

Sorption of heavy metal ions by new complexing anion exchanger on the basis of epoxy derivative of vinyl ether of monoethanolamine, allyl glycidyl ether and polyethylene imine

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Abstract. The results of studies on extraction of ions of heavy metals – copper (II), nickel (II), cobalt (II) and zinc (II) from aqueous model sulfate solutions under static conditions by a new anion exchanger based on epoxidized monoethanolamine vinyl ether, allyl glycidyl ether and polyethylene imine are presented. Electron microscopy data showed that the anionite has a developed folded surface with a great number of macropores ranging in size from 0.985 to 8.677 nm. The sorption properties of a new anion exchanger with respect to ions of copper (II), nickel (II), cobalt (II) and zinc (II), the initial and equilibrium concentration of which were determined by the classical polarography were studied. The effect of concentration and pH of solutions of heavy metal salts as well as time of their contact with an anion exchanger on its extracting ability is studied. The optimum values of pH of sulfate solutions at which a maximum sorbing ability of the anion exchanger is observed are found: for Cu^{2+} – 4.1; Ni^{2+} – 6.1; Zn^{2+} – 0.8 and Co^{2+} – 5.4. It is stated that its sorption capacity under optimum conditions reaches the following values for the ions Cu^{2+} , Ni^{2+} , Zn^{2+} and Co^{2+} : 705.2; 598.8; 536.4 and 436.0 mg/g, respectively. The degree of their extraction is 75.6-80.7%. It has a higher extracting ability in regard to these cations than industrial anion exchangers AMP, AM-2b, ANKB, BP-1P, AB-17 and AH-31. Because of this, it can be used for effective group extraction of heavy metal ions in hydrometallurgical processes of non-ferrous metallurgy.

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Introduction

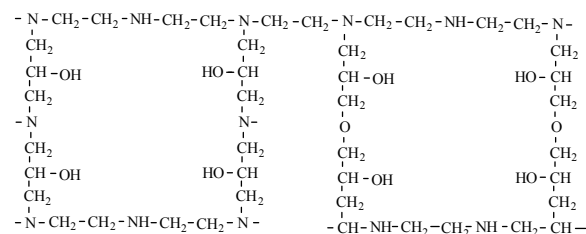
In order to develop resource-saving production processes, of great interest is the development of sorption methods of purification of aqueous solutions of different nature from heavy metal ions [1]. Their compounds refer to the poisons of a cumulative, additive, carcinogenic, mutagenic action and are components of wastewaters of many non-ferrous metallurgical, machine-building, processing, electroplating, radio engineering and other industries [2]. The content of heavy metals in the liquid waste is 10-20 times higher than the maximum permissible concentration (MPC) [3]. Current technologies do not provide effective purification of waste water from them, so after a chemical treatment, most often used at enterprises, the residual content of metal makes up 5.1 mg/l at MPC for most of them being equal to 0.001-0.100 mg/l. Moreover, due to the imperfection of the technologies and equipment being used for extraction of heavy metal ions there take place their significant losses [4]. For example, in electrodeposition, loss of heavy metal salts makes up 60-70%. Electrodeposition refers to environmentally hazardous productions with harmful conditions of

work and a great amount of waste water [3]. Annually, a significant amount of toxic electroplating wastewater containing about 50 tons of heavy metals is released into the environment in the Russian Federation. Typically, the average volume of wastewater generated by a galvanic production is 600-800 m³/per day. A significant environmental problem of mining and metallurgical industries is also mine water containing harmful compounds of heavy metals that pollute water basins [5, 6]. Hydrolytic purification of effluents, as a traditional method of processing, does not solve the problem because it is related to formation of hardly utilizable sludge. Of more expedience can be implementation of ion exchange technology which prevents formation of secondary waste. It is believed that a significant disadvantage of sorption processes is the high cost of synthetic ion exchange materials but here the price of the extracted metals is not taken into account. The advantages of the sorption purification of wastewater are high efficiency, manageability, the ability to extract several heavy metal ions and their recovery [7]. Values of capacity and selectivity with respect to the target ions are the main characteristics, when selecting a sorbent for practical

use [8]. In this connection, development of new effective sorbents having high sorption and kinetic properties with respect to heavy metal ions is relevant.

The most promising compounds for synthesis of polycondensation of ion exchangers are epoxy compounds due to their high reactivity, high thermal and chemical stability, as well as the possibility to control permeability of final products on account of using monomers with different distances between the active groups [9]. In order to create a three-dimensional macromolecular carcass of polycondensation ionites, the initial substances must contain at least three reactive groups or atoms in the molecule.

From the epoxidized vinyl ester of monoethanolamine (EVEMEA), allyl glycidyl ether (AGE) and polyethyleneimine (PEI) we have synthesized a new anion exchanger (EVEMEA-AGE-PEI) of supposed network structure:



The purpose of the work is to study sorption of heavy metal ions by EVEMEA-AGE-PEI new anionine from the model sulfate solutions.

Experimental

EVEMEA-AGE-PEI anionite was synthesized by polycondensation of epoxidized vinyl ether of monoethanolamine, allyl glycidyl ether and polyethyleneimine with a weight ratio EVEMEA:AGE:PEI of 1:1:2.5, temperature 75° C and the duration of 2 hours, followed by solidification of the reaction mass at 110° C for 48 hours. Then it was milled and ionite with particle sizes of 0.5-1.0 mm was obtained. It was found by potentiometric titration that EVEMEA-AGE-PEI in the OH-form is a weak base anionite exchanger. Static exchange capacity (SEC) of the anion exchanger with 0.1 n HCl solution is 14.7 mEq/g.

Sorption of ions Cu^{2+} , Ni^{2+} , Co^{2+} and Zn^{2+} by EVEMEA-AGE-PEI anionite in OH-form (particle size is 0.5-1.0 mm) was studied under static conditions at the ratio of sorbent:solution equal to 1:400, room temperature $20 \pm 2^\circ C$, varying the concentration of metals in sulfate solutions from 0.2 to 2.6 g/l in the range of pH from 0.8 to 6.1 with 0.1 n solution of H_2SO_4 . Duration of the contact of the

sorbent with solutions is from 30 minutes to 7 days. For preparation of model solutions, salts $CuSO_4 \cdot 5H_2O$, $NiSO_4 \cdot 7H_2O$, $CoSO_4 \cdot 7H_2O$, $ZnSO_4 \cdot 7H_2O$ of analytical grade were used.

Sorption capacity (SC) was calculated from the difference between the initial and equilibrium concentration of solutions which was determined by the method of classical polarography against 0.5 n H_2SO_4 solution on the waves of recovery Cu^{2+} ($E_{1/2} = -0.16$ B), Ni^{2+} ($E_{1/2} = -1.12$ B), Co^{2+} ($E_{1/2} = -136$ B) and Zn^{2+} ($E_{1/2} = -1.02$ B). Polarograms were taken on universal polarograph PU-1 in a thermostatted cell at $25 \pm 0.5^\circ C$ using the dropping mercury electrode. Oxygen from the test solutions was removed by blowing argon for 5 min. A saturated calomel electrode was used as a reference electrode.

The structure of the anionite surface was examined by the method of electron microscopy on the scanning electron microscope JSM 6510LA of the JEOL company (Japan) at the resolution of the microscope $30 \text{ \AA} \cdot \text{cm}^{-1}$.

Results and Discussion

The effect of the concentration of sulfuric acid solutions on the extraction of ions Cu^{2+} , Ni^{2+} , Co^{2+} and Zn^{2+} by EVEMEA-AGE-PEI anionite in the OH-form (Figures 1, 2) was studied.

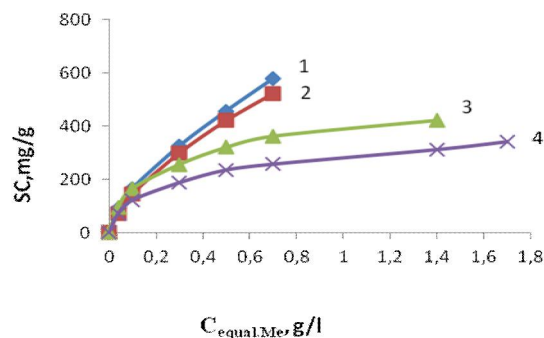


Figure 1. Isotherms of sorption of Cu^{2+} (1), Ni^{2+} (2), Zn^{2+} (3) and Co^{2+} (4) ions from sulfuric acid solutions by EVEMEA-AGE-PEI anionite. The contact time is 7 days

As can be seen in Figure 1, EVEMEA-AGE-PEI anionite has a high absorption capacity for cations Cu^{2+} and Ni^{2+} but it slightly worse absorbs ions Zn^{2+} and Co^{2+} . When removing heavy metal ions from solutions containing metals in the amount of 2.0-2.6 g/l, SC of EVEMEA-AGE-PEI anionite reaches the values over the ions Cu^{2+} , Ni^{2+} , Zn^{2+} and Co^{2+} , 565.6, 522.8, 433.2 and 341.6 mg/g, respectively.

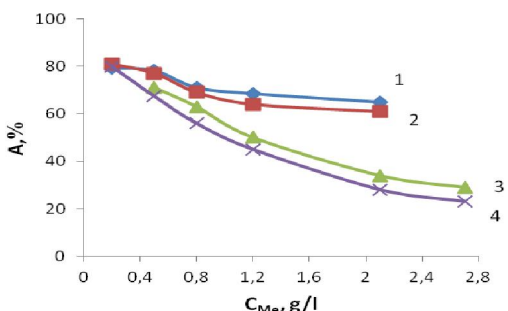


Figure 2. Dependence of the extraction degree of ions Cu²⁺ (1), Ni²⁺ (2), Zn²⁺ (3) and Co²⁺ (4) by EVEMEA-AGE-PEI anionite on the concentration of sulfuric acid solutions. The contact time is 7 days

From Figure 2 it follows that the degree of extraction (A) of heavy metal ions decreases with the increase of their concentration in the sulfuric acid solutions.

In this case, for ions Zn²⁺ and Co²⁺ there is a greater drop in the values of A than for cations Cu²⁺ и Ni²⁺. At the absorption of heavy metal ions from solutions of sulfates with their concentration 0.2 - 0.3g/l, the degree of extraction of ions Cu²⁺, Ni²⁺, Zn²⁺ and Co²⁺ is practically the same 75.6 - 80.7%.

Sorption of heavy metal ions largely depends on pH of solutions as well as the kinetic activity of ion exchangers. We have stated the optimal values of pH sulfate solutions in which maximum absorption capacity of the EVEMEA-AGE-PEI anion exchanger with respect to the ions Cu²⁺, Ni²⁺, Zn²⁺ and Co²⁺ (Table) is observed.

Table. The sorption properties of EVEMEA-AGE-PEI anion exchanger in relation to heavy metal ions

Cation	pH	SC		$\tau_{\text{equil, h}}$
		mg/g	mg-Eq/g	
Cu ²⁺	4.1	705.2	22.2	48
Ni ²⁺	6.1	598.8	20.4	24
Zn ²⁺	0.8	536.4	16.4	5
Co ²⁺	5.4	436.0	14.8	1

As can be seen from the table data, selectivity series of heavy metal ions for EVEMEA-AGE-PEI anion exchanger is as follows: Cu²⁺ > Zn²⁺ > Ni²⁺ > Co²⁺, which is slightly different from the series for chelate nitrogen-phosphorus containing ion exchangers based on ethylene diamine and diethyltriamine (Cu²⁺ > Ni²⁺ > Zn²⁺ > Co²⁺) [10]. It was shown [4] that the sorption capacity of the mineral – brucite in regard to metals decreases in the series: Cu²⁺ > Zn²⁺ > Co²⁺ > Ni²⁺. The time to reach the equilibrium state between EVEMEA-AGE-PEI

anion exchanger and CuSO₄, ZnSO₄, NiSO₄, CoSO₄ solutions changes in the reverse order.

SC values of amine containing chemisorption polyamide fiber POLAN-OG fiber when extracting from solutions containing 1 g/l of heavy metal ions is by Cu²⁺, Ni²⁺, Zn²⁺, 98.36, 99.24, 99.44, mg/g respectively [11]. The best results for extraction of Cu²⁺ ions at pH 4-5 from solutions obtained by leaching ores of Zhezkazgan and Kalmakyr fields with sulfuric acid and containing 1.50-6.25 g/l of copper were shown by industrial ANKB polyampholyte, which contains carboxyl groups in addition to amine [12]. SC on it by Cu²⁺ ions reaches 120-160 mg/g. SC of AM-2b porous anion exchanger of mixed basicity and gel of AMP highly anion resin by Zn²⁺ ions during their extraction from solutions of ZnSO₄, containing 14.6 - 15.0 g/l of zinc is equal to 88 and 151 mg/g, and the recovery 6 and 10 mass %. [13]. Industrial anionite BP-1P, AB-17, AN-31 and ANKB-35 have SC by ions Zn²⁺, respectively equal to 3.4 (pH 4.5), 3.0 (pH 11.0), 2.2 (pH 3.8) and 0.57 (pH 2.9) mEq/g [14]. In the adsorption of Zn²⁺ on the new cyclodextrin polymer it was stated [15] that the equilibrium in the system is achieved for 300 minutes, the optimum value of pH is 5-5.6 and SC is 0.78 mmol/g (51.0 mg/g). On the biosorbent – waste production of the enzyme preparation-megatherium at the extraction of Co²⁺ ions from solution containing cobalt in the amount of 0.2 g/l equilibrium is reached after 30 min, the SC and the recovery was 2.9 mg/g and 27 % [16]. When using cassava peels as a sorbent, the maximum capacity for Co²⁺ ions reaches 41.8 mg/g [17]. Comparison of the found values of SC of new EVEMEA-AGE-PEI anion exchanger with the literature data shows that it has a higher extracting ability in relation to heavy metal ions than conventional and industrial anion exchangers. This is obviously due to the chemical structure of the EVEMEA-AGE-PEI polymer matrix and the structure of its surface (Figure 3).

The data of electron microscopy show that EVEMEA-AGE-PEI anion exchanger has a developed folded surface, with a great number of macropores ranging in size from 0.985 to 8.677 nm.

Sorption of heavy metal cations by anion exchangers proceeds due to the formation of coordination bonds by the donor-acceptor mechanism between the electron-donor atoms of the ion exchanger (N, O) and the vacant orbital of the metal ion [18]:



Thus, the change in the acidity of the solution will affect binding of metal ions by functional groups of the sorbent as the coordination energy $L \rightarrow H^+$ is greater than the binding energy L

→ M (L and M , respectively, ligand and metal) [19]. That is why, to study sorption of heavy metal ions, we used a fully deprotonated OH⁻ form of EVEMEA-AGE-PEI anion exchanger.

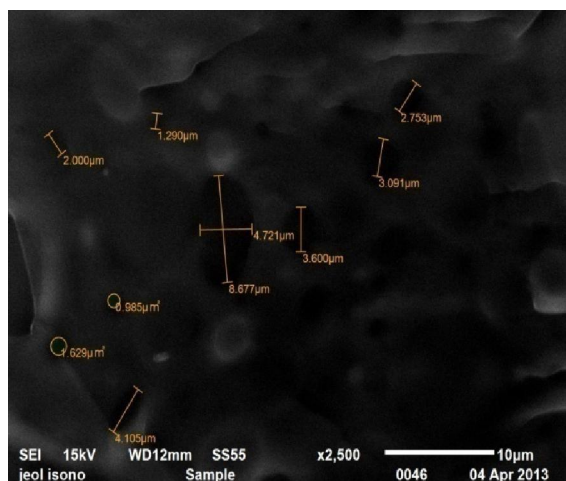
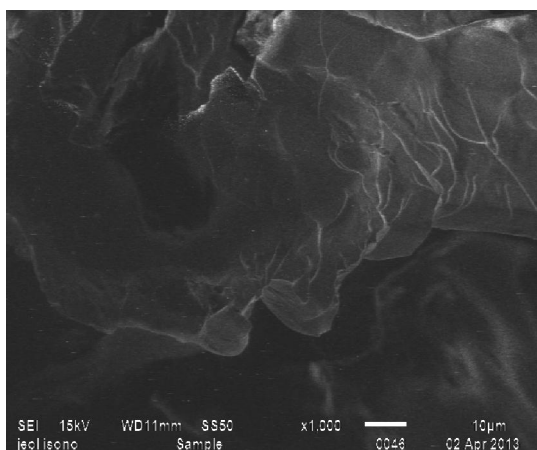


Figure 3. Electron micrographs of the surface of EVEMEA-AGE-PEI anion exchanger

Conclusion

Thus, sorption and kinetic properties of the new anion exchanger based on epoxidized vinyl ether of monoethanolamine, allyl glycidyl ether and polyethylene imine under static conditions are studied. The selectivity series of heavy metal ions for anion exchanger EVEMEA-AGE-PEI has the form: $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+}$. It was found that anionite EVEMEA-AGE-PEI has a higher extracting capacity, relative to cations Cu^{2+} , Ni^{2+} , Zn^{2+} and Co^{2+} , than industrial anion exchanger. Because of this, it can be used for effective group extraction of heavy metal ions in hydrometallurgical processes.

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