SCANNING ELECTRON MICROSCOPY (SEM) METHOD IN A COMBINATION WITH THE ENERGY-DISPERSIVE SPECTROSCOPY (EDS) FOR ANALYSIS THE SURFACE OF HYDROUS IRON OXIDE-IMPREGNATED HYBRID POLYMER USED FOR SELENIUM ADSORPTION

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Abstract

The scanning electron microscopy (SEM) method in a combination with the energy-dispersive spectroscopy (EDS) was applied to analyze the surface area of the hydrous iron oxide-impregnated hybrid polymer (ER/DETA/FO/FD) used to adsorb selenium (Se) from water. Specified morphological characteristics important for the assessment of selenium adsorption efficiency were not observed by comparison the SEM micrographs of the adsorbent surface ER/DETA/FO/FD before and after Se adsorption. Analyzing the surface of the ER/DETA/FO/FD adsorbent by the EDS method, the signals characteristic of Se that were not present in the starting sample were detected.

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

1 INTRODUCTION

Selenium (Se, atomic number 34) exists naturally in the four oxidation states including selenide (−II), selenium (0), selenite (IV), and selenate (VI). The two most common inorganic forms of Se in natural water are selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}). Selenite is the most toxic of the four states due to its higher bioavailability resulting in its toxicity being 10 time higher than selenate [1].

Despite the nutritional benefits of Se, the reported adverse effects of its excess intake include induction of cancer, Type 2 diabetes, diseases of the nervous and endocrine systems, and skin [2]. Thus, the WHO (World Health Organization) provisional guideline of Se has been set at 40 $\mu g\ L^{-1}$ for drinking water [3]. In comparison, the maximum permissible limit suggested by the European Union (EU) is 10 $\mu g\ L^{-1}$, while the maximum contamination level in the USA is 50 $\mu g\ L^{-1}$ [4,5].

Selenium removal is summarized by the three categories of treatment: (I) physical (e.g., reverse osmosis, nanofiltration, ion exchange, and evaporation), (II) chemical (iron reduction and precipitation, ferric coagulation and filtration, cementation, electrocoagulation, and photoreduction), and (III) biological (microbial reduction, and phytoremediation) treatment. Adsorption is an established versatile physical removal method due to its relatively low cost and its overall technological simplicity [6]. Iron oxides and oxyhydroxides (magnetite, Fe_3O_4; maghemite, γ-Fe_2O_3; hematite, α-Fe_2O_3; goethite, α-FeOOH, etc.) and aluminum oxides/oxyhydroxides (activated alumina, γ -

Al_2O_3 and gibbsite, $Al(OH)_3$) have been used for decades due to their high affinity for selenite species attributed to the formation of the Lewis acid–base complexes [6].

2 MATERIAL AND METHODS FOR TESTING THE Se ADSORPTION FROM WATER

The material used to test selenium adsorption is a microporous poly (GMA-co-EGDMA) crosslinked resin called the ER/DETA/FO/FD, prepared by the radical suspension copolymerization as described in the works of I.D. Vukoje et al. and K. Taleb et al. [7,8]. Synthetic solutions of Se were prepared by dissolving an appropriate amount of Na_2SeO_4 (p.a. degree of purity, Sigma Aldrich) in the milli-Q water. The conditions under which selenium adsorption experiments were performed are: $C_{Se,i}$ = 1 mgL^{-1}, temperature 24°C, mixing speed 170 o min^{-1}, pH 4, contact time 300 min. Based on the results concerning the adsorption process, the following conclusions were drawn: the studied process was pH dependent, with the best performance at pH 4; the pseudo-first model gave the best description of adsorption kinetics; the experimentally determined maximum adsorption capacity of the tested adsorbent for selenate is 22.5 mg g^{-1}, while the value calculated using the Langmuir model was 28.8 mg g^{-1}, confirming its high adsorption capacity [9].

2.1 Characterization of adsorbent ER/DETA/FO/FD by the SEM-EDS method

The surface morphology of solid phases is a very important characteristic of adsorbents. For morphological analysis the surface and registration the morphological characteristics of the adsorbent ER/DETA/FO/FD, used during the process of selenium adsorption, the SEM method (Instrument: JOEL JSM-IT300LV operated at 20 keV) was applied in a combination with the EDS. The SEM-EDS microscopy is a method not only for obtaining the 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 the adsorbent ER/DETA/FO/FD are shown in Figure 1. In parallel, this method determined the elemental composition of an adsorbent sample before and after Se adsorption and the results are shown in Figure 2, a) and b).

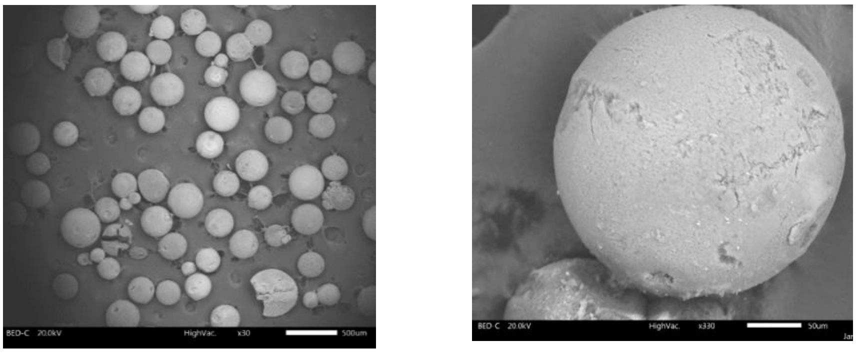
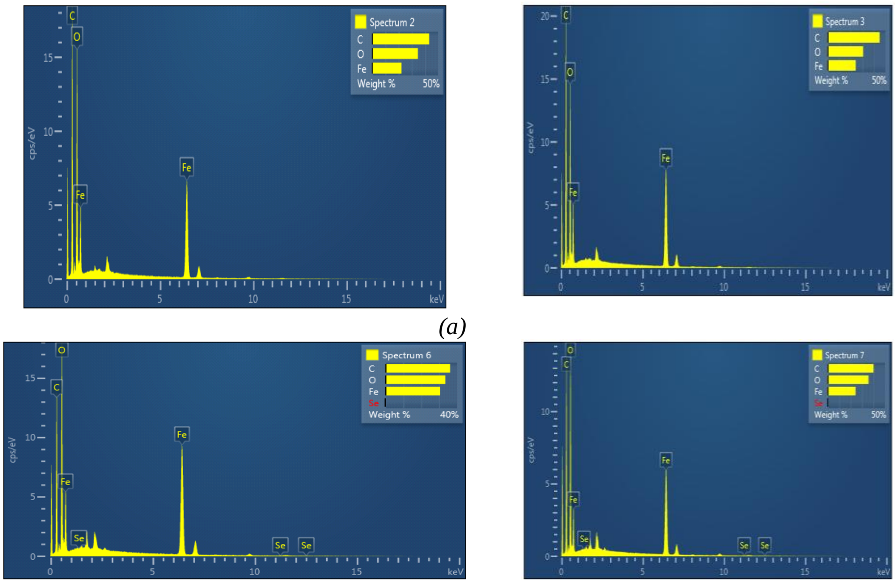


Figure 1 *SEM image of the adsorbent ER/DETA/FO/FD*

As it can be seen from Figure 1, the surface of spherical particles is very smooth without sharp edges, uniform morphology and mean diameter of 200–500 nm.

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

The EDS did not show Se signals before adsorption, and after adsorption, peaks characteristic of Se was registered, confirming its adsorption. On the sample surface, the C content is in the range from 36.06 to 44.99%, O is from 26.83 to 36.36%, Fe from 22.23 to 35.89%, while the Se content is ≈0.01%, as a consequence of a low initial concentration in solution of 1 mg L^{-1}, Figure 2.



(a)

(b)

Figure 2 *EDS analysis of the ER/DETA/FO/FD adsorbents (a) before and (b) after Se adsorption*

3 CONCLUSION

Specified morphological characteristics, important for assessment the efficiency of selenium adsorption, were not observed by comparison the SEM micrographs of the ER/DETA/FO/FD adsorbent surface before and after adsorption. The material was comparable in both observed samples, which indicates that the process of selenium adsorption from aqueous solution does not affect a change of the same. The EDS analysis of tested samples confirmed the efficiency of Se anion adsorption on the surface of the ER/DETA/FO/FD adsorbent because the analysis has detected the new Se signals. The SEM-EDS analysis of the ER/DETA/FO/FD adsorbent after adsorption confirmed the hypothesis that the mechanism of adsorption of selenates by the ER/DETA/FO/FD arises by the formation of complexes in the inner and outer spheres. The highest removal efficiency and maximum adsorption capacity were obtained at pH 4, due to the formation of a complex between $FeOH_2^+$ on the solid phase and SeO_4^{2-} that is predominantly present in the liquid phase at this pH value (V. Marjanovic et al., 2020).

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