

SYNTHESIS AND STUDYING OF NITROGEN AND OXYGEN-CONTAINING COMPLEXING SORBENTS DURING THE SORPTION OF SOME D-METALS

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Abstract. *The purpose of the work is the synthesis and study of sorbents that form stable complex compounds with high sorption properties for the concentration and separation of various rare and non-ferrous metals during wastewater treatment of industrial and hydrometallurgical enterprises. To achieve this goal, a polymer ligand containing nitrogen and oxygen based on aminoacetic acid, epoxy resin and polyethylene polyamine was synthesized and studied. The article analyzes the surface morphology and elemental analysis of a polymer ligand obtained by covalent addition of an amino acid to an epoxy matrix, static and dynamic exchange. Using IR spectroscopy methods, the structure of the resulting sorbent was established and proposed. The structural and sorption properties of the sorbent were determined by the Brunauer, Emmett and Teller (BET) method, based on the absorption of water vapor at low pressure, and it was found that the resulting sorbent is mesoporous and has high sorption properties. When studying the static exchange ability of sorbents synthesized on the basis of amino acids, it was found that the sorbent obtained on the basis of aminoacetic acid has the greatest ability.*

Keywords: *covalent immobilized ligand, aminoacetic acid, microstructure, scanning electron microscopy, structural sorption properties*

1. Introduction. Around the world, a number of industrial enterprises discharge wastewater of various concentrations into the environment. This, of course, has a negative impact on any acceptable part of the environment. Of great importance is the synthesis and study of sorbents that form complex compounds with high sorption properties for the concentration and separation of various rare and non-ferrous metals in the treatment of industrial wastewater and hydrometallurgical enterprises. Ion exchangers have acquired particular importance in the processes of neutralizing wastewater from metal salts, phenol and its derivatives, cyanide, arsenic, and sulfur compounds.

Ion-exchange polyion exchangers are used in all areas of industry. They are widely used in thermal and nuclear power plants for water softening, in chemical plants for water desalination, hydrometallurgy to isolate rare, valuable, and heavy metals from process solutions, as well as to reduce environmental damage, to clean wastewater from poisonous ions (1). Ions of heavy metals such as nickel, cobalt, zinc, chromium, copper, lead, and cadmium cause serious environmental problems for animals, plants, and humans due to their extreme toxicity [2]. The reactivity of these elements is determined by the shape and arrangement of the electron shells of the atom, affecting their tendency to complex formation and, thus, contribute to physiological and biochemical activity [3]. Heavy metals are generally toxic in nature and are not easily degraded by simple biological treatment, like other organic materials [4,5]. The removal of these contaminants from discharged water is a necessary step in wastewater treatment processes[6]. Extensive work is being done in this area to remove toxic metals using a range of advanced technologies such as polymer-

enhanced ultrafiltration [7], flocculation [8], adsorption [9-11], ion exchange [12], and various membrane separation technologies [13,14]. Of great interest is the adsorption process, a surface phenomenon in which a multi-component liquid (gas or liquid) mixture is attracted to the surface of a solid adsorbent and forms bonds through physical or chemical bonds, the most effective, promising, and widely used fundamental approach in wastewater treatment processes is recognized [15], mainly depends on its simplicity, economically viable, technically feasible and socially acceptable [16]. There are also many theories for evaluating the ion exchange process [17,18]. In the present work [19], the use of a new environmentally friendly amino polycarboxylate chelating agent of the trisodium salt methyl glycine diacetic acid (MGDA) for the inactivation of various metal ions by complexation in microporous anion exchangers was considered, and the sorbents were tested. And in this review [20], the modern development in the field of application of biosorbents for water purification with an emphasis on adsorption is critically assessed.

In the last few decades have studied a sorbent based on o-aminobenzoic acid, epoxy resin, and polyethylene polyamine [21]. In addition, an ion exchanger based on guanidine, epoxymol, and polyethylene polyamine was synthesized [22], the physicochemical properties of a chelating polymer sorbent based on urea, formaldehyde, and amino acetic acid were studied [23] and obtained by sulfonation of a polymer synthesized by polycondensation of bottom waste from the Shurtan gas chemical complex (ShGChC, Uzbekistan) with furfural [24]. The sorption properties of new types of fibrous sorbents modified with hydroxylamine, ethylenediamine, or hexamethylenediamine were studied [25]. In this paper [26], some features of the sorption of a neutral aromatic amino acid (phenylalanine) by heterogeneous ion exchange membranes from propped surfaces are discussed. In [27–28], the results of a study of the adsorption characteristics of a polymer matrix modified with new-generation chelating agents are presented.

2. Experimental Part

Reagents of the brand “pure” and “chemically pure” were used in the work. Reagent solutions were prepared by dissolving an accurate sample in a known volume of solvents..

2.1. Material and Methods

To prepare the material, the following chemicals and equipment are required: aminoacetic acid, epoxy resin (ED-20), polyethylene polyamine, distilled water, a thermostable glass, a magnetic stirrer, and an oven.

IR spectroscopic studies have been carried out on an IRTracer-100 SHIMADZU infrared Fourier IR spectrometer (Japan) (range 400–4000 cm^{-1} , resolution 4 cm^{-1}) by the powder method. Morphological studies of the surface of the samples were carried out using a scanning electron microscope SEM - EVO MA 10 (Zeiss, Germany). To determine the elemental composition, energy-dispersive X-ray spectroscopy (EDS) was carried out in a local area, in which it was determined using an energy-dispersive elemental analyzer brand - Oxford Instrument - Aztec Energy Advanced X-act SDD. Thermoanalytical studies were carried out on a Netzsch Simultaneous Analyzer STA 409 PG instrument (Germany), with a K-type thermocouple (Low RG Silver) and aluminum crucibles. The surface-structural properties of the obtained sorbents were studied by measuring the sorbents on a McBen-Bakr balance as a result of an increase in mass during the absorption of gaseous bromine at a temperature of 20°C and reduced pressure. The results obtained were calculated by the BET method [29].

3. Results and Discussion.

3.1. Study of the Physical and Chemical Properties of the Synthesized sorbent. *Infrared spectroscopic analysis of the synthesized sorbent.*

IR spectroscopy was used to establish the structure of the obtained ionite. Here are the absorption bands in the IR spectra: $\nu(\text{NH})$ 3408 cm^{-1} , $\nu_s(\text{CH}_2)$ 2927 cm^{-1} , $\nu_s(\text{O-CH}_3)$ 2852 cm^{-1} , $\nu(\text{C}_6\text{H}_5-)$ 1606 cm^{-1} , $\nu(\text{CH})$ 1456 cm^{-1} , $\nu(\text{NH})+\nu(\text{CN})$ 1296 cm^{-1} . In the spectra of the synthesized ion exchanger, there are no characteristic frequencies (cm^{-1}) of epoxy groups (810-950, 1250, 3000-3050), which indicates their chemical transformation. On the other hand, bands of bending vibrations N-H (1456) and stretching vibrations C-N (1236) of amino group bonds appear (Fig. 1).

As a result of the synthesis carried out by us, by polycondensation of epoxy resin, aminoacetic acid, and polyethylene polyamine at a molar ratio of 1.5:1:0.05, an EAAP ion exchanger was obtained, which has good prospects in terms of its exchange capacity. As can be seen from the structure of the product obtained as a result of the modification, the sorbent contains an amino and carboxyl group, which gives the sorbent, which has both basic and acidic properties, a polyampholytic character. The formula of the resulting polyampholyte can be represented as follows (Fig. 2).

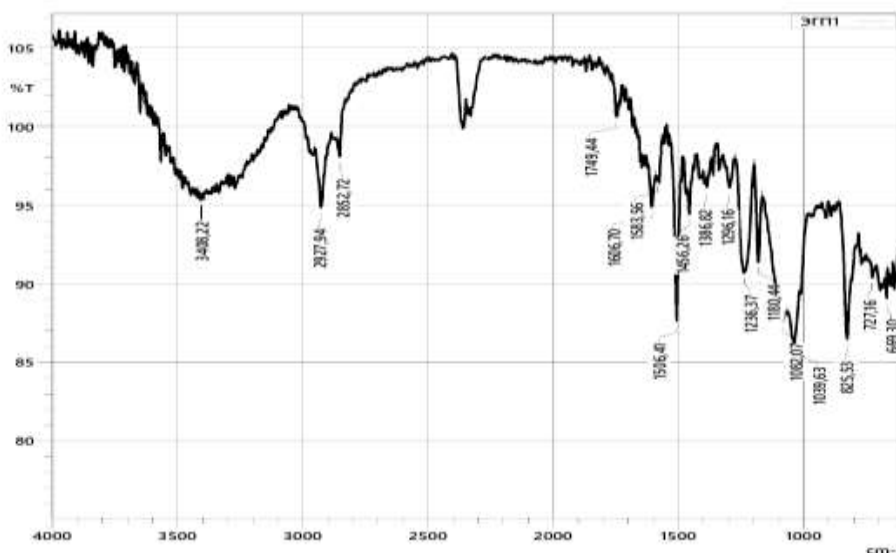


Figure 1. IR spectrum of a polymeric ligand.

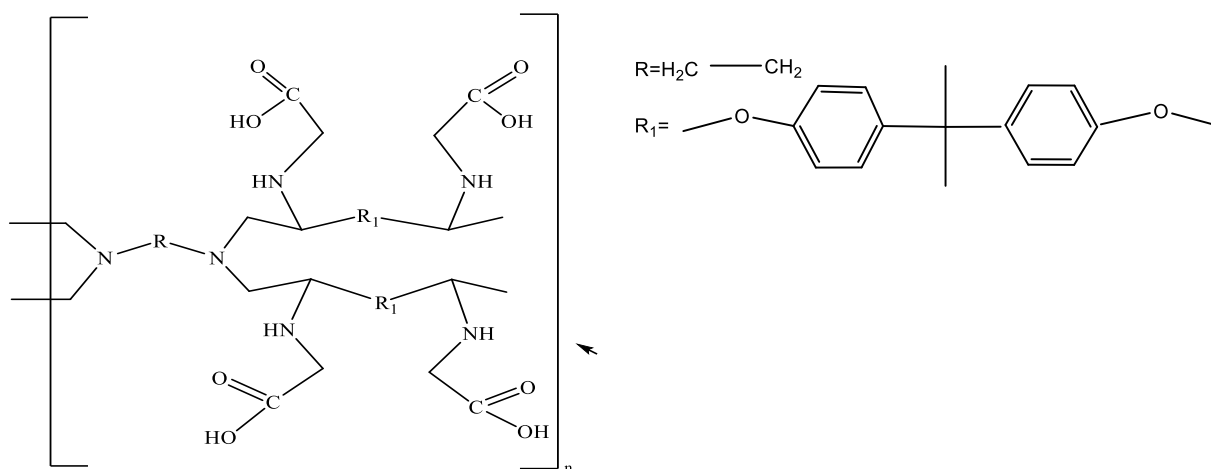


Figure 2. The structure of the resulting polymeric ligand.

The influence of the molar ratio of the initial substances on the composition and sorption properties of sorbents synthesized on the basis of amino acids has been studied. Among the obtained polymeric ligands, it was found that the sorbent based on aminoacetic acid has the highest static and dynamic exchange capacity (Table 1). In table. 2 shows the ion-exchange capacities of complex compounds of some d-metal ions (Cu^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Ag^{+}) with a complexing sorbent based on EAAP.

Table 1.

Influence of molar ratios of initial substances on the composition and physicochemical properties of synthesized sorbents

| № | Sorbents | | The ratio mol | *SEC, 0,1N solution, mg-ekv/g, CuSO_4 pH=4,2 | *DEC |
|----------|-----------------|---|----------------------|---|-------------|
| | EAAP | Epoxyamol ED-20, aminoacetic acid, PEPA | | 13,3 | |
| | OABA-EP | Ortho-aminobenzoic acid, ED-20, PEPA | 0,7:0,7:0,6 | 1 1 | |
| | PABA-EP | Para-aminobenzoic acid, ED-20, PEPA | | 8,33 | |

Note: *SEC – static exchange capacity, mg-eq/g, *DEC - dynamic exchange capacity, g/dm³

Table 2.

Sorption studies of the polymeric ligand synthesized on the basis of aminoacetic acid

| Sorbents | Salts in which the sorption process is studied | Volume 0,1 N Saline solutions, ml | Weight sorbent, gr | Absorption time (hours) | Sorption mg-eq/gr |
|-----------------|---|--|---------------------------|--------------------------------|--------------------------|
| 1 | CuSO_4 | 10 | 0.03 | 24 | 13.3 |
| 2 | NiCl_2 | 10 | 0.03 | 24 | 8.8 |
| 3 | AgNO_3 | 10 | 0.03 | 24 | 5.5 |
| 4 | $\text{Co}(\text{NO}_3)_2$ | 10 | 0.03 | 24 | 7.2 |
| 5 | ZnSO_4 | 10 | 0.03 | 24 | 6.8 |

3.2. Surface morphology and elemental analysis of the synthesized polymer ligand.

Scanning electron microscopy (SEM) (photographs, elemental analysis) was used to study the microscopic structure of the immobilized polymeric ligand and the coordination compound of the EAPM sorbent with Cu^{2+} copper ions.

Figure 3 shows photographs of the microstructure of the surface of the immobilized ligand before (a) and after (b) sorption of copper (II) ions taken at 100 μm . The image shows that the surface has a heterogeneous structure, the ion exchanger has a mesoporous structure, in which spherical, slit-like pores are traced, and there are larger and smaller particles. This indicates that the resulting ligand has a sufficiently high sorption capacity (Fig. 3).

Also in Table. 3 shows the elemental analysis of the obtained ligand and its coordination compound with Cu(II).

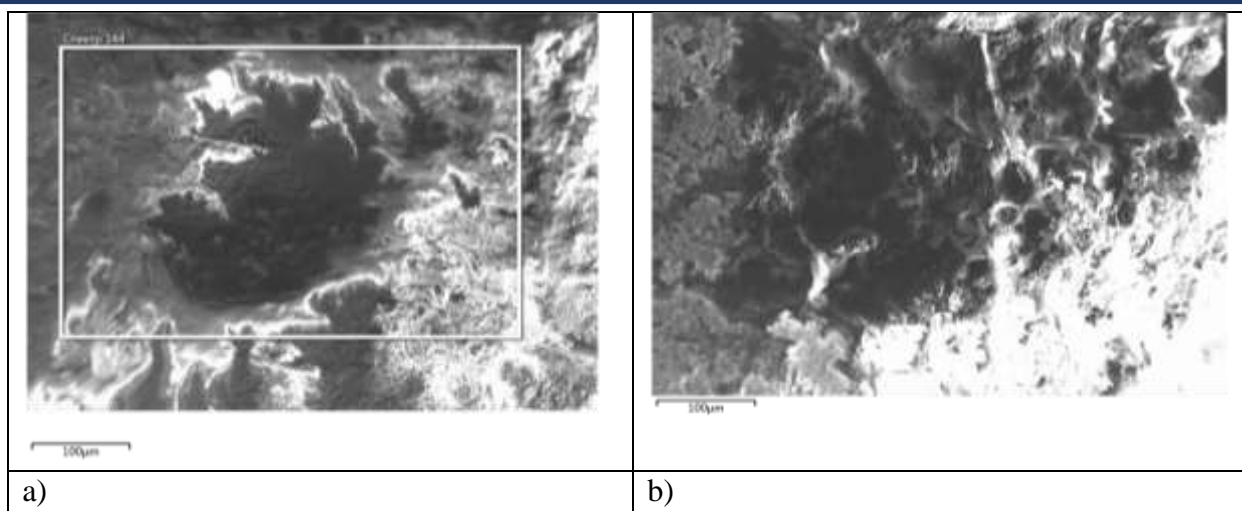


Figure 3. Scanning electron microscopic image of the polymer ligand surface before (a) and after (b) sorption of copper (II) ions.

Table 3.
Results of elemental analysis of the immobilized ligand and its complex compound with copper (II) ions

| Element | Quantity, % | Sigma weight, % | Quantity, % | Sigma weight, % |
|---------|--|-----------------|--|-----------------|
| | [C ₅₄ H ₇₂ N ₆ O ₁₂] _n | | [C ₅₄ H ₆₈ N ₆ O ₁₂ Cu ₄] _n | |
| C | 65,6 | 0,65 | 52,06 | 0,62 |
| O | 26,86 | 0,78 | 21,75 | 0,89 |
| N | 7,54 | 0,18 | 5,93 | 0,15 |
| Cu | - | | 20,26 | 0,33 |
| Total | 100,0 | | 100,0 | |

It is known that to study the structural features of polymers, their ability to sorb water vapor is studied.

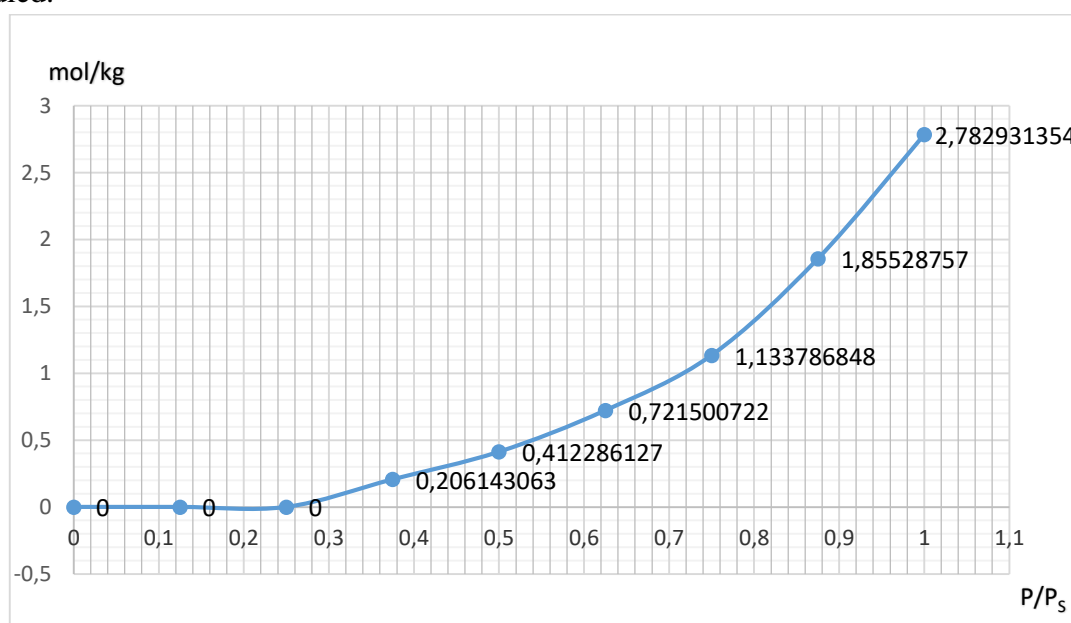


Figure 4. Water vapor isotherm at 20°C according to EAAP.

Table 4.

Structural and surface characteristics of EAAP

| № | Sorbent | Capacity of monolayers, mol/kg | Comparison surface, m ² /g | Saturation volume, l | Pore radius, Å |
|---|---------|--------------------------------|---------------------------------------|----------------------|----------------|
| 1 | EAAP | 0,122 | 7,90 | 0,05 | 126,8 |

Water vapor is an active sorbate for most polymeric materials with hydrophilic functional groups, and sorbent pores also play a role in water vapor sorption to one degree or another.

When determining the sorption characteristics of the structure, an isotherm of water absorption on the surface of the sorbent was built depending on the relative pressure (Fig. 4). Based on the results obtained, the calculated surface properties of the sample are presented in Table 4.

As can be seen from the isotherm shown in this figure (Fig. 5), the studied sorbent is mesoporous (Table 4.) and has a fairly high sorption capacity, and the sorption value increases significantly even in a small pressure field.

4. Conclusions.

Thus, polyampholyte EAUP was obtained by immobilizing aminoacetic acid in an epoxy resin matrix. It also has a high sorption capacity for non-ferrous metals due to the mesoporous surface structure. During the synthesis of sorbents, the influence of the molar ratios of the starting substances on the composition and physicochemical properties of the synthesized sorbent was studied, and the optimal synthesis conditions were determined. The composition of the resulting sorbent was determined using IR spectroscopy methods, and the microscopic structure of the synthesized polymer sorbent was studied using scanning electron microscopy (SEM) (photography, elemental analysis). Sorptive polyampholytes obtained by the proposed method are light yellow products that are stable in acidic and alkaline solutions and when heated. They can be used for the concentration and separation of various rare and non-ferrous metals during the treatment of industrial wastewater and the sorption extraction of precious and precious metals in the form of powders or in the form of fibrous materials filled with these polymers.

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