectrum. Amine groups were observed in the ranges of 1605.62 cm⁻¹ and 1455.76 cm⁻¹, and OH-groups were observed in the range of 3400-3500 cm⁻¹,

in contrast to aliphatic alcohols, probably because they do not form hydrogen bonds [6]. Since anionite was synthesized on the basis of styrene macromolecule, the absorption bands characteristic only for the aromatic system should appear in the IR spectrum. These bands were observed in the range of 1605.62 (more intense than when they overlap with amine groups); 1510.38 cm^{-1} . The mentioned bands belong to the oscillations of C-C bonds of the benzene ring. The band observed in the range of 3019.47 cm^{-1} corresponds to the oscillations of C-H bonds of the aromatic cycle. The

oscillations in the range of 1258.39; 857.21 and 811.91 cm^{-1} can probably be attributed to the oscillations of the substituents (-CH₂-CH-) in the benzene nucleus. There is no need to present those spectra since the complex hydroxyl groups formed by anionite with germanium, and the complex formed by copper (II) was realized through nitrogen atoms; however, there is no significant shifts were observed in the absorption bands at 1605.62 and 1455.76 cm^{-1} belonging to hydroxyl (3400-3500 cm^{-1}) and amine groups.

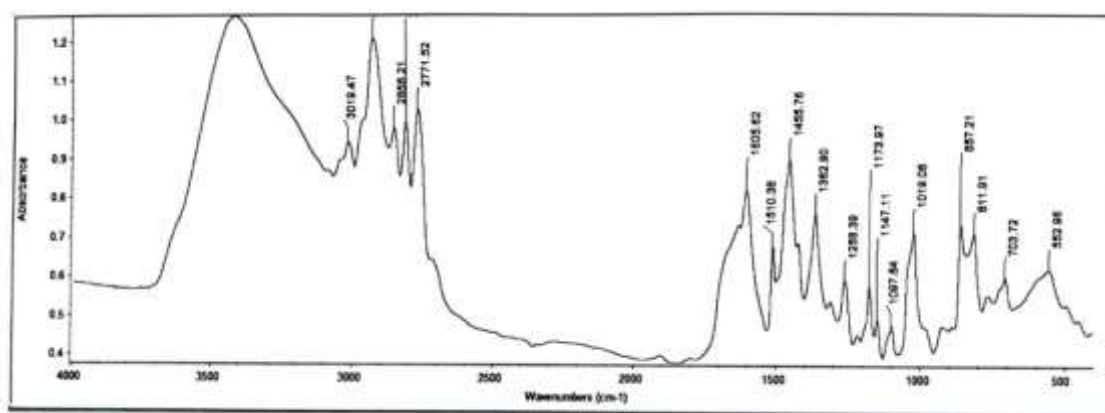


Fig.1. IR spectrum of diaion CRBO₂ anionite

Results and discussion

The sorption isotherm of germanate ions with anionite was distinguished by a clear convexity. The linear part of the isotherm was characterized by a high distribution coefficient- K_d , confirming its high selectivity to anionic germanate ions. Regarding equilibrium of Cu^{2+} ions, a serious effect of the concentration of chloride ions was established in the shape of the isotherm and the sorption capacity of anionite. Thus, the initial part of the sorption isotherm from a pure CuCl_2 solution has an S-like shape. Of course, such an isotherm cannot be written

with sufficient accuracy by any of the known classical adsorption models. Although many isotherm equations of Langmuir, Florey-Huggins, Redlich-Peterson, Freundlich, Tiomkin, Toth and other authors are known for the mathematical writing of isotherms [7-8], after preliminary checks, we preferred Langmuir, Freundlich and Tiomkin equations. Because the possibility of writing the isotherms obtained with certain small errors with these equations was confirmed. The attached Table also confirms the above.

Table 1. Equilibrium parameters of sorption from pure GeO_2 and chloride solutions of different concentrations by diaion CRBO₂ anionite

c (Cl ⁻), mol/l	0	1	4
Langmuir model R_L^2	$a = 2.56 \cdot \frac{6760C_t}{1 + 6760C_t}$	$a = 2.24 \cdot \frac{9685C_t}{1 + 9685C_t}$	$a = 1.40 \cdot \frac{18980C_t}{1 + 18980C_t}$
	0.995	0.995	0.990

Freundlich model R_F^2	$a = 7.76 \cdot C_t^{0,19}$ 0.977	$a = 14.1 \cdot C_t^{0,20}$ 0.964	$a = 7.82 \cdot C_t^{0,21}$ 0.972
Tiomkin model R_T^2	$a = 3.75 + 0.29 \ln C_t$ 0.978	$a = 4.21 + 0.33 \ln C_t$ 0.984	$a = 2.81 + 0.22 \ln C_t$ 0.985
ST, mmol/g	2.45	2.22	1.42
K_d , ml/g	16210	21096	26500
K_s (Ge/Cl)	7.75	12.56	18.84
N	0.78	0.72	0.79

Note that in Tables 1 and 2, C_t represents the equilibrium concentrations of the analyzed ions, and ST represents the sorption capacity.

The S-like shape of the sorption isotherm with Cu^{2+} ions, in our opinion, was due to the hydrolysis process at low concentrations of the ion in solution [9]. By adding NaCl solution to the solution, the curvature in the initial part of the isotherm is lost due to the formation of a structure which is well sorbed by

anionite, and the value of the distribution coefficient increase appreciably. As a result, the sorption capacity of anionite against Cu^{2+} ions increase significantly. According to the Tiomkin model, the high values of the correlation coefficients during the studying of the isotherm in the sorption of Cu^{2+} ions indicate the significant role of intermolecular interactions between adsorbate particles.

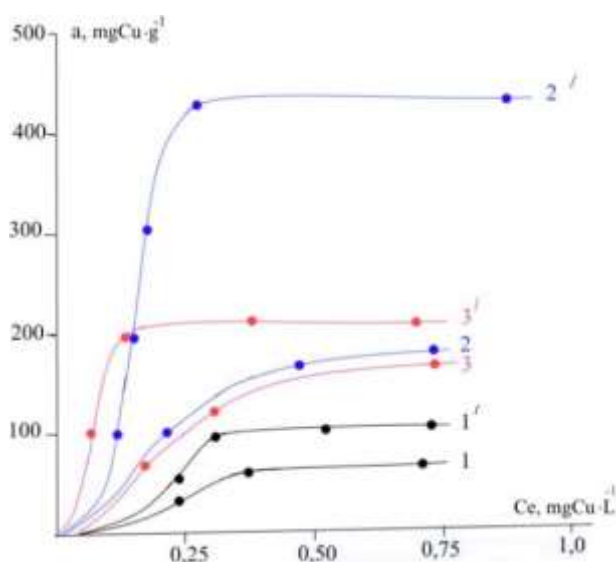


Fig. 2. From solutions with different compositions (pH 5-6) sorption isotherms of copper ions: of germanate ions:
1-sorption from pure copper solution;
2-C(Cl⁻) 1mol/l; 2'-C(Cl⁻) 4 mol/l;
1¹-Cl⁻- free solution; 2¹-C(Cl⁻)1mol/l
3¹-C(Cl⁻) -4 mol/l

For isotherms 1¹, 2¹, and 3¹, the Ge:Cu ratio was 1:1.

As can be seen from Fig. 2, while the maximum sorption capacity of anionite from a pure $CuCl_2$ solution fluctuates around 65 mg/g,

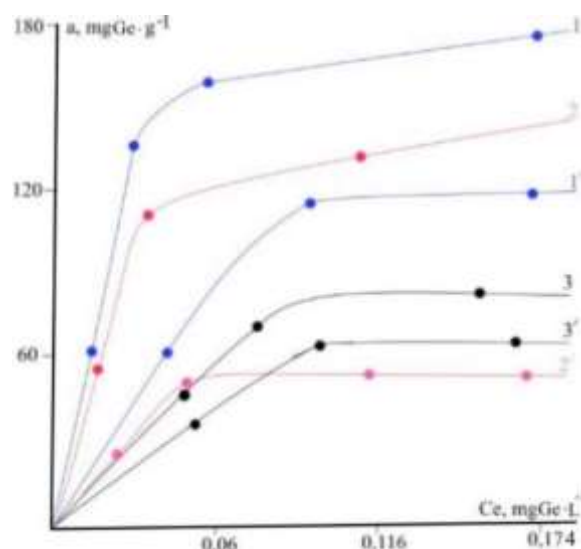


Fig. 3. From solutions with different contents (pH 5-6) sorption isotherms of germanate ions:
1-sorption from pure GeO_2 solution;
2-C(Cl⁻) 1mol/l; 3-C(Cl⁻) 4 mol/l;
1¹-Cl⁻- free solution; 2¹-C(Cl⁻)1mol/l;
3¹-C(Cl⁻) -4mol/l

this amount increases 7.5 times reaching 470 mg/g at a 1:1 ratio of Cu:Ge mixture and a concentration of Cl⁻ ions of 1 mol/l.

Dependence of logarithmic analyzes of ion distribution coefficients on equilibrium concentrations in non-linear parts of isotherms made it possible to calculate total absolute

values of charges of sorbed ions: $\log K_d = \log A - n \log C_t$. n - in this formula indicates the total absolute value of the charges of the adsorbed ions.

Table 2. Equilibrium parameters of sorption of Cu^{2+} ions from pure and different concentrations of CuCl_2 solutions by diaion CRBO₂ anionite

c (Cl ⁻), mol/l	0	1	4
Langmuir model R_L^2	$a = 2.04 \cdot \frac{296C_t}{1+296C_t}$ 0.90	$a = 5.76 \cdot \frac{164C_t}{1+164C_t}$ 0.98	$a = 5.95 \cdot \frac{144C_t}{1+144C_t}$ 0.96
Freundlich model R_F^2	$a = 10.2 \cdot C_t^{0.45}$ 0.90	$a = 7.98 \cdot C_t^{0.21}$ 0.96	$a = 8.05 \cdot C_t^{0.20}$ 0.95
Tiomkin model R_T^2	$a = 3.76 + 0.52 \ln C_t$ 0.90	$a = 8.25 + 1.15 \cdot \ln C_t$ 0.96	$a = 6.95 + 0.75 \cdot \ln C_t$ 0.94
Q_∞ , mg/g	121.6	338	342.5
K_d , ml/g	588	896	820
$K_s(\text{Ge/Cl})$	3.2	10.4	8.60
n	0.14	1.4	1.45

As it can be seen, irrespective of the concentration of Cl^- ions, the charge of germanate ions is not expressed by values close to the integer, but by fractional numbers. This gives reason to believe that germanium is sorbed in the anionite phase as germanate acid H_2GeO_3 molecular, as well as metagermanate HGeO_3^- and germanate GeO_3^{2-} anions. Unlike germanium, the total charge of copper ions is significantly different from either pure solutions or chloride solutions. The approach of n to zero can be explained mainly as molecular sorption of neutral $\text{Cu}(\text{OH})_2$ molecules. Addition of electrolyte to the studied solution led to an increase in the total charge ($1 < n < 2$) to indicate the sorption of uncharged Cu^{2+} , $\text{Cu}(\text{OH})^+$ and other ions [10]. The results of sorption from binary solutions of components in 1:1 molar ratio are illustrative that, despite the sharp decrease in the sorption of germanate ions (30-35% on average), the sorption of copper is noticeably increased. Copper sorption isotherm from 1 mol/l NaCl solution is of particular interest. In the presence of an isomolar amount of germanium ions, the total sorption capacity of Diaion CRBO₂ anionite for copper increases by about 1.55 times (from 5.15 to 8 mmol/g). To our thinking, this may be related to the

change in the composition of sorbate due to the formation of uncharged and ionic associates of copper and germanium complexes. This result can be explained by the increase in the share of uncharged particles of germanium and copper in the adsorbate phase. This is also confirmed by the values of n -calculated due to the distribution of the total charges of the particles.

The conducted research and analysis of isotherms confirmed that the sorption of ions from 1mol/l chloride solutions is characterized by the reversibility of ionite selectivity, effective sorption of copper ions is observed at low concentrations of germanate ions in a 1:4 ratio of germanium and copper ions. This, in turn, gives reason to think that both ions are sorbed in the form of polynuclear complex compounds [11].

Proceeding from the fact that the sorption mechanism would be further clarified by studying the kinetics of the processes, it was verified that the sorption of ions was under the control of external, mixed and internal diffusion by using the proposed models.

As is known, a share of external and internal diffusion in sorption processes is expressed by the Bio criterion of the value of diffusion coefficients [12]:

$$B_i = R^2 / 3 \cdot D_{in} \cdot \beta = \frac{D_{ex} \cdot R}{D_{in} \cdot \delta \cdot K_d}$$

In this formula: R – radius of ionite grains, cm; D_{in} – internal diffusion coefficient, cm^2/sec ; D_{ex} – external diffusion coefficient, cm^2/sec ; δ – the thickness of the layer formed in contact with the ionite grain of the solution ($0.5 \cdot 10^{-2}$ cm is accepted); K_d – distribution coefficient, ml/g; It is calculated according to the appropriate parameters from the $\beta = R \cdot \delta \cdot K_d / 3 \cdot D_{ex}$ formula.

The process is carried out according to the intradiffusion mechanism if $B_i \geq 2$ and the external diffusion mechanism if $B_i \leq 1$. If the value of the Bio criterion varies within the range of 1-5, a share of internal and external diffusion in the process is considered to be approximately equal. The mentioned results are related to the linear part of the isotherm [13].

When calculating D_{ex} and D_{in} from low-density germanate solutions, it can be assumed

$$t_{in} = R^2 / 15 \cdot D_{in} \quad \text{v} \quad t_{ex} = K_d \cdot \delta \cdot R / 3 \cdot D_{ex}$$

Using the internal and external diffusion coefficients, the average radius of anionite grains and distribution coefficients, the values of t_{in} and t_{ex} were calculated: average values of 25.34 minutes for t_{ex} (from the solutions with a concentration of 1.00 g GeO_2/l) and 3.38 hours for t_{in} (from the solutions with a concentration of 1.00 g Cu^{2+}/l CuCl_2) were obtained. When adjusted for the fact that the quantities we calculated agreed with the theoretical values to a certain extent, we did not find it necessary to make calculations for all cases.

From the experiments conducted within the temperature range of 25-45 °C, it was determined that the activation energy of the sorption of germanium ions dropped from 17.4 to 12.6 kJ/mol with the experiments conducted with the presence of copper. On the contrary, during the sorption of copper, the activation energy increased approximately by 3.5 times (from 18.5 to 64.75 kJ/mol). Activation energy values were calculated from the Arrhenius equation from the dependence of $\ln D - (1/T) \cdot 10^3$. This confirms that the sorption of copper is completely transferred to the internal

diffusion area. If we consider that the presence of germanate ions in the medium does not affect the diffusion parameters of the sorption of copper ions, the significant increase of the activation energy can, in our mind, only be related to chemical processes. In considering that the joint presence of both ions promotes the sorption of germanate ions to the anionite phase, it can be claimed that copper-germanium complexes are formed in the object under investigation.

As is known complex-forming ionites, in view of weak dissociation of functional groups have low kinetic indicators [14]. On the other hand, the more selectively an ion is sorbed, the more difficult it is subject to desorption from the ionic phase. At the same time, desorption requires more time and reagent consumption. The conditions for the optimal concentration of copper from the ionite phase with 2.5% hydrochloric acid were established by us as follows: the flow rate of the solution for 1 g of anionite is 0.6 liters/hour, the total time for sorption is 1.5 hours, the desorption time from the ionite phase is 2 hours. For

germanate ions, after sorption from a joint solution (Cu and Ge), the parameters of desorption with 2.5% NaOH solution are about

1.5 times higher than copper desorption parameters in the selected concentration interval (1gCu/ and 1gGe/l).

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XELATƏMƏLƏGƏTİRİCİ DİAİON CRBO₂ ANİONİTİ – GeO₂-Cu(II)-NaCl SİSTEMİNİN TARAZLIQ ŞƏRAİTİ, KİNETİKASI, İŞLƏNMİŞ KOLONKALARIN DESORBSİYA REJİMİ

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Xülasə: Stiol makromolekulu əsasında sintez edilmiş, qlükamin funksional qruplu Diaion CRBO₂ anionitinin İQ-spektri incələnməmiş, anionitlə germanium(IV)-mis(II)-Cl sisteminin sorbsiya özəllikləri

araşdırılmış, anionitin hidrosil və amin qruplarının germanat və mis(II) ionları ilə qarşılıqlı təsirlərinin kompleksmələgəlməyə əsaslandığı göstərilmişdir. Fərqli variantlar üçün sorbsiya izotermələri qurulmuş, izotermələrin tabe olduqları hesablama tənlikləri təklif olunmuş, proseslərin kinetik mexanizmi bio kriteriyasına əsasən proseslərdə xarici, qarışıq və daxili diffuziyanın rolu aydınlaşdırılmış, işlənmiş anionit kolonkasının araşdırılan komponentlərə görə desorbsiya rejimi müəyyənləşdirilmişdir.

Açar sözlər: İonit, germanat-, mis(II), Cl⁻ ionları, sorbsiya, sorbsiya izotermələri, izoterm tənlikləri, kinetik parametrlər, Bio kriteriyası, işlənmiş kolonkaların desorbsiyası

УСЛОВИЯ РАВНОВЕСИЯ, КИНЕТИКА АДСОРБЦИИ СИСТЕМЫ GeO₂-Cu(II)-NaCl НА АНИОНИТЕ DIAION CRBO₂ И РЕЖИМ ДЕСОРБЦИИ С ОТРАБОТАННЫХ КОЛОНК

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Резюме: Исследован ИК-спектр анионита DIAION CRBO₂, синтезированного на основе хелатирующего агента, макромолекулы стирола с функциональной группой глюкомина. Изучены сорбционные свойства анионита по отношению к системе германий(IV)-медь(II)-Cl⁻. Показано, что взаимодействие гидроксильных и аминогрупп анионита с ионами германата и меди(II) основано на образовании соответствующих комплексов. Построены различные варианты изотерм сорбции, предложены расчетные уравнения, которым следуют изотермы, уточнена роль внешней, смешанной и внутренней диффузии на основе кинетического механизма процессов. Определен десорбционный режим исследуемых компонентов с обработанной анионитовой колонны.

Ключевые слова: анионит, германат- ионы, ионы меди(II), Cl⁻, сорбция, изотермы сорбции, уравнение изотермы, кинетические параметры, критерий Био, десорбция