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Д.В. Сокольский атындағы «Жанармай,
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ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
АО «Институт топлива, катализа и
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NEWS

OF THE ACADEMY OF SCIENCES
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NAS RK is pleased to announce that News of NAS RK. Series of chemistry and technologies scientific journal has been accepted for indexing in the Emerging Sources Citation Index, a new edition of Web of Science. Content in this index is under consideration by Clarivate Analytics to be accepted in the Science Citation Index Expanded, the Social Sciences Citation Index, and the Arts & Humanities Citation Index. The quality and depth of content Web of Science offers to researchers, authors, publishers, and institutions sets it apart from other research databases. The inclusion of News of NAS RK. Series of chemistry and technologies in the Emerging Sources Citation Index demonstrates our dedication to providing the most relevant and influential content of chemical sciences to our community.

Қазақстан Республикасы Ұлттық ғылым академиясы "ҚР ҰҒА Хабарлары. Химия және технология сериясы" ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Web of Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Химия және технология сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді химиялық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАН РК сообщает, что научный журнал «Известия НАН РК. Серия химии и технологий» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по химическим наукам для нашего сообщества.

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KINETICS AND MECHANISM OF SORPTION OF COPPER (II) IONS BY ION EXCHANGER

Abstract. In this article the kinetics of the process of sorption of copper (II) ions from aqueous solutions by polymer sulfonic cation exchanger, an elementary unit containing a heterocycle and a sulfonic group, under static conditions at a temperature of 298 K and a copper concentration of 2 mmol / mg is investigated. The sulfonic cation exchanger was preliminarily obtained by the reaction of polycondensation of diphenyl oxide and furfural with further sulfonation to obtain functional ionogenic groups in order to increase the extraction efficiency. The obtained kinetic curves of the dependence of the degree of extraction of copper ions from solution on time were processed using the Boyd, Adamson, and Myers equation, which describes diffusion in a limited volume of solution. The kinetic parameters of the sorption process (effective diffusion coefficient, etc.) are calculated, and the results obtained are compared with the data for the traditionally used industrial cation exchanger, which is a copolymer of styrene and divinyl benzene. It has been established that the process of sorption of copper (II) ions in the sulfonic cation exchanger phase is of an intra diffusion nature and corresponds to second-order kinetic equations.

Key words: kinetics, sorption, copper (II) ions, photometry, diffusion, mechanism.

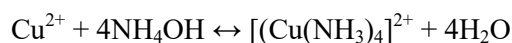
Introduction. Heavy metal ions are dangerous and widespread pollutants of the hydrosphere that have a toxic effect on the ecosystem. Among them, copper ions are considered especially unfavorable for living organisms, which belong to the group of highly toxic substances with a wide spectrum of toxic effects with diverse manifestations [1, 2].

In this regard, a very promising direction of research is the development of methods for purifying industrial and domestic wastewater from heavy metal ions, in particular, from copper ions. Currently, most enterprises use the ion-exchange method as the main method of water purification from ions of heavy metals, which has significant advantages over other methods, for example, high selectivity with respect to the recovered metal. This allows the process to be carried out with a short duration of the technological cycle, relatively low costs and consumption of chemical reagents [3]. Nevertheless, the use of this method with known ion-exchangers does not allow reducing the content of toxic ions of heavy metals to the norm of the maximum permissible concentration [4]. The solution to this problem can be the use of more efficient cation-exchanger based on polymers modified with various functional groups [5–10], for example, carboxyl [9–12], amine [13], phosphoric acid [7, 14, 15], alkylthiophosphoric [16], sulfogroups [17,18], etc. At the same time, to establish the optimal parameters of the sorption of metal ions, it is necessary to know the kinetic laws and the mechanism of the sorption process. In connection with the above, the purpose of this study was to determine the kinetic characteristics of the sorption process of copper (II) ions from aqueous solutions using a new sulfonic cation exchanger of the polycondensation

type, to establish the sorption mechanism, and also to compare the obtained parameters with the data for the known cation exchanger used in industry.

Methods. In the study, we used two types of cation exchanger - industrial sulfonic cation exchanger grade KU-2-8 (strongly acidic cation exchanger, copolymer of divinylbenzene and styrene, Anta LLC, Russia) and sulfonic cation exchanger obtained by polycondensation of diphenyl oxide and furfural, followed by sulfonation. The synthesis of the latter is described in [17], where the static exchange capacity for copper was 2.4–3.2 mg-eq/g.

For the determine of the copper ions in the solution used photometric method. The method is based on measuring the optical density (A) of a blue solution of copper (II) ammonia, obtained as a result of the reaction:



and using the functional dependence of optical density on the concentration of Cu (II) ions according to the Bouguer-Lambert-Beer law

$$I = I_0 \exp(-\varepsilon \cdot c \cdot \ell),$$

where I_0 is the intensity of the incident light, c - is the concentration of the absorbing substance (mol/l), ε - is the molar absorption coefficient (l / mol · cm).

A sample weighing 3.927 g of chemically pure copper sulfate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was transferred into a volumetric flask with a capacity of 1000 ml, dissolved, added 5 ml of concentrated sulfuric acid (density 1.84 g/cm³) and brought up to the mark with water. 1 ml of this solution contains 1 mg of Cu^{2+} ion. 5 standard solutions were prepared from standard solution 1. For this purpose, 20, 15, 10, 5, and 2.5 ml of a standard copper salt solution were measured with a burette in five volumetric flasks with a capacity of 100 ml. To each of the flasks, 10 ml of diluted (1: 3) ammonia solution was added and the volume was brought to the mark with distilled water. To plot a calibration graph, 10 ml of diluted (1: 3) ammonia was transferred into a 100 ml volumetric flask, one drop of concentrated sulfuric acid was added and distilled water was brought to the mark (zero solution). A solution with an average concentration was photometrically measured in the wavelength range of 400–750 nm. We chose a light filter at which the absorption maximum of the solution is observed - 670 nm. This light filter was used for further work [19].

Measurement of absorbance A was started with the solution having the highest copper concentration. To do this, the solution from the flask was poured into a cuvette with a working width of 1 cm, the cuvette was closed with a lid, and the absorption of the solution was measured with a yellow filter. Having measured the absorption A of all solutions, a calibration graph was built.

Experiments to determine the kinetics of sorption were carried out at a temperature of 298 K, in a time interval from 1 to 120 min, while the concentration of copper in the solution was 2 mmol / mg.

Results and its discussion. In order to identify the peculiarities of the kinetics of ion exchange in the work, we compared the sorption of copper (II) ions from aqueous solutions by two types of polymer sulfonic cation exchangers - industrial sulfonic cation exchanger based on divinylbenzene and styrene (KU-2-8) and sulfonic cation exchanger, previously synthesized by the polycondensation reaction of diphenyloxide and furfural followed by sulfonation (SKDF) [17]. Figure 1 shows the kinetic curves representing the time dependences of the amount of sorbed copper ions from the solution.

The obtained dependences make it possible to conclude that the achievement of sorption equilibrium on the SKDF cation exchanger occurs within 30 minutes, and on the KU-2-8 cation exchanger, respectively, within 20 minutes. The difference in achieving equilibrium between SKDF and KU-2-8 is small, which indicates the possibility of using the obtained cation exchanger for the extraction of copper ions from wastewater solutions.

Further, the obtained kinetic curves were processed using the Boyd, Adamson and Myers equation [20], which describes diffusion in a limited volume of solution:

$$F = \frac{Q_t}{Q_\infty} = 1 - 6/\pi^2 \sum \frac{1}{n^2} \exp(-Bt \cdot n^2),$$

where F is the degree of ion exchange; Q_t and Q_∞ are the amount of sorbed ion at time t (sampling time) and at the time of reaching equilibrium, respectively; $Bt = \frac{D\pi^2 t}{r^2}$ - dimensionless parameter or Fourier homochronism criterion; D is the diffusion coefficient (cm²/g); r - is the radius of the ion exchanger grain, cm.

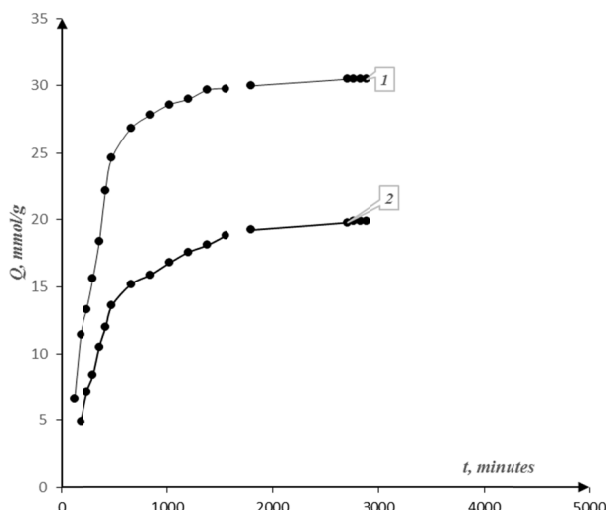


Figure 1 - Kinetic curves of sorption of copper (II) ions from aqueous solutions by industrial sulfonic cation exchanger KU-2-8 (curve 1) and sulfonic cation exchanger based on a copolymer of diphenyl oxide and furfural SKDF (curve 2)

The value of F was determined experimentally and a graph of the dependence of the degree of exchange of ions F on t was plotted (figure 2). Then, using the table of dependence of F on Bt [21], the value of Bt was found for the corresponding values of F and t , and then the diffusion coefficient was calculated according to the method described in the literature [22].

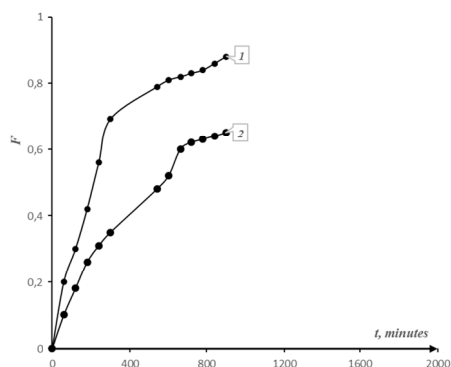


Figure 2 - Dependence of the degree of ion exchange F on time for sulfonic cation exchangers KU-2-8 (1) and SKDF (2)

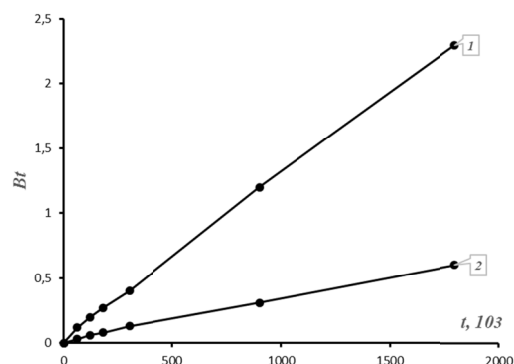


Figure 3 - Dependence of the kinetic coefficient of sorption Bt on time for sulfonic cation exchangers KU-2-8 (1) and SKDF (2)

In figures 2 and 3 the time dependences of the kinetic parameters F and Bt is shown. As can be seen, in the case of the dependence of the function F on time t (figure 2) at small values of F from 0 to 0.15, the obtained dependences are linear, which indicates the internal diffusion character of the kinetics. The dependences of the parameter Bt (kinetic coefficient of sorption) on time t (figure 3) are linear, which suggests a "gel" type of kinetics. In figure 4 shows the kinetic curves of the dependence $-\ln(1 - F) = f(t)$.

As can be seen from figure 4, only in the initial sections of the dependence is the linear character of the function $-\ln(1 - F) = f(t)$ observed. At the next time intervals, the kinetic curves do not meet the criteria of a pure "external diffusion" mechanism. This indicates that, at the initial stage, the sorption process on the indicated cation exchangers proceeds according to the external diffusion mechanism, and over time the influence of the external diffusion factor decreases, and the internal diffusion factor, on the contrary, increases. This means that the process as a whole proceeds in a mixed diffusion mode, i.e. controlled by diffusion in the solution film and diffusion in the grain of the cation exchanger [23].

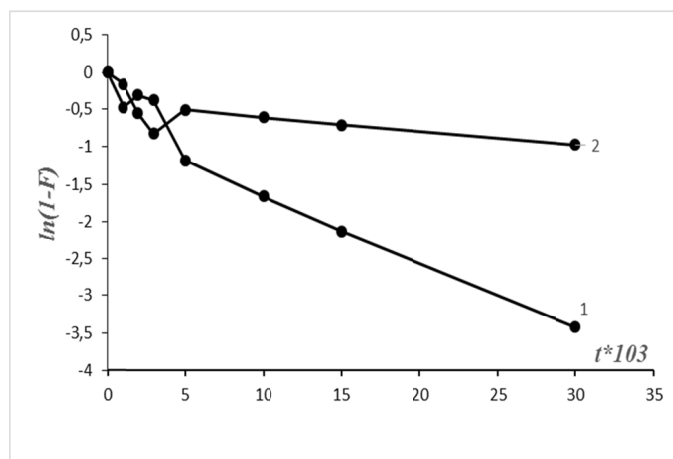


Figure 4 - Dependence $-\ln(1-F) = f(t)$ for the sorption of copper (II) ions by sulfonic cation exchangers KU-2-8 (1) and SKDF (2)

Assigning the kinetic curves to one of the kinetic types makes it possible to calculate the effective diffusion coefficients from the experimental curves, which are kinetic coefficients that take into account both the diffusion features of the transport of molecules in the sorption system and the parallel processes of swelling of the ion-exchange agent, protolysis, and sorbate solvation [24]. Thus, the diffusion coefficients can be calculated using the following formula:

$$D = \frac{Bt \cdot r_0^2}{\pi^2 \cdot t}$$

where D - is the diffusion coefficient, cm^2/s ; t - is the contact time of the solution with the ion exchanger; r - is the radius of an ion exchanger grain in a swollen state, cm .

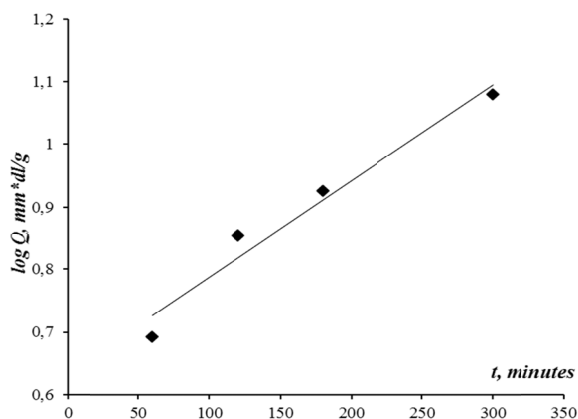


Figure 5 - Dependence of $\log Q$ on time of SKDF sulfonic cation exchanger

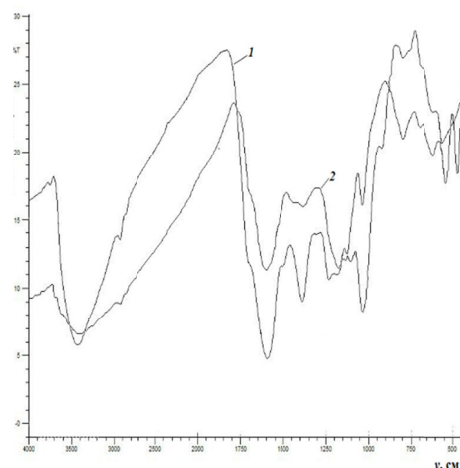
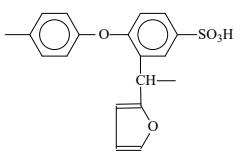
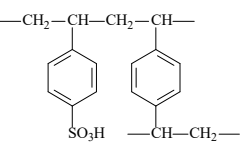


Figure 6 - IR spectra of SKDF sulfonic cation exchanger before (1) and after (2) sorption of copper (II) ions

Stages 1, 5 and 2, 4 are different in the direction, but not in the nature of the movement of ions. Therefore, we can restrict ourselves to considering only the first three stages. In this case, the third stage proceeds instantly in systems not complicated by side processes, including complexation with ionogenic groups [25]. Sorption kinetics expresses the rate of absorption of copper ions on the sorbent, as well as the time of equilibrium regulation of the rate. Kinetic data were processed using kinetic equations of various orders. Representing the equations for the concentration of the reagent at different times, the values of the rate constant are calculated, which make it possible to reveal the contribution of the chemical interaction stage to the sorption process [26]. Dependences of the processed kinetic data showing the second order in

linearized coordinates according to the equation $1/C=k\tau + 1/C_0$ showing a high determination value $R^2 = 0.9628$ is shown in Fig. 5. The IR spectrum of sulfonic cation exchanger before and after adsorption is shown in Figure 6. The IR spectrum of the sulfonic cation exchanger is characterized by the presence of intense absorption bands in the range of $3000-3600\text{ cm}^{-1}$ ($\nu_{\max}=3406\text{ cm}^{-1}$), $1500-1700\text{ cm}^{-1}$ ($\nu_{\max}=1599\text{ cm}^{-1}$) и $950-1250\text{ cm}^{-1}$ ($\nu_{\max}=1031, 1103, 1173\text{ cm}^{-1}$). In addition, in the “fingerprint” region, absorption bands are found due to bending vibrations (out-of-plane vibrations) of aromatic fragments [27] with less (at $792, 686, 615\text{ cm}^{-1}$) and medium intensity (at $920, 539, \text{ and } 472\text{ cm}^{-1}$). According to the literature data [28, 29], the absorption band at $\nu_{\max} = 3406\text{ cm}^{-1}$ can be attributed to the stretching vibrations of the OH group of sulfonic acid. A relatively broad absorption band with a maximum $\nu_{\max} = 1599\text{ cm}^{-1}$ is due to in-plane vibrations of aromatic fragments. The characteristic bands of O=S=O groups, caused by symmetric and asymmetric vibrations, usually lie in the range of $1010-1080$ and $1150-1260\text{ cm}^{-1}$, respectively [30]. On this basis, the absorption bands at 1031 and 1173 cm^{-1} can be attributed to symmetric and asymmetric vibrations of O=S=O groups. Difficult to assign is the absorption band at 1103 cm^{-1} in the initial cation exchanger. Since, the cation exchanger contains C-O-C groups of furan and diphenyl oxide, which can give absorption bands at a given frequency [31]. The high sensitivity of this band to the formation of the SO_3^- anion makes it possible to assign this band to the C-O-C group of diphenyl oxide, which undergoes a high-frequency shift by 20 cm^{-1} after absorption. After sorption, the relative intensity of the absorption band at 1031 cm^{-1} decreases significantly, the position does not change. The absorption band of sulfonic cation exchanger at 1173 cm^{-1} , caused by asymmetric vibrations of O=S=O groups, undergoes a high-frequency shift ($\nu_{\max} = 1227\text{ cm}^{-1}$) after sorption. This band of naphthalene-2-sulfonic acid [29] is found at 1189 cm^{-1} and after (sorption of the copper ion) the formation of the SO_3^- -anion is shifted to the high-frequency region - 1224 cm^{-1} . Similar absorption bands are observed in complexes with the participation of copper (II) ion, cobalt (II) and other metals and aromatic sulfonic acid [32]. In these complexes, the tetraaqua cation $[\text{Me}(\text{OH}_2)_4]^{2+}$ is formed, coordinating with two anions - SO_3^- . A wide absorption band in the region of $3000-3600\text{ cm}^{-1}$ with a maximum at 3431 cm^{-1} , an absorption band in the region of double bonds (in the form of a shoulder at $\sim 1700\text{ cm}^{-1}$), and broad low-intensity absorption bands in the region of $450-900\text{ cm}^{-1}$. The table lists some parameters that determine the nature of the kinetics of the sorption of copper (II) ions on the used sulfonic cation exchangers [33,34].

Table - Elementary unit structure and kinetic parameters of cation exchangers

Cation exchanger type	Elementary link	Kinetic parameters *		
		R^2	$D \cdot 10^{-9}$	k
SKDF		0.9978	31.69	0.0370
			31.69	0.0211
			28.17	0.0298
			27.46	0.0064
			21.834	0.0037
KY-2-8		0.9994	12.67	0.0317
			10.56	0.0220
			9.50	0.0628
			84.52	0.0096
			84.52	0.0022

Note: * R^2 -values of the coefficient of determination; $D \cdot 10^{-9}$ diffusion coefficient (cm^2 / s); k - second-order sorption rate constant, respectively, g / mmol / min.

Conclusion. Thus, the results of studying the kinetics of sorption of copper (II) ions from aqueous solutions by sulfonic cation exchangers of two types under static conditions, as well as the performed mathematical processing of the kinetic curves, made it possible to establish that the sorption mechanism is of a mixed nature and is determined by the total effect of diffusion and chemical reaction.

The results obtained allow us to conclude that the small difference in reaching equilibrium between the SKDF sulfonic cation exchanger obtained by us and on the KY-2-8 cation exchanger indicates the possibility of using the cation exchanger for the extraction of copper ions from wastewater solutions in

certain working time intervals. The peculiarities of the study are represented by the "gel" type of kinetics. The graph constructed according to the experimental data for the obtained sulfonic cation exchanger turned out to be rectilinear to the coordinates $\log Q = f(\tau)$ shows the second order of kinetics determining the process of ion exchange inside the grain of the ion exchanger.

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СУЛЬФОКАТИОНИТПЕН МЫС (II) ИОНДАРЫН СОРБЦИЯЛАУ КИНЕТИКАСЫ ЖӘНЕ МЕХАНИЗМИ

Аннотация. Сорбция кинетикасын зерттеу практикалық қызығушылық тудырады, өйткені тәжірибе барысында өлшенетін сорбция жылдамдығы сорбцияны жүргізу үшін мынадай шарттарды – сорбент түрін, сорбент түйіршіктерінің мөлшерін, температуралық жағдай және басқа параметрлерді таңдау тәрізді практикалық мәселелерді шешуде үлкен рөл атқарады. Сорбция кинетикасын анықтау бойынша тәжірибелер 298 К температурада 1-120 минут уақыт аралығында жүргізіледі, ерітіндідегі мыс концентрациясы 2 ммоль/мг болады. Иониттер фазасындағы мыс (II) иондарының катиондармен сорбциясын зерттеу үшін келесідей физико-химиялық талдау әдістері қолданылады. Екітипті катиониттер арқылы мыс иондарының сорбция кинетикасын зерттеу үшін шектеулі көлем әдісі қолданылады. Салмағы 1 г зерттелетін сорбент сынама-ларының өлшенген бөліктеріне 0,1 г/дм³ концентрациясы бар 100 дм³ CuSO₄·5H₂O ерітінділері құйылады, колбаларды кезеңімен шайқап, 1-120 минутқа дейін сақтайды. Белгіленген уақыттан кейін ерітіндіні декантирлейді және мыс иондарының қалдық мөлшері анықталады. Кинетикалық қисықтар «A –t» коорди-наттарында құрылады, мұнда A – таңдалған уақыт аралығында байқалатын адсорбция, мг / г, t – фаза арасындағы байланыс ұзақтығы. Алынған мәліметтерді математикалық өңдеу Origin Lab Pro бағдарламасы арқылы жүзеге асырылады. ИК спектрлері Перкин-Элмер (АҚШ) фирмасының System-2000 ИК- Фурье спектрометрінде нығыздалған KBr түйіршіктері түрінде анықталады.

Алдын ала болжағанымыздай, сульфокатионитпен мыс иондарының сорбциялану кинетикасы ион алмасу реакциясының жылдамдығымен анықталады. Ион алмасу процесінің жалпы жылдамдығы ерітіндіде жүретін (дәнге қарсы ион және иониттер дәнінен диффузиясы) және ионитте (ионит дәнінің орталығына жоғарғы бетінен қарсы иондар диффузиясы және қарама-қарсы бағытта; ерітіндіден қарсы иондармен ионитте қарсы иондарының алмасуы) процестердің жиынтығы ретінде ұсынылады. Ион алмасу процесі күрделі, көпсатылы, гетерогенді қатты-сұйық жүйеде жүреді. Осыған байланысты ион алмасу кинетикасы гетерогенді реакциялардың жалпы теориясы тұрғысынан қарастырылады. Бұл теорияға сәйкес, ион алмасу процесі қатты фазада жүретін химиялық өзгерістермен ғана емес, зат массасының бір фазадан екінші фазаға өту процестері, реактив шығынын толтыру және реакция өнімдерін жою негізінде сипатталады. Мыс иондары d-элементтер және қисық сутекті байланыстармен сульфо тобы байланысқан түрлі құрылымдар кешенін құрайды, бұл сульфо тобының оттегі атомдары әсерінің нәтижесі болып саналады.

Өндірістік катиониттермен салыстырғанда синтезделген сульфокатионит үшін орнатылған механизм мен алынған кинетикалық сипаттамалары көрсеткендей, біріншісінің Cu²⁺ иондарын алудың технологиялық процестерінде, сонымен қатар оны ауыр металл иондарынан ағынды суды тазарту технологиясында қолдану мүмкіндігінің болашағы бар.

Кестедегі мәліметтерде көрсетілгендей, сорбцияның бастапқы кезеңінде диффузияның тиімді коэффициентінің мәні артады, одан кейін төмендеу негізінде тұрақты мәнге жуықтайды. Диффузия коэффициентінің жоғарылауы сорбцияның бастапқы сатысында ионит бөлшектерінің (катиониттің бастапқы үлгісі құрғақ күйде болады) ісінуі барысында күрделене түсетін сипатын түсіндіреді. Иониттің ісіну уақыты, кезектегі диффузия коэффициентінің өсуі тәжірибелік жағдай, иониттің сорбцияланған иондарының табиғаты, өзара байланысу дәрежесі және басқа факторлармен анықталады. Осы сульфокатиониттерде H⁺ → Cu²⁺ иондары алмасқан жағдайда ион алмасудың ұзақтығы 30 минутты құрайды.

Алынған сульфокатиониттің тәжірибелік мәліметтері бойынша құрылған график, $\log Q = f(\tau)$ координаттарында түзу сызығы ионит дәнінің ішіндегі ион алмасу процесін анықтайтын кинетиканың екінші

реттілігін көрсетеді. ИК-спектрлік және әдебиеттер мәліметтеріне негізделген нәтижелерде, сульфокатионитпен мыс (II) иондарының тетрааква кешені түрінде байланысуы – $[\text{Cu}(\text{OH}_2)_4]^{2+} \cdot 2\text{SO}_3^-$ байқалады.

Осылайша, статикалық жағдайда екі түрдегі сульфокатиониттің сулы ерітінділерден мыс (II) иондарын сорбциялану кинетикасын зерттеу нәтижелері, сонымен қатар кинетикалық қисықтарды математикалық өңдеу анықтағандай, сорбция механизмі аралас сипатқа ие және диффузия мен химиялық реакцияның жалпы әсері арқылы анықтауға мүмкіндік береді.

Түйін сөздер: кинетика, сорбция, мыс (II) иондары, фотометрия, диффузия, механизм.

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КИНЕТИКА И МЕХАНИЗМ СОРБЦИИ ИОНОВ МЕДИ(II) СУЛЬФОКАТИОНИТОМ

Аннотация. Исследование кинетики сорбции представляет практический интерес, так как скорость сорбции, измеряемая в ходе эксперимента, играет главную роль при решении таких практических задач, как выбор условий проведения сорбции типа сорбента, размера гранул сорбента, температурных условий и других параметров. Эксперименты по определению кинетики сорбции осуществляли при температуре 298 К, во временном интервале от 1 до 120 мин, при этом концентрация меди в растворе составляла 2 ммоль/мл. Для исследования сорбции ионов меди(II) катионами в фазе ионитов использовали следующие физико-химические методы анализа. Для изучения кинетики сорбции ионов меди с помощью катионитов двух типов использовали метод ограниченного объема. К навескам исследуемых образцов сорбента массой 1 г приливали по 100 дм^3 растворов $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ с концентрацией 0.1 г/дм^3 и оставляли в течение времени от 1 до 120 мин, периодически встряхивая колбы. По истечении заданного времени раствор декантировали и определяли в нем остаточное содержание ионов меди. Кинетические кривые строили в координатах «А – t», где А – адсорбция, наблюдаемая в выбранный временной промежуток, мг/г, t – продолжительность контакта фаз. Математическую обработку полученных данных проводили в программе Origin Lab Pro. ИК-спектры были сняты на ИК-Фурье спектрометре System-2000 фирмы Перкин-Эльмер (США) в виде прессованных таблеток с КВг.

Предполагалось, что кинетика сорбции ионов меди сульфокатионитом должна определяться скоростью протекания ионообменной реакции. Общая скорость процесса ионного обмена может быть представлена как совокупность процессов, происходящих в растворе (диффузия противоионов к зерну и от зерна ионита) и в ионите (диффузия противоионов от поверхности к центру зерна ионита и в обратном направлении; обмен противоионов ионита на противоионы из раствора). Процесс ионного обмена является сложным, многостадийным, протекающим в гетерогенной системе твердое тело – жидкость. В связи с этим кинетику ионного обмена следует рассматривать с позиций общей теории гетерогенных реакций. Согласно этой теории процесс ионного обмена должен характеризоваться не только химическим превращением, протекающим в твердой фазе, но и процессами переноса массы вещества из одной фазы в другую, для восполнения расхода реагентов и удаления продуктов реакции. Ионы меди является d-элементами и образуют комплексы различного строения, связанные с сульфогруппой искривленными водородными связями, что является результатом влияния атомов кислорода сульфогрупп.

Установленный механизм и полученные кинетические характеристики для синтезированного сульфокатионита по сравнению с промышленным катионитом указывают на перспективность использования первого в технологических процессах извлечения ионов Cu^{2+} , а также возможность его применения в технологии очистки сточных вод от ионов тяжелых металлов.

Из данных таблицы видно, что значения эффективного коэффициента диффузии в начальный период сорбции возрастают, затем, снижаясь, приближаются к постоянной величине. Рост коэффициента диффузии, по-видимому, объясняется тем, что на начальной стадии сорбция осложняется набуханием частиц ионита (исходная навеска катионита была в сухом состоянии). Время набухания ионита, а, следовательно, рост коэффициента диффузии определяется условиями опыта, природой сорбируемых ионов ионита, степени сшивки и другими факторами. В случае обмена ионов $\text{H}^+ \rightarrow \text{Cu}^{2+}$ на данных сульфокатионитах продолжительность ионного обмена составляет 30 мин.

График, построенный по опытным данным для полученного сульфокатионита, оказался прямолинейным к координатам $\log Q = f(\tau)$, показывает второго порядка кинетики, обуславливающим процесс ионного обмена внутри зерна ионита. Результаты на основании ИК спектральных и литературных данных можно предположить связывание ионов меди(II) сульфокатионитом в виде тетрааква комплекса – $[\text{Cu}(\text{OH}_2)_4]^{2+} \cdot 2\text{SO}_3^-$.

Таким образом, результаты исследования кинетики сорбции ионов меди(II) из водных растворов сульфокатионитами двух типов в статических условиях, а также проведенная математическая обработка кинетических кривых, позволили установить, что механизм сорбции носит смешанный характер и определяется суммарным эффектом диффузии и химической реакции.

Ключевые слова: кинетика, сорбция, ионы меди(II), фотометрия, диффузия, механизм.

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