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STUDY OF SORPTION OF LEAD (II) IONS BY ANIONITE OBTAINED ON THE BASIS OF ANILINE, EPICHLOROHYDRIN AND POLYETHILENPOLYAMINE

Abstract. Polyfunctional anionit based on aniline, epichlorohydrin, and polyamines were synthesized. The composition and structure of the anion exchanger were studied by IR spectroscopy and elemental analysis. Lead sorption was studied by classical polarography. Dependences on the sorption of lead (II) ions on the solution acidity, concentration of metal ions, and duration the contact of resins with solution $Pb(NO_3)_2$ were determined. This anionite exhibits high capacity in sorption of lead ions. The developed sorbents with increased sorption ability can successfully solve problems of removing lead (II) ions from process effluents in nonferrous metallurgy.

Keywords: sorption, lead ions, anion exchanger, sorption capacity.

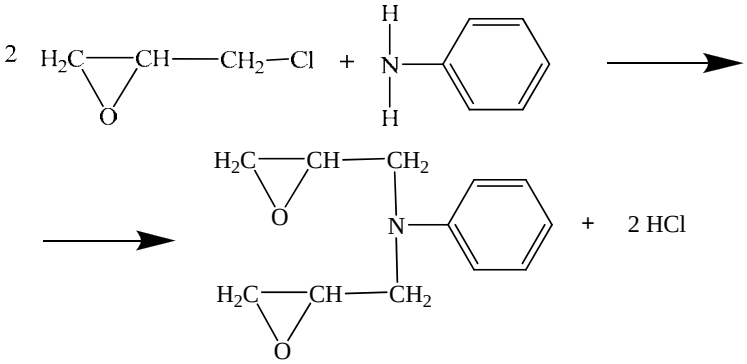
Introduction. Lead is known as a toxic metal that accumulates in the human body throughout the lifetime [1]. The World Health Organization (WHO) has established the maximum allowable limit of 0.01 mg/l for lead in drinking water [2]. Therefore, highly sensitive determination methods of trace lead in environmental samples need to be established and contamination occurs industrial activities such as mining, electricity generation, sewage application, fertilization and petrochemical. Although some of them play important roles in biological function, they are likely to have a potential to destroy ecosystems and human health through the food chain [3-5]. The US Environmental Protection Agency (USEPA) priority list regards Pb pollution as one of the top 20 pollutants. Therefore, the possibility of reducing its contamination must be taken into consideration. Due to the fact that heavy metals are non-biodegradable, they are contained in the soil continual [6]. So it is extremely important to search an environmentally way to harness the environmental pollution of heavy metal, and then reduce the deteriorating effect of heavy metals to the environment [7]. Traditional physical and chemical treatments effective in some cases. The drawback of these methods are that they expensive, disruptive, and impractical under natural environmental conditions. Therefore, ion exchange can be used as a relatively new, economical and highly effective technology to solve the heavy metal problems and restore the fertility of soil. Sorption is also the most advantageous and most promising procedure for purifying and separating substances. The sorbents should be sufficiently selective, exhibit high sorption ability, and be resistant to high temperatures [8, 9].

This study deals with the physicochemical properties of polyfunctional anion exchangers based on aromatic hydrocarbons, epichlorohydrin and polyethyleneimine in relation to lead (II) ions onto them.

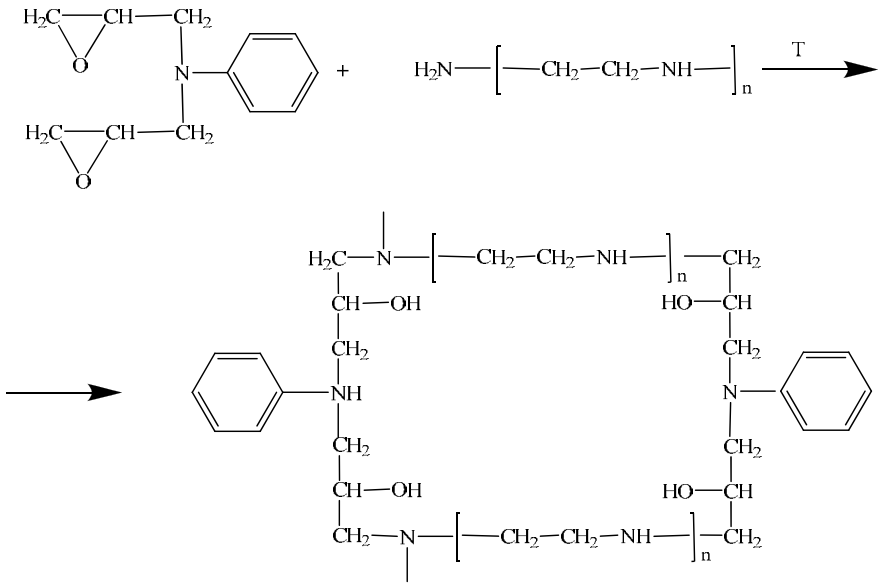
EXPERIMENTAL PART

Epoxy amine was synthesized from aniline (A) and epichlorohydrin (ECH). Polyfunctional anion exchanger A–ECH–PEPA was prepared by condensation of the epoxy amines with polyethylenepolyamine (PEPA).

Glycidyl amine derivatives (epoxy amines) was synthesized in the first step from A and ECH in the presence of NaOH (50°C, 6 h).



In the second step, the condensation of the epoxy amines with PEPA was performed in a dimethylformamide (DMF) solution at different molar ratios of the components at 60– 65°C for 5–6 h, after which the reaction mass was cured at 100°C for 16–24 h. The optimum conditions for preparing the ion-exchange materials were found previously.



The composition and chemical structure of the anion exchanger was studied by IR spectroscopy with a Nicolet 5700 Fourier IR spectrometer (Thermo Electron Corporation, the United States) and by elemental analysis with a CHN628 analyzer (LECO, the United States).

As seen from figure 1, in IR spectra, characteristic bands (cm^{-1}) of epoxy groups (810–920, 1250, 3000–3010) are absent, but N–H bending (1599–1600) and C–N stretching (1020–1220) vibration bands of amino groups appear, suggesting the occurrence of a chemical reaction of aniline diglycidyl derivative with polyamine. The absorption at 1502–1504, caused by stretching vibrations of the benzene ring, confirms the presence of aromatic fragments in the structure of the anion exchangers [10].

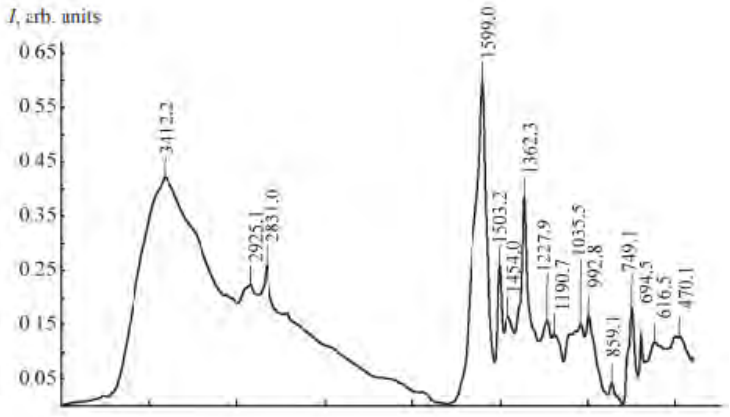
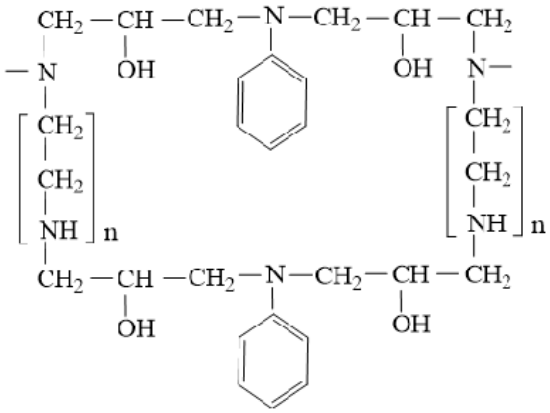


Figure 1 – IR spectra of anion exchanger A–ECH–PEPA.
(I) Intensity and (ν) wavenumber

The elemental composition of the anion exchanger A–ECH–PEPA (found/calculated, %) is as follows: C 74.23/73.84, H 16.32/16.48, N 5.76/5.50, O 3.69/4.18.

The results of chemical and spectroscopic analysis of the synthesized polymers suggests the following structure:



The physicochemical characteristics of the synthesized anion exchanger is given in the table 1.

Table 1 – Physicochemical properties of the synthesized anion exchanger

Anion exchanger	SEC_{HCl}, mg-equiv/g	V_{sp}, ml/g	Chemical stability in solutions, %			Thermal stability in water, %
			5 N H_2SO_4	5 N NaOH	10% H_2O_2	
A–ECH–PEPA	3,03	4,2	89,9	91,4	70,0	91,8

Sorption of lead (II) ions onto A–ECH– PEPA ion exchanger in the OH form was studied in batch experiments under the following conditions: sorbent : solution ratio 1 : 400, room temperature (20 ± 2°C), concentration of lead ions in $Pb(NO_3)_2$ solutions from 0.227 to 2.072 g/l, pH 1.1–5.8 (adjusted by adding 5 N HNO_3). The pH values were measured with a pH-150 MI pH meter with an accuracy of ±0.05 pH unit. The sorbent–solution contact time was from 0.5 h to 7 days. Model solutions were prepared using chemically pure grade $Pb(NO_3)_2$.

SC was calculated from the difference between the initial and equilibrium concentrations of the solutions, which were determined by classical polarography in 0.5 M NH_4Cl supporting electrolyte from the Pb (II) reduction wave ($E_{1/2}$ = −0.46 V). The polarograms were recorded with a PU-1 universal polarograph with an accuracy of ±0.5% in a temperature-controlled cell at 25±0.5°C using a dropping mercury electrode. Oxygen was removed from the solutions by argon bubbling for 5 min. A saturated calomel electrode was used as a reference electrode. The conditions of our sorption experiments (sorbent : solution ratio, concentration and pH of molybdenum-containing model solutions, contact time) were close to those of the industrial processes.

RESULTS AND DISCUSSION

To use ion exchangers in the practice, it is necessary to study how the sorption of metal ions depends on the process conditions. To determine the optimum parameters of the sorption, we studied the infl uence exerted on the sorption of lead (II) ions by the concentration and pH of $Pb(NO_3)_2$ solutions and by the time of their contact with the ion exchanger (figures 2–4).

From figure 2, can be seen the isotherm of sorption Pb^{2+} ions and the SC anion exchanger is represented, and show increase of SC with the content of lead ions in solutions. The rise of the curve at their small equilibrium concentrations indicates that the anion exchanger extracts lead (II) ions with sufficient completeness. The recovery rate reaches at 91% and maximum SC of A–ECH– PEPA anion exchanger reaches at 228 mg/g.

One of the most important factors controlling sorption of metal ions from solutions is pH of the solution. The pH infl uences both the metal speciation in the solution and the state of the ionogenic groups [11]. The dependence of the sorption capacity of the anion exchanger for lead ions on the acidity of $Pb(NO_3)_2$

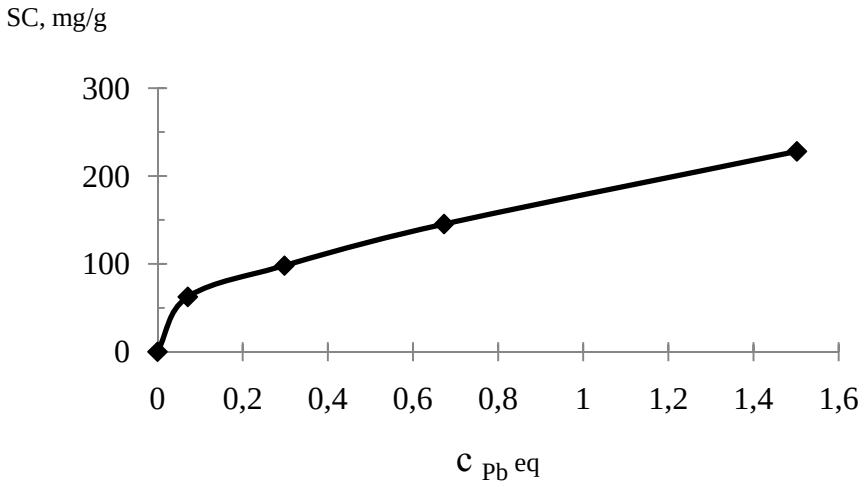


Figure 2 – Isotherm of Pb^{2+} sorption onto A–ECH–PEPA anion exchanger. Contact time 7 days, pH 5.8. SC – sorption capacity (mg/g), C_{Pb} eq – equilibrium concentration (g/L)

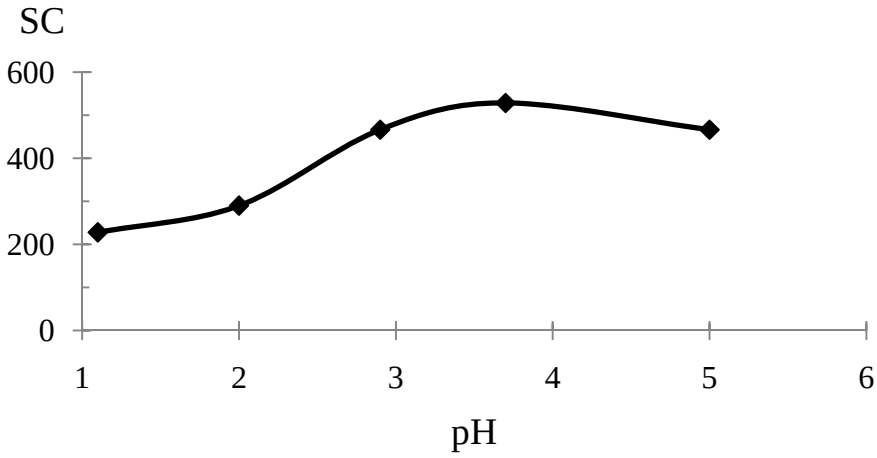


Figure 3 – Dependence sorption capacity of A–ECH–PEPA anion exchanger on the acidity of solution $Pb(NO_3)_2$. C_{Pb} = 2.072 g/L; contact time 7 days

solutions is shown in figure 3. As can be seen, the optimum pH for the uptake of lead ions is 3.7. Under these conditions, the uptake of Pb (II) ions and SC of A–ECH–PEPA anion exchanger reach maximal values and SC is 528.4 mg Mo/g.

Figure 4 shows the lead ions sorption isotherm for A–ECH–PEPA anion exchanger. The equilibrium between the resins and solution containing 2.072 g/l Pb and having pH 3.7 is attained in 1 h, and the SC of the A–ECH–PEPA anion exchanger is 528.4 mg/g.

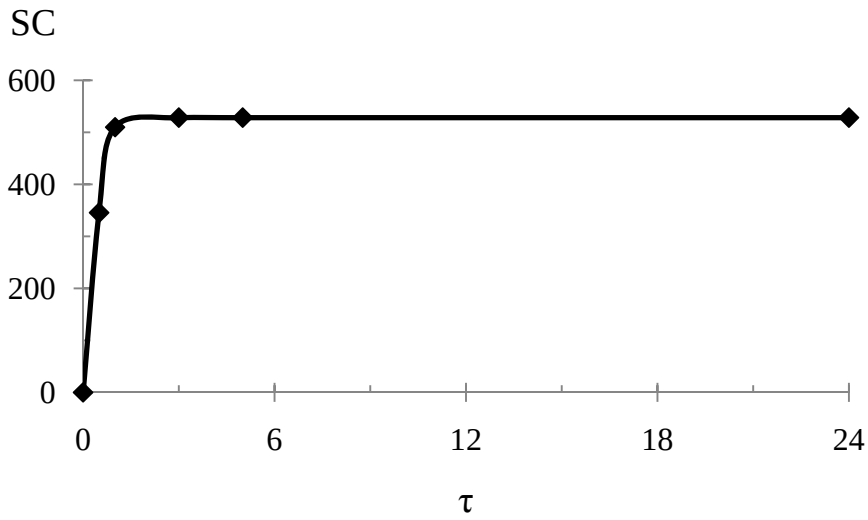


Figure 4 – Dependence sorption capacity of A–ECH– PEPA anion exchanger on the duration contact time (τ) of resin with $Pb(NO_3)_2$ solution. C_{Pb} = 2.072 g/L; pH 3.7

Conclusion. Thus, the sorption ability of polyfunctional anion exchanger based on aniline, epichlorohydrin and polyethilenpolyamine with respect to lead ions is studied. It is established that it possesses unique sorption properties with respect to Pb^{2+} ions. It is shown that the acidity of the medium has a significant effect on the sorption of lead ions. Thanks to high sorption and kinetic properties, the investigated anion exchanger can be recommended for wastewater treatment of hydrometallurgical production from lead ions.

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Резюме

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АНИЛИН, ЭПИХЛОРГИДРИН ЖӘНЕ ПОЛИЭТИЛЕНПОЛИАМИН НЕГІЗІНДЕ АЛЫНҒАН АНИОНИТПЕН ҚОРҒАСЫН (II) ИОНЫНЫҢ СОРБЦИЯСЫН ЗЕРТТЕУ

Анилин, эпихлоргидрин және полиэтиленполиамин негізіндегі полифункционалды анионитпен классикалық поляграфия әдісі арқылы қорғасын ионының сорбциясы зерттелді. Ерітінді концентрациясымен pH көрсеткіші қорғасын (II) ионын бөліп алу қасиетін зерттеу барысында, ерітіндідегі Pb концентрациясының көбеюімен иониттің сорбциялық сыйымдылығы артатындығын көрсетті. Анионитің оңтайлы pH мәні 3.7, тең болған жағдайда сіңіру сыйымдылығы 528.4 мг Pb/г құрайды.

Түйін сөздер: сорбция, қорғасын иондары, анион алмастырғыш, сорбциялық сыйымдылық.

Резюме

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ИЗУЧЕНИЕ СОРБЦИОННОЙ СПОСОБНОСТИ АНИОНИТА, ПОЛУЧЕННОГО НА ОСНОВЕ АНИЛИНА, ЭПИХЛОРГИДРИНА И ПОЛИЭТИЛЕНПОЛИАМИНА, ПО ИОНАМ СВИНЦА

Синтезирован полифункциональный анионообменник на основе анилина, эпихлоргидрина и полиэтиленполиамина; были изучены состав и структура анионита методами ИК-спектроскопии и элементного анализа. Исследован процесс сорбции свинца методом классической полярографии и найдены зависимости сорбции ионов Pb^{2+} в статическом режиме от кислотности растворов, концентрации ионов металлов и продолжительности контакта ионитов с раствором $Pb(NO_3)_2$. Установлено, что данный ионообменник обладает высокими сорбционными свойствами по отношению к ионам свинца. Научная новизна исследования состоит в том, что впервые была изучена сорбционная зависимость по отношению к ионам Pb^{2+} синтезированным ионитом. Практическая значимость данной работы заключается в том, что разработанный сорбент с повышенной сорбционной способностью может успешно решить проблемы очистки технологических стоков цветной металлургии от ионов свинца (II).

Ключевые слова: сорбция, ионы свинца, анионит, сорбционная емкость.