IMPROVEMENT OF ADSORPTION-ION-EXCHANGE PROCESSES FOR WASTE AND MINE WATER PURIFICATION

*Myroslav Malovanyy[1, *], Kateryna Petrushka[1], Ihor Petrushka[1]*

Abstract. The increase of ecological safety level of the hydrosphere as a result of the improvement of the adsorption processes for waste and mine water purification by using natural sorbents and desalting processes *via* electrodialysis has been investigated. The optimal parameters of improved sorption processes with natural sorbents have been established. The mechanism of diffusion was studied by the "kinetic memory" method. Effective coefficients of pore diffusion were determined during sorption of pollutants by natural sorbents. The optimal parameters of electrodialysis with intermembrane filling by ion exchangers for demineralization of waste and mine water have been established.

Keywords: ecological safety, electrodialysis, natural sorbents, sorption, waste and mine water, intermembrane filling.

1. Introduction

Ukraine belongs to the least water-dependent countries of Europe, since the local reserves of river runoff is about 1000 m^3/year per person. The main reason of surface water pollution is the dumping of untreated and insufficiently treated industrial waste water. Wastewater of light or mining industries is especially dangerous because it is not only highly mineralized, but also contains high molecular compounds in significant concentrations. Among them there are organic dyes from textile enterprises. The specific volume of wastewater from painting industry is 150–489 m^3/t. In some mining regions of Ukraine there is a shortage of drinking water, whereas a large amount of mine water is pumped out from underground openings and negatively affects the environment. Using purified mine water would help to solve two problems at once: to reduce its negative impact on the environment and to overcome the shortage of technical water in the regions with poor water resources.

Effective method for purification of municipal wastewaters and landfill filtrates are aerobic biological methods [1, 2]. One of the promising methods of waste and mine water demineralization is electrodialysis, due to which desalting and concentration of water with a salt content of up to 12,000 mg/l can be achieved; the purification efficiency would be up to 94 %. As a result, the initial solution can be concentrated by almost 20 times. It is important that the service life of the membranes is economically attractive and durable [3-7].

The high effect is achieved by using ion exchangers. Electrodialysis is an effective desalination method, in particular for seawater which may be used in drinking water supply. Electrochemical, as well as reagent methods are versatile, well exposed to automation and provide high efficiency of purification [8-10].

Adsorption using natural sorbents of mineral and plant origin is also economically viable method of waste and mine water purification [11-13]. The prospect of using natural minerals in the process of wastewater treatment is determined not only by their high adsorption capacity but also by the existence of effective methods for improving the adsorption properties of minerals and the nature of their surfaces *via* modification. Exhausted natural adsorbents often do not require regeneration (the sorbents saturated with the withdrawn component receive new qualitative characteristics and can be used in other technologies).

Therefore, the investigations aimed at improving the adsorption-ion-exchange processes of waste and mine water purification are relevant and important for increasing the ecological safety of the hydrosphere.

The aim of this work is to increase the ecological safety level of the hydrosphere as a result of the improvement of the adsorption processes for waste and mine water purification by using natural sorbents and desalting processes *via* electrodialysis.

2. Experimental

The kinetics of dyes sorption by natural sorbents was investigated in a thermostated apparatus equipped

[1] Lviv Polytechnic National University,
12, S.Bandery St., 79013 Lviv, Ukraine
* *mmal@lp.edu.ua*

with a stirrer using activated bentonite, glauconite and palygorskit as the sorbents. The design of the setup allowed to vary the speed of rotation of the mixing device for various experiments. The contaminated media were artificially prepared wastewater, contaminated with anionic red 8C and active scarlet 4ZhT dyes. In the experiments with interrupted stirring, the mixing device was stopped after 5 min, the interruption time was 10 min ($\Delta\tau = 10$ min).

A method for comparing experimental values with the theoretical ones for intradiffusion sorption process on the basis of effective coefficients of pore diffusion was that adsorption occurred in the volume of the fluid, which in a weight ratio significantly exceeded the content of the solid phase (sorbent). It means that at the initial moment of time the concentration of pollutions in the fluid changes slightly. In the beginning of the process, it is accepted as a constant on the surface of the adsorbent grain, and the mathematical problem was formulated as a problem of diffusion with the first-type boundary conditions.

To investigate ion-exchange processes for highly mineralized waste and mine water purification the model system of ion exchange resin KU 2–NH$_4$Cl solution was used. The ion exchanger was placed in a measuring cell (U-shaped tube) and alternately led to the equilibrium with the test solution (solutions of 0.1–0.5 M were investigated). The values of back resistance of the pure solution and the ionite–solution system depending on the solution concentration (1/R) were plotted. The point of intersection of the received dependences allowed to determine the concentration of the iso-conductive solution (under which the concentration conductivity is the same as that of ion exchanger). Then the resin was transferred to a centrifuge cell (the ion exchange cell with a porous bottom and two platinum electrodes, folded against each other in the cell wall). The equilibrium solution was removed by centrifugation. The centrifugation of the cell lasted 15 min at the increase in gravity by 373 times. Using an AC bridge (1000 Hz), the resistance of the cell (R_x) was measured, the value of which was used to calculate the specific electrical conductivity of the ion exchanger. The obtained results allow to study the concentration dependence of the resin specific conductivity in the NH$_4$Cl solution.

3. Results and Discussion

The selectivity of adsorption by clay minerals is caused not only by the presence of micro-, meso-, macropores, but also by participation of nanotubes in the adsorption processes and formation of the pores between them. It was investigated that the pore radius of the modified bentonite of the Ilnitsky deposit shifts toward the

transition pores and macropores [14], which suggests an expansion of selective sorption range. The increase in the number of transition pores indicates that the main mass transfer occurs precisely in these pores. In addition, the capillary condensation is observed in such pores, which takes place when the non-compensated superficial forces act over the pores entire volume.

Forecasting of the adsorption kinetics on the example of direct dyes sorption from wastewater can determine the speed of achieving the process equilibrium and its mechanism, as well as the maximum sorption capacity of the adsorbent. In this case, the possibility of calculating the diffusion coefficients of mass transfer allows to construct an optimization profile of the industrial process.

The solution of the problem for the intradiffusion adsorption process at the initial concentration in the solution ($\tau = 0$; C_0) and in the adsorbent grain C_{a0}, and the first-type boundary conditions, with the assumption that the particles shape being spherical, is the equation that determines the change in the component concentration in the liquid phase with time [15]:

$$\frac{C_1}{C_0} = 1 - \frac{1}{1+a}\left[1 - \sum_{n=1}^{\infty}\frac{6a(1+a)\exp\left(-m_n^2 t\right)}{9+9a+a^2 m_n^2}\right] \quad (1)$$

$$\frac{tg\,m_n}{m_n} = \frac{3}{3+a\cdot m_n^2} \quad (2)$$

where C_0 is the initial concentration of the component in the solution, g/dm^3; C_1 is the component concentration at the given moment of time, g/dm^3; μ_n are positive roots of characteristic equation; a is the coefficient of adsorbent pores filling by an adsorbate.

Theoretical calculations of the coefficient of pore filling in natural sorbents by direct dyes (Fig. 1) are carried out taking into account the hydrodynamic conditions of the process and the effective coefficients of pore diffusion. The granulometric composition of sorbents and their distribution by fractions are the same.

From the presented graphic dependences it is observed that the maximum coefficient of pores filling by direct dyes for natural adsorbents is achieved at $n = 6\,\text{s}^{-1}$. On the basis of constructed dependences, calculated effective coefficients of pore diffusion and the shape of kinetic curves, we may assert that the process transfers from the external diffusion or mixed area to pore diffusion area, which is characterized by Bio number Bi $\to 0$.

$$Bi = \frac{bR}{D_p} \quad (3)$$

where β is the mass transfer coefficient, m/s; D_p is the coefficient of pore diffusion, m^2/s; R is the radius of the adsorbent grain, m.
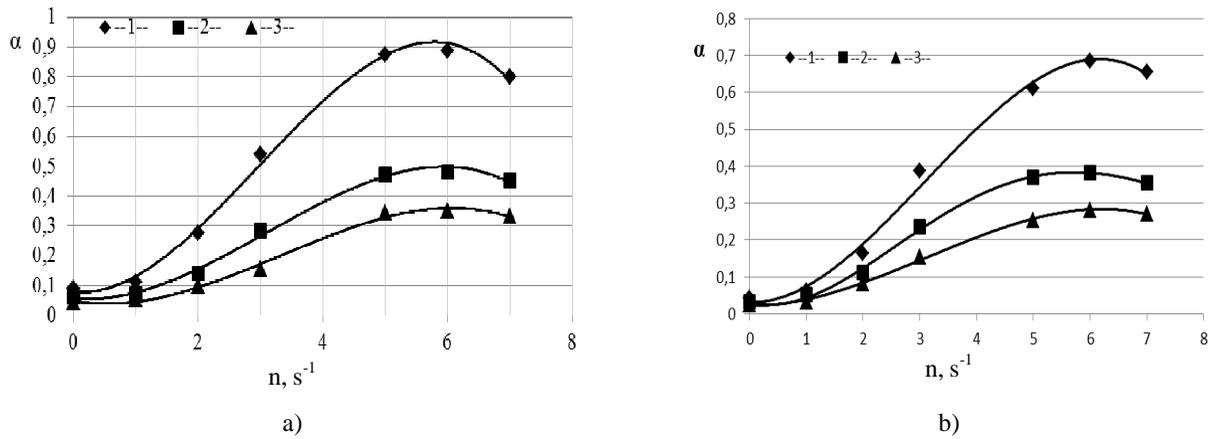
Fig. 1. Effect of the process hydrodynamic conditions on the coefficient of pore filling of the adsorbent (activated bentonite (1); palygorskit (2); glauconite (3)) by anionic red 8C (a) and active scarlet 4ZhT (b)
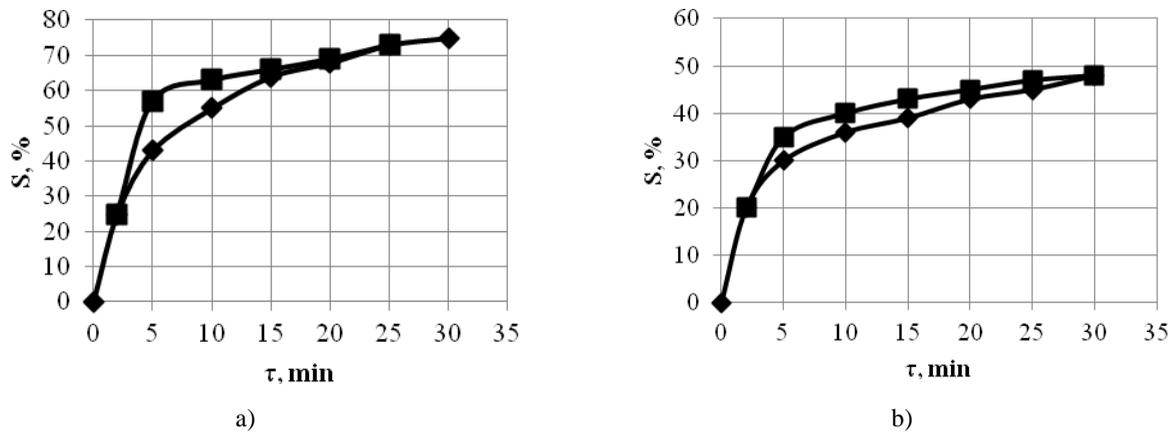
Fig. 2. Kinetic curves of anionic red 8C (a) and active scarlet 4ZhT (b) sorption

by activated bentonite for variable stirring modes (♦ – continuous; ■ – periodical)

At the external diffusion Bi > 50. Within the range of Bi = 0.2–50 the diffusion mixed area takes place and at Bi → 0 there is a pore diffusion.

In order to confirm the diffusion mechanism, we used an interrupt method, or the so-called "kinetic memory" method, the essence of which is described above. Concentration gradients in the adsorbent grain were aligned during the period of contact between the sorbent and the solution, *i.e.*, when the diffusion process was retarded. After the contact was restored, the mass transfer rate increased in comparison with that before interruption. Thus, the increase in the sorption rate confirms the proceeding of pore diffusion (Fig. 2).

To calculate the level of achievement of adsorption equilibrium (*F*), we used a model of gel diffusion from a limited volume to the elementary spheroidal particle of the adsorbent [16]:

$$F = 1 - \frac{6}{p^2} \cdot e^{\frac{-p^2 \cdot D_p \cdot t}{R^2}} \tag{4}$$

where *t* is the adsorption time, s.

If the process approaches the equilibrium one, the final value of the component concentration in the solution has the form:

$$\frac{C_{1f}}{C_0} = \frac{a}{1+a} \tag{5}$$

Parameter *t* is the dimensionless value which is similar to the Fourier number ($Fo = \dfrac{D \cdot t}{R^2}$) and takes into account physical and sorption characteristics of the sorbent:

$$t = \frac{D \cdot t}{R^2} \cdot \frac{e_p}{1 - e_p} \cdot \frac{C_0}{r_s \cdot q_0} \tag{6}$$

where t is the adsorption time, s; D is the diffusion coefficient, m²/s; R is the particle radius, m; ρ_s is the density of solid porous phase, kg/m³; ε_p is the particle porosity, m³/m³.

Obviously, the low values of the exponential correspond to the high time values, therefore, since some time we can neglect the roots of the characteristic equation m_n. Eq. (4) can be submitted as a straight dependence:

$$\ln\left(\frac{C_1}{C_0} - \frac{a}{1+a}\right) = \ln B - m^2 t \tag{7}$$

We determine the effective diffusion coefficient using a slope angle:

$$D = \frac{tg a R^2}{m_1^2} \cdot \frac{1 - e_p}{e_p} \cdot \frac{r_s q_0}{C_0} \tag{8}$$

The obtained results allow to determine effective diffusion coefficients of pollutants sorption by natural sorbents in the modified form and to estimate the intensity of the adsorption process.

To determine the parameters of the external diffusion process of adsorption, we proposed a model based on the theory of local isotropic turbulence for apparatus with a mechanical stirring [16]. This theory is applied to describe dissolution of the solid particles, the sizes of which exceed the thickness of the diffusion boundary layer. The theoretical coefficient of mass transfer is calculated according to the dependence:

$$b_{theor} = 0.267 \cdot (e_0 \cdot n)^{1/4} \cdot Sc^{3/4} \tag{9}$$

where e_0 – specific energy of dissipation; n – kinematic viscosity, m²/s; $Sc = \dfrac{n}{D}$ – the Schmidt number.

The diffusion coefficient of dissolved pollutants (D_d, m²/s) is determined according to Wilk-Chang equation:

$$D_d = 7.4 \cdot 10^{-8} \frac{T(x \cdot M_{water})}{m \cdot u^{0.6}} \tag{10}$$

where T is the temperature, K; x is an initial concentration of pollutant in water, g/dm³; M_{water} is the molecular weight of water, g/mol; m is a dynamic viscosity of water, Pa·s; u is a volumetric molecular weight of the pollutant, cm³/mol.

The specific energy of dissipation e_0, and mixing power N were determined according to known dependences:

$$e_0 = \frac{N}{r \cdot V} \tag{11}$$

$$N = K_N \cdot r \cdot n^3 \cdot d^5 \tag{12}$$

where K_N is the coefficient of mixing, which depends on the Reynolds number; ρ is the density of the fluid, kg/m³; d is a diameter of the mixer, m; n is the number of mixer revolutions, 1/s.

According to Ref. [16], an increase in the coefficient of mass transfer is observed compared to the calculated Eq. (9) due to the radial separation of solid particles. Theoretical values of β were compared with those determined experimentally.

Fig. 3 shows the experimental and calculated values of the coefficients of mass transfer β depending on the number of revolutions n. The obtained graphic dependences allow us to confirm the adequacy of the proposed calculating method in order to predict the intensity of the sorption process.
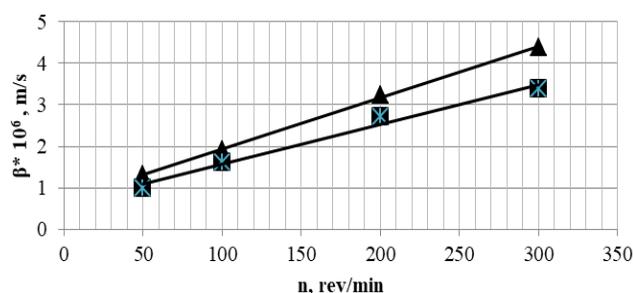
Fig. 3. Coefficient of mass transfer *vs.* number of revolutions for the model solution "pollutant-sorbent":

▲ – theoretical results; ■ – experimental results

The character of the kinetic curves in Fig. 3 confirms the dominant mechanism of pore diffusion in the adsorption process of direct dyes from wastewater by natural sorbents. Thus, using the correction factor k_β, which takes into account the radial separation of the sorbent solid fraction in a limited volume of fluid, the value of the experimental coefficient of mass transfer will approach the theoretical value.

Reverse water supply systems contain ions of sodium, phosphates, chlorides and sulfates. It is important to choose how to remove these ions in a form easy to be used. It is expedient to recycle sodium chloride *via* electrodialysis to obtain alkali and active chlorine. Electrodialysis with filling the intermembrane space by ion-conducting turbulators, *e.g.* granulated ion exchange materials, is a promising method. The role of these ion-exchange materials is that irreversible dissociation of water occurs on their heteropolar boundaries with ion-exchange membranes, during which hydrogen and hydroxyl ions are generated, which are involved in the continuous electrochemical regeneration of the ion-exchange material. There is a combined transport with ions of water mineral impurities. The use of insulating fillers results in a significant increase of the voltage drop and decrease of the membranes working surface. Therefore, the use of ion exchangers in the form of granules as intermembrane filling is of considerable interest. But for the successful application of insulating

fillers for the electrodialysis, a prerequisite is the preliminary study of the electrical conductivity of materials that will be used for intermembrane filling.

We obtained dependences for the pure solution (1) and the system ionite – solution (2), allowing to determine the concentration of insulating solution. They are shown in Fig. 4. The point of intersection of the resulting dependences allows to determine the concentration of the insulating solution, which is equal to 0.51 mol/dm^3.

When using the dependence of specific electric conductivity of NH$_4$Cl solution $y = 11.136x+0.061$ we found $k_{iso} = 5.8296$ Ohm^{-1}·m^{-1} or S/m.

The cell constant is calculated according to Eq. [17]:

$$\Gamma = k_{iso} \cdot R_{iso} \qquad (13)$$

where Γ is the cell constant, determined by the known electrical conductivity of the ionite at the point of isoelectric conductivity, R_{iso} is the measured resistance of the cell after centrifugation with resin, brought to equilibrium with an isoelectric conductivity solution. So, $\Gamma = 5.8229$ Ohm^{-1}·m^{-1} · 596 Ohm = 3474.442 m^{-1}.
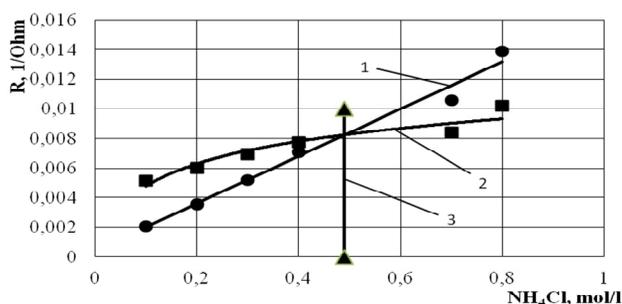
Fig. 4. Determination of the isoelectric conductivity point of KU-2 resin in a U-shaped tube: NH$_4$Cl solution (1); ionite (2) and line of isoelectric conductivity (3)

The obtained data can be used to calculate the electrodialysis process of solutions with NH$_4$Cl, using intermembrane filling by the ion exchanger KU-2.

4. Conclusions

The proposed mathematical models of the adsorption process, which are based on the calculation of external and pore diffusion parameters, allow us to determine the limiting step of adsorption. This enables to predict the degree of pollutants absorption from wastewater. The experimental results regarding the electrical conductivity of KU-2 resin, which will be used for intermembrane filling during electrodialysis, allowed to determine the cell constant and establish the concentration dependence of the KU-2 conductivity. The obtained results can be used for the calculation of real processes.

References

[1] Malovanyy M., Zhuk V., Sliusar V. *et al.*: East Eur. J. Adv. Technol., 2018, **1**, 23. https://doi.org/10.15587/1729-4061.2018.122425
[2] Malovanyy M., Shandrovych V., Malovanyy A. *et al.*: J. Chem., 2016, **2016**, 9. https://doi.org/10.1155/2016/6874806
[3] Tedesco M., Brauns E., Cipollina A. *et al.*: J. Memb. Sci., 2015, **492**, 9. https://doi.org/10.1016/j.memsci.2015.05.020
[4] Daniilidis A., Vermaas D., Herber R., Nijmeijer K.: Renew. Energy, 2014, **64**, 123. https://doi.org/10.1016/j.renene.2013.11.001
[5] Tufa R., Curcio E., van Baak W. *et al.*: RSC Adv., 2014, **4**, 42617. https://doi.org/10.1039/C4RA05968A
[6] Chang D., Choo K., Jung J. *et al.*: Desalination, 2009, **236**, 152. https://doi.org/10.1016/j.desal.2007.10.062
[7] Wang Q., Yang P., Cong W.: Separ. Purif. Technol., 2011, **79**, 103. https://doi.org/10.1016/j.seppur.2011.03.024
[8] Nosachova Yu., Zeleniuk O., Gomelya M.: Khim. Inzhener. Ekolohiia ta Resursozb., 2010, **1**, 48.
[9] Bezdieniezhnykh L., Sviatenko A.: Ekol. Bezpeka, 2015, **2**, 78.
[10] Gomelya M., Trus I., Shabliy T.: Chem. Chem. Techol., 2014, **8**, 197. https://doi.org/10.23939/chcht08.02.197
[11] Melnyk L., Bessarab O., Matko S., Malovanyy M.: Chem. Chem. Technol., 2015, **9**, 467. https://doi.org/10.23939/chcht09.04.467
[12] Malyovanyy M., Sakalova G., Chornomaz N. *et al.*: Chem. Chem. Technol., 2013, **7**, 355. https://doi.org/10.23939/chcht07.03.355
[13] Shmandii V., Bezdenezhnykh L., Kharlamova E. *et al.*: Chem. Chem. Technol., 2017, **11**, 242. https://doi.org/10.23939/chcht11.02.242
[14] Petrushka I., Malovanyy M., Yatchyshyn Y., Petrushka K.: Naukovi Pratsi ONAKhT, 2015, **47**, 48.
[15] Kul A., Caliskan N.: Adsorpt. Sci. Technol., 2009, **27**, 85. https://doi.org/10.1260/026361709788921632
[16] Brahynskyi L., Behachev B., Barabash B.: Peremeshyvanye v Zhydkykh Sredakh. Khimik, Leninhrad 1984.
[17] Gnusin N., Grebenyuk V., Pevnitskaya M.: Elektrokhimiya Ionitov. Nauka, Novosibirsk 1972.

УДОСКОНАЛЕННЯ АДСОРБЦІЙНО-ЙОНООБМІННИХ ПРОЦЕСІВ ОЧИЩЕННЯ СТІЧНИХ ТА ШАХТНИХ ВОД

Анотація. Досліджено підвищення рівня екологічної безпеки гідросфери в результаті удосконалення адсорбційних процесів очищення стічних та шахтних вод від забруднень із застосуванням природних сорбентів та процесів знесолювання електродіалізом. Встановлені оптимальні параметри удосконалення процесів сорбції забруднень природними сорбентами. Механізм дифузії досліджений методом «кінетичної пам'яті». Визначені ефективні коефіцієнти внутрішньої дифузії в процесі сорбції забруднень природними сорбентами. Встановлені оптимальні параметри реалізації електродіалізу із міжмембранною засипкою йонітом для демінералізації стічних та шахтних вод.

Ключові слова: екологічна безпека, електродіаліз, природні сорбенти, сорбція, стічні та шахтні води, міжмембранна засипка.