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ANALYSIS THE SURFACE OF MODIFIED LIGNIN BASED MICROSPHERES USED FOR SELENIUM ADSORPTION BY THE SEM-EDS ANALYTICAL METHOD

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Abstract

This paper presents the results of the morphological and elemental analysis of the material tested for evaluation the adsorption of selenium (Se) from water, obtained applying the SEM-EDS method. The tested material was obtained from a natural polymer - kraft lignin by the process of suspension copolymerization and additional modification with nanoparticles of iron oxide in the form of magnetite, called the A-LMS Fe_3O_4. According to the obtained morphological data, the A-LMS Fe_3O_4 material is highly porous, and the particles are irregularly spherical. The elemental analysis of material after the process of Se adsorption from water, using an EDS detector, detected the characteristic signals for Se.

Keywords: *selenium, SEM-EDS analysis, adsorption, magnetite*

1 INTRODUCTION

Selenium is a naturally occurring metalloid, which is found in low concentrations in the earth crust, water and atmosphere [1]. Selenium is unevenly distributed in the earth' crust leading to the zones with a lack of selenium and zones with an increased content. Inorganic selenium (IV) and selenium (VI) are the predominant species in the natural water resources.

The toxic effect of selenium depends on its chemical form. In its elemental form, selenium is biologically inactive, because it has a low solubility, on the other hand, inorganic compounds, such as selenium (IV) or selenium (VI) are highly toxic due to their high solubility. Selenium (IV) is known to be twenty times more toxic than selenium (VI) due to the variations in its mobility, distribution and bioavailability [2]. The toxicity of organic compounds, such as selenomethionine, is lower compared to the inorganic compounds. Selenium has the largest range between dietary deficiency (<40 μg/day) and toxicity (> 400 μg/day) given its intake. The presence of selenium (IV) above the limit values in water resources is of a great interest to the ecologists and technologists.

Sorption is known to play an important role in transport and control of pollutants in the ecosystem [3]. Bearing in mind that selenate in soil and sediments primarily reacts with Fe(III) oxide and hydroxides [4], the synthetic and natural iron-based adsorbents were used to remove selenate.

High prevalence, low price and favorable impact on the environment increased the interest in development the adsorbents based on natural polymers for removal the pollutants from water. The most common polymers in wood are: cellulose, hemicellulose and lignin. Lignin also occurs as a by-product in the pulp and paper industry, and biomass processing processes [5].

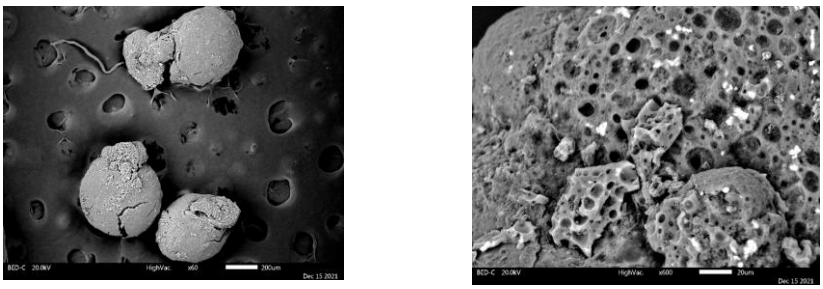
The adsorbent, based on lignin microspheres, was synthesized by a modified process, based on inverse suspension copolymerization [6] of kraft lignin with branched poly(ethylene-imine) (PEI), in order to obtain an amino-functionalized adsorbent and using epichlorohydrin as an agent for networking [5]. The synthesized material was named as follows: A-LMS, and after functionalization with amino-modified magnetite nanoparticles: A-LMS Fe_3O_4. A detailed description of the synthesis of this adsorbent is given in the works of Popović et al. [5,7,8].

Characterization of microstructure the A-LMS Fe_3O_4 adsorbent is an important step to confirm the adsorption of selenium. Scanning Electron Microscopy (SEM) combined with Energy Dispersive Spectroscopy (EDS) is a widely used technique for the micron-scale microstructure analysis [9].

2 MATERIAL AND METHODS FOR TESTING THE ADSORPTION OF SE FROM WATER

Selenium adsorption test by the adsorbent A-LMS Fe_3O_4 was done with the synthetic solutions of Se, prepared by dissoltion an appropriate amount of Na_2SeO_4 (p.a. degree of purity, Sigma Aldrich) in demineralized water. The conditions under which selenium adsorption experiments were performed are: $C_{Se,i}$ = 10 mgL^{-1}, pH 6.46, temperature 24°C, mixing rate 170 o min^{-1}, contact time 300 min.

For morphological analysis, the surface and registration of morphological characteristics of the adsorbent A-LMS Fe_3O_4, used during the process of selenium adsorption, the SEM method (Instrument: JOEL JSM-IT300LV operated at 20 keV) was applied in combination with the EDS method. The SEM-EDS microscopy is a method not only for obtaining information on morphology, but also on the elemental composition and other surface properties of the tested samples [10,11]. The EDS spectra were recorded using an X-ray spectrometer (Oxford Instruments) attached to the scanning electron microscope and Aztec software. Representative images of the surface morphology of adsorbent A-LMS Fe_3O_4 are shown in Figure 1.



a) *b)*

Figure 1 *SEM images of the adsorbent A-LMS Fe_3O_4*

Figure 1 (a,b) shows a micrographic view of the synthesized hybrid sample of A-LMS Fe_3O_4 adsorbent, and as it can be seen on the microspheres there are small irregularities in the shape and porous structure with a large number of micropores. Irregularities in the shapes of synthesized microspheres probably occur due to the

additional functionalization with magnetite nanoparticles. The mean diameter of A-LMS Fe_3O_4 microspheres is approximately 400±40 μm.

The EDS spectra clearly indicate the presence of expected elements (C, O, Cl, Fe and Se). The most intense peaks belong to the elements C, Cl and O, which is in accordance with the chemical composition of the starting lignin. The presence of Fe peaks clearly indicates the incorporation of magnetite from the adsorbent preparation process.

On a sample surface, the C content is in the range from 56.82 to 67.00%, O from 19.89 to 24.21%, Cl from 19.89 to 24.21%, Fe from 0.7 to 2.98%, while the Se content is from 10.73 to 18.53%, Figure 2, a), b). The EDS did not show the Se signals before adsorption, Figure 2, a), and after adsorption, the peak characteristic of Se was registered Figure 2, b), confirming its adsorption.

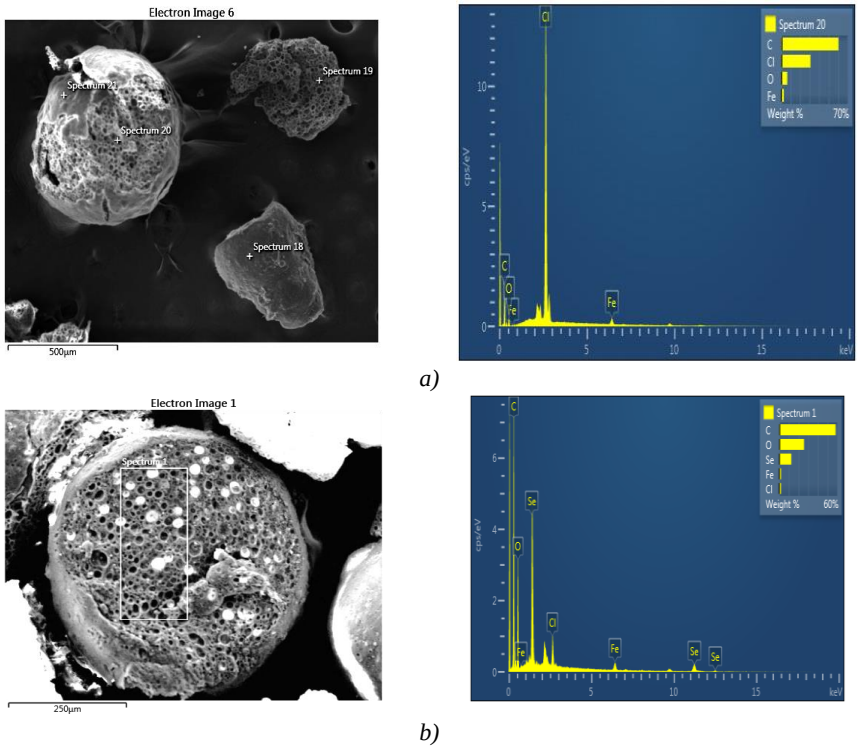


Figure 2 *EDS analysis of the A-LMS Fe3O4 adsorbents (a) before and (b) after Se adsorption*

3 CONCLUSION

Based on the analysis of samples of adsorbent A-LMS Fe_3O_4:

- Using the SEM analysis method, it can be concluded that the material used for adsorption is highly porous, and particles are of the irregular spherical shape;
- The EDS analysis method confirmed the presence of the elements C, O, Cl and Fe, which is in accordance with the chemical composition of lignin and synthesis process of the obtained adsorbent;

- The EDS analysis of material after adsorption detected the characteristic signals for Se;
- Based on the EDS analysis of A-LMS Fe_3O_4 after adsorption, the content of Se on the surface was in the range from 10.73 to 18.53 %.

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