Physicochemical and Sorption Properties of Anionites Based on Aromatic Amines, Epichlorohydrin and Polyethylenimine with Regard to Strontium (II) Ions

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Abstract
Multifunctional anion exchangers based on aromatic amines, epichlorohydrin and polyethylenimine have been synthesized. Their composition, structure, and thermal stability have been studied using IR spectroscopy, elemental and thermogravimetric analyses. Extraction of strontium ions has been studied using classical polarography, and sorption of strontium (II) ions in static regime has been determined as a function of solution acidity, metal ion concentration, and contact duration of ionites with SrCl₂ solution. It has been established that the obtained ion exchangers are characterized by high sorption properties with regard to strontium ions. The novelty of these studies is that the sorption dependence of synthesized ionites with regard to Sr²⁺ ions has been studied for the first time. The practical importance of this work is the development of anion exchangers with higher extractability, which could successfully solve the issues of elimination of strontium (II) ions from process wastes of nonferrous metallurgy.

Keywords: Sorption, Strontium, Sorption capacity, Anion exchanger, Extraction

1 Introduction
Development of nuclear power engineering and accompanying industries results in contamination of environmental objects by radioactive metal ions, which poses a health risk, since long-living radionuclides tend to accumulation, can easily be transferred to high distances and quite often participate in the biological cycle [1]. In this regard it is very important to develop efficient sorbents produced by simple and inexpensive process as well as characterized by high capacity and selectivity with regard to extracted cations and reliably holding radionuclides extracted from contaminated solutions in the form suitable for long-term storage, processing, or disposal [2].

Strontium is one of the main contaminants of radioactive waste waters widely occurring in nuclear fuel, medicinal and industrial radioactive wastes [3, 4]. It is well known that strontium is characterized by long half-life, high solubility, and high bioaccessibility. After penetration with contaminated food into organism strontium will accumulate in bones and marrow, which can cause cancer of adjacent tissues and leukemia. Therefore, systematic and efficient methods of elimination are especially important to provide steady development of humans and environmental protection [3–6].

Sorption is one of the most efficient approaches to treatment of wastes with heavy metals due to its low cost, high efficiency and readily recovered sorbents [7]. A significant number of publications are devoted to studying the features of separation and extraction of strontium and its purification from the impurities using anionites of various structure [3, 8–10]. In [3], the authors studied the sorption capacity of new adsorbent obtained from almonds in relation to strontium ions, where the sorption capacity (SC) reached 11.45 mg·g⁻¹ at pH = 10.8. At strontium concentration of 20 mg·l⁻¹ and pH = 7.0 ± 0.1 of the solution, the SC values of the modified ion exchangers approached the value of 1.6 mg·g⁻¹ [4]. In [5], the authors analyzed the environmental conditions impact on the sorption behavior of Sr (II) and identified that the Sr (II) sorption was greatly affected by ionic strength at pH <9.5, and no effect at pH> 9.5 was found. This fact indicated that in the mechanism of Sr (II) sorption, outer-sphere surface complexation or ion exchange at low pH prevailed; at pH = 7.0 ± 0.1 and cS₀ = 15 mg·l⁻¹, the SC value reached 20 mg·g⁻¹. In [6], the authors found that the SC of complexing polymeric sorbents based on EDE-10P and chlorine-containing quinones was 358.2 - 420.4 mg·g⁻¹ at pH = 4.6, cS₀ = 1.926 mg·l⁻¹. Thus, in [8] it was established that maximum SC of polymer complexing sorbents of various structure with regard to strontium ions was 50 mg·g⁻¹ at pH of solution from 2.2 to 7.0. Thus, certain interest is attracted to analysis of strontium ions sorption on specially produced anionites characterized by high SC and containing

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active groups in their structure. This work is aimed at analysis of physicochemical and sorption properties of multifunctional anionites based on epoxy derivatives of aromatic amines and polyethylenimine with regard to strontium (II) ions.

2 Methods

On the basis of aniline (A) or benzylamine (BA) and epichlorohydrin (ECH) we synthesized epoxy amines, and then, by condensing them with polyethylenimine (PEI), multifunctional anionites A–ECH–PEI and BA–ECH–PEI [11]. At first, using A or BA and ECH in the presence of caustic soda at 50°C for 6 h, glycidyl derivatives of amines (epoxy amines) were synthesized. Then, their polycondensation with PEI was carried out in dimethylformamide (DMFA) solution at various ratios, 60–65°C for 5–6 h, then the reacted mass was solidified at 100°C for 16–24 h. Composition and chemical structure of the anionites were analyzed by IR spectroscopy using a Nicolet 5700 Fourier spectrometer (Thermo Electron Corporation, USA) and by elemental analysis using a CHN628 instrument (LECO, USA). As can be seen in Fig. 1, a, b , the IR spectra of A–ECH–PEI and BA–ECH–PEI anionites are very similar, which probably could be attributed to close chemical structure. These spectra do not contain characteristic bands (cm⁻¹) of epoxy groups (810–920; 1,250; 3,000–3,010), there appear bands of N–H bending vibrations (1,599–1,600) and C–N stretching vibrations (1,020–1,220) of amine group bonds, which evidences chemical interaction of diglycidyl derivatives of A and BA with PEI. The frequency at 3,500 characterizes occurrence of hydroxyl groups. Absorption in the 1,502–1,504 area, stipulated by stretching vibrations of benzene ring, confirms existence of aromatic fragments in the anionite structure [12]. The elemental composition of anionites (detected/predicted), % for A–ECH–PEI: C – 73.32/73.86; H – 17.60/17.34; N – 5.89/5.60; O – 3.19/3.20; and for BA–ECH–PEI: C – 70.72/70.92; H – 17.61/17.48; N – 7.81/8.09; O – 3.86/3.51. On the basis of chemical and spectral analyses, the structure of synthesized polymers can be presented as follows (Figure 2):

![Figure 1: IR spectra of BA–ECH–PEI (a) and A–ECH–PEI (b). I – intensity, ν – wave number (cm⁻¹)](image)

![Figure 2: Structures of synthesized polymers](image)
The morphology and chemical structure of polymer matrix, as well as the structure of surface of the given anionites are similar to that studied previously and described in [13]. Thermal resistance of anionites in OH form was studied by thermogravimetric analysis (TGA). Thermograms were obtained using TGA/DSC1 thermogravimetric analyzer (Mettler Toledo, Switzerland) in air in the range of 20–600°C at heating rate of 10°C/min. In order to determine static exchange capacity (SEC) of anionites using 0.1N HCl solution, a sample of anionite in the OH form from in the amount of 1 g on dry basis measured with the accuracy of 0.0002 g was poured with 100 ml of 0.1N titrated solution of hydrochloric acid in 250 ml flat bottom flask and sealed. Reaching equilibrium (24 h), 25 ml of filtrate was titrated by 0.1N solution of sodium hydroxide in the presence of three droplets of methyl red until pink color changed into yellow. The concentration of functional groups in polymer phase corresponding to the ionite SEC (mg eq·g⁻¹) was calculated as follows: SEC = (100 – 4V)/10 P, where V was the exact volume of 0.1N solution of sodium hydroxide consumed for titration (ml); P was the ionite sample on dry basis (g). In order to determine the volume occupied by mass unit of dry ionite after swelling in water, a sample of about 10 g was placed into cylinder and poured with 70 ml of water. The cylinder was tightly sealed and agitated up to complete wetting of lower layers of ionite and held in horizontal position for 12 h. Then the cylinder was positioned vertically, water was refilled to 100 ml, and compacted to constant volume by tapping cylinder bottom against wooden surface. After the compaction, the volume occupied by ionite was measured. The specific volume of swelled ionite (Vₛ, ml·g⁻¹) was determined as follows: Vₛ = V/G, where V was the volume of swelled ionite, ml; G was the sample of dry ionite, g.

In order to determine chemical resistance of the ionites with regard to solutions of acids and alkalis, two ionite samples, 0.1 g on dry basis each, were placed into 250 ml round bottom reflux flask. One sample was poured with 100ml of 5N solution of sulfuric acid, the other sample was poured with 100 ml of 5N solution of sodium hydroxide. The content of the flasks was held for 30 min on boiling water bath. Then the mixture was cooled in air to ambient temperature and the ionite was separated by filtration. The anionite was converted into hydroxyl form when air to ambient temperature and the ionite was separated by filtration. The anionite was converted into hydroxyl form when

Table 1: Main physicochemical properties of the synthesized anionites

<table>
<thead>
<tr>
<th>Anionites based on</th>
<th>SEC_{HCl} (mg eq·g⁻¹)</th>
<th>Vₛ (ml·g⁻¹)</th>
<th>Chemical resistance in solutions, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A–ECH–PEI</td>
<td>4.83</td>
<td>4.5</td>
<td>92.5, 94.9, 70.1</td>
</tr>
<tr>
<td>BA–ECH–PEI</td>
<td>8.95</td>
<td>5.7</td>
<td>97.9, 98.7, 72.0</td>
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</table>

Stringent requirements to thermal resistance are set to ion exchangers intended for long-term operation at higher temperatures [16]. The thermal resistance is an important property of polymer materials allowing to detect destruction processes at higher temperatures, leading to impairment of operational properties and environmental pollutions. Destruction of ionites in dry state allows better estimation of the thermal stability of matrix and ionogenic groups and determination of initial temperatures of destruction of these structural elements. Thermograms of A–ECH–PEI and BA–ECH–PEI are illustrated in Figure 3. The use of TGA allows to determine the weight loss of ionite during thermal destruction. The results of TGA of anionites based on epoxy derivatives of aromatic amines and polyethylenimine are summarized in Table 2. The TGA curves (Fig. 1, a, b), the shapes of which are identical, illustrate that the initial temperature of their destruction, after which the weight loss is significant, is 260°C for A–ECH–PEI and 280°C for BA–ECH–PEI. These temperatures on the curves of differential scanning calorimetry correspond to occurrence of exothermal maximums, which can be probably attributed to heat evolution upon further structuring of ionites, then the polymer matrix is destructed. Herewith, their weight loss is 8%. The commercial sorbent EDE-10p upon heating to 100–200°C loses more than 20% of its weight [17].
Figure 3: Thermogravimetric analysis of anionites based on A–ECH–PEI (a) and BA–ECH–PEI (b). T is the temperature (ºC), DSC is the thermal capacity dependence (J·10^3·mg⁻¹), TG is the weight loss (%)

Table 2: Weight loss of A–ECH–PEI and BA–ECH–PEI at various temperatures

<table>
<thead>
<tr>
<th>T, °C</th>
<th>Weight loss, %</th>
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<tr>
<td></td>
<td>A–ECH–PEI</td>
</tr>
<tr>
<td>100</td>
<td>5</td>
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<tr>
<td>200</td>
<td>8</td>
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<td>300</td>
<td>20</td>
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<td>350</td>
<td>55</td>
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<tr>
<td>400</td>
<td>90</td>
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</table>

It has been established that these anion exchangers are characterized by sufficiently high thermal resistance. The structure of their polymer matrix exerts significant effect on thermal stability of anionites, which at 300–350°C decreases as follows: A–ECH–PEI > BA–ECH–PEI

Figure 4: Sorption isotherms of Sr²⁺ ions by A–ECH–PEI (1) and BA–ECH–PEI (2). Duration of contact is 7 days; pH = 1.0; c_{Sr eq} is the equilibrium concentration; SC is the sorption capacity (mg·g⁻¹); c_{Sr eq} is the equilibrium concentration (g·l⁻¹)

It can be seen in Figure 3 illustrating the sorption isotherms of Sr²⁺ ions that the anionite SC increases with the content of strontium ions in solutions. The curve rising at low equilibrium concentrations evidences that these anionites extract strontium (II) ions with sufficient completeness. Herewith, the extraction rate reaches 83%. The sorption capacity of BA–ECH–PEI upon extraction of Sr²⁺ ions is higher in comparison with A–ECH–PEI, their SC is 507.7 mg·g⁻¹ and 491.36 mg·g⁻¹, respectively. One of the main factors upon extraction of metal ions from solution is the medium acidity, which influences both the form of the considered ion in solution, and the state of ionogenic groups [11]. It can be seen in Fig. 5 illustrating sorption capacity of anionites with regard to lead ions as a function of acidity of SrCl₂ solutions that the optimum pH for their extraction is 1.0. Under such conditions, the absorption of strontium (II) ions is maximum.

It also follows from Figure 5 that the sorption capacity of ionites is determined mainly by the ionic state of strontium in the solution. The acidity range corresponding to maximum SC, is stipulated, on the one hand, by the ratio of the interaction energy of metal cations and hydrogen with active polymer centers, and on the other hand, by pH values determining the started formation of hydroxide deposits and main metal salts. Further decrease in the solution acidity leads to deposition of strontium hydroxide. The mentioned facts evidence the necessity to achieve certain pH of acidity of purified water. Figure 6 illustrates the isotherms of sorption of strontium (II) ions by BA–ECH–PEI and A–ECH–PEI. Equilibrium state between the ionites and the solution...
containing 2.015 g·l⁻¹ strontium and having pH 1.0 is reached for BA–ECH–PEI in 1 h, and for A–ECH–PEI – in 3 h. Herewith, the SC of BA–ECH–PEI is 507.7, and of A–ECH–PEI is 491.36 mg·g⁻¹.

![Graph](image)

Figure 6: Sorption of strontium (II) ions by BA–ECH–PEI (I) and A–ECH–PEI (2) as a function of duration of its contact with SrCl₂ solution (c₀ = 2.015 g·l⁻¹, pH = 1.0)

It has been established in [8] that the polymer complexing sorbents of various structure, which contain –CH₂–NH– ion exchanging groups, more completely extract Sr²⁺ ions in acid mediums. The maximum performance of the sorbent, used in [18] for extraction of strontium ions, is 40.6 mg·g⁻¹. On the basis of experimental data, it has been established that the most promising for practical application are the sorbents with the best kinetic properties and maximum SC, which is 3.5–50.0 mg·g⁻¹, that is, by 50 times less than that of the synthesized ion exchangers characterized by the best kinetic properties.

### 4 Conclusions

1. The main physicochemical and thermal properties of the obtained sorbents have been studied. Their composition and structure are detected.
2. Sorption capacity of the synthesized anionites based on epoxy derivatives of aromatic amines and polyethylenimine with regard to strontium (II) ions has been studied. It has been established that they are characterized by high affinity to Sr²⁺ ions upon their extraction from individual model SrCl₂ solutions.
3. It has been determined that the medium acidity in the range of pH = 1.0–6.3 exerts influence on sorption of strontium (II) ions. Maximum sorption is observed at pH = 1.0.
4. The obtained BA–ECH–PEI and A–ECH–PEI anionites are characterized by superior kinetic properties. Complete chemical equilibrium is achieved in 1 and 3 h, respectively.

### Findings

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### Conflict of interests

The authors confirm that the submitted data do not contain conflict of interest.

### Authors’ contribution

All authors of this study have a complete contribution for data collection, data analyses and manuscript writing.

### References


