

Sorption of Rhenium on Carbon Fibrous Materials Modified with Chitosan

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Sorption behavior of rhenium with respect to new sorption materials was the object of this study in order to define the possibility of its extraction and concentration from dilute solutions. The sorption materials were prepared by modifying of high-area carbon cloth with a natural biopolymer – chitosan. The three types of sorption materials with different degree of amino groups protonation were obtained. Modified materials have higher sorption capacity as compared to initial carbon cloth. Sorption behavior of the materials was found to be conditioned by the number of the protonated amino groups. We propose that electrostatic interaction of perrhenate ion ReO_4^- with the protonated amino groups $-\text{NH}_3^+$ takes place.

Nitrogen containing anionites and complexing ionites as well as amino containing impregnates are used for sorption of rhenium, one of the least distributed rare metals. Chitosan, a natural organic polymer containing amino groups can adsorb ReO_4^- and sorption depends on the ionic strength and pH of its solutions. Specifically, chitosan has primary amino groups with pK_a values close to 6.3. At pH below pK_a most of the amino groups are protonated making chitosan a water-soluble cationic polyelectrolyte. At pH above the pK_a chitosan's amino groups are deprotonated, and this polymer becomes insoluble¹. These properties of chitosan were used for obtaining of new sorption materials. It is known that for adsorption of some pollutants (such as organic compounds, metals) from water some high-area carbon cloth samples which have the advantage of having large specific area are used.^{2,3} It was also reported⁴ that adsorbate could be almost quantitatively desorbed by anodic or cathodic polarization of C-cloth configured as a porous electrode.

The C-cloth used as initial material for preparing of the sorbents was received from Svetlogorsk PC “Khimvolokno” and coded as Busofit-T having specific area $\sim 700\text{--}800 \text{ m}^2/\text{g}$. It was modified with chitosan by means of electrochemical process and adsorption on C-cloth. Thus, the three types of the sorption materials were obtained by the following ways: by cathodic and anodic polarization (in potentiostatic regime) and at open-circuit condition in electrolyte solutions. The amount of precipitated chitosan depends on the treatment method at the same concentration. To determine the types of nitrogen containing groups we used the X-ray photoelectron spectra. X-ray photoelectron N 1s spectra of some samples are presented in Figure 1. Deconvolution of these spectra gives two peaks with a difference in energy of 2.6 eV corresponding to amino groups $-\text{NH}_2$ and protonated amino groups $-\text{NH}_3^+$. It was found that the chitosan film precipitated at the negative electrode had much less amount of protonated amino groups.

Comparison of the sorption properties of the three series of sorption materials as regards to rhenium was carried out. Rhenium sorption from neutral solutions with phase ratio 1:1000 was studied. Figure 2 compares kinetic characteristics of the sorption materials obtained. All the samples modified

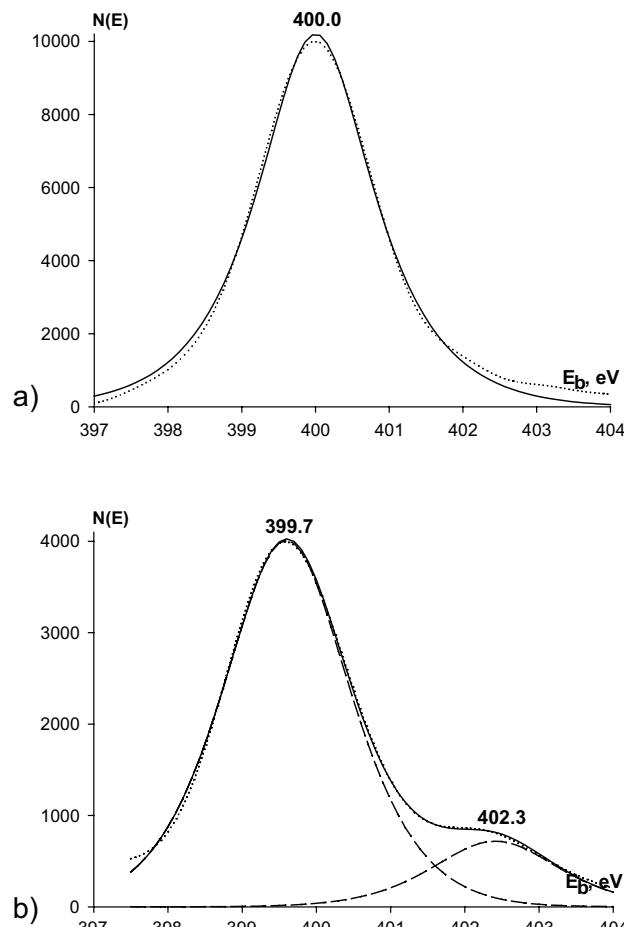


Figure 1. X-Ray photoelectron N 1s spectra after smoothing and background subtraction of carbon-fibers modified with chitosan by cathodic (a) and anodic (b) polarization.

with chitosan under various conditions have higher sorption capacity as compared to the initial C-cloth. Thus, sorbent samples prepared by anodic polarization have better kinetic features (curve c). This difference helps us to understand the role of amino groups in rhenium sorption. We suppose that sorption behavior of materials is conditioned by the number of protonated groups.

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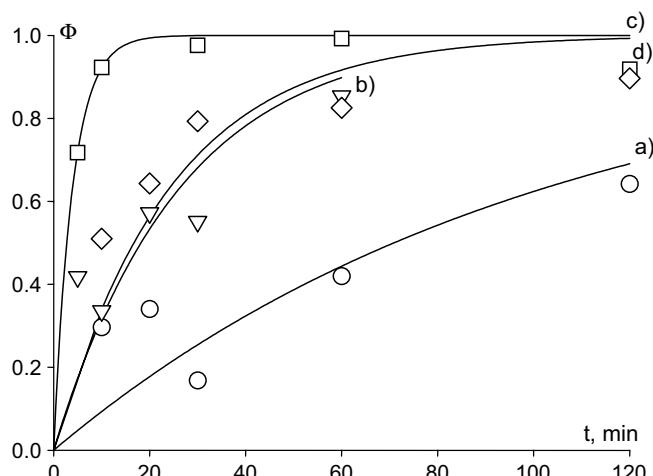


Figure 2. The kinetics of ReO_4^- sorption on original C-cloth (a) and C-cloth modified with chitosan by cathodic (b) and anodic (c) polarization and at open-circuit potential (d). Here Φ is the degree of the sorption against the equilibrium sorption.

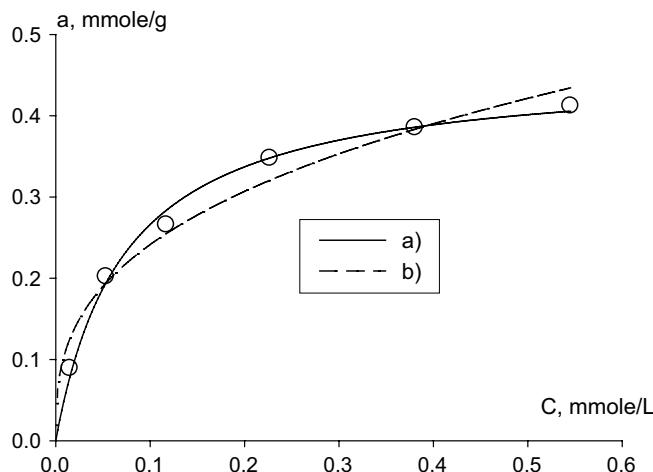


Figure 3. The isotherm of ReO_4^- sorption on C-cloth modified with chitosan by anodic polarization and its approximation by Langmuir (a) and Freundlich (b) isotherms. Here a is the sorption and C is the equilibrium concentration.

Figure 3 shows the adsorption isotherm of rhenium on the sorbent sample prepared by anodic polarization. The experimental data were fitted using both Langmuir and Freundlich isotherms. The best correlation between experimental data and fit-line as obtained for Langmuir isotherm with the following parameters – the constant value $13.6 \pm 1.5 \text{ L/mmole}$, the maximum capacity – $0.46 \pm 0.01 \text{ mmole/g}$. We propose that in adsorption process the protonated amino groups can interact with the negatively charged perrhenate anion ReO_4^- via electrostatic interaction as in Reference 5. Rhenium desorption from the sorbent in result of change of its charge may confirm this proposal. In order to desorb previously adsorbed rhenium

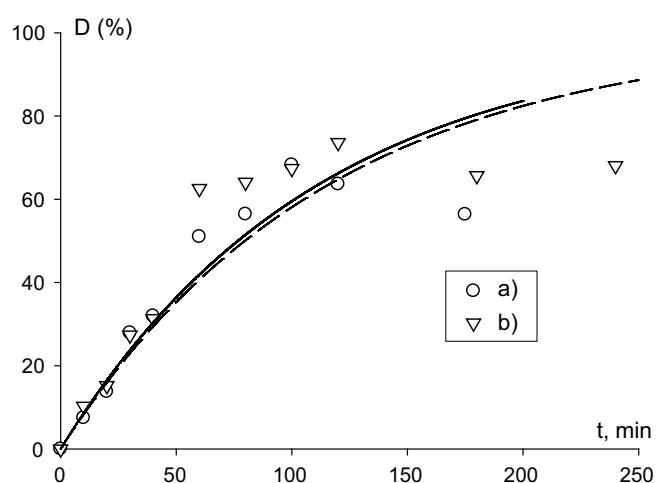


Figure 4. The kinetics of ReO_4^- desorption at 0 mV (a) and at -100 mV (b). Here D is the degree of desorption.

the modified sorbent was negatively polarized with the rate 0.1 mV/sec up to potentials 0 and 100 mV (Ag/AgCl reference electrode) and then was exposed to these potentials. The time of the electrode charging since stationary potential up to desorption one was about 1 hour (Figure 4). Exposure to desorption potentials lets to desorb up to 80% of rhenium. Some decrease of amount of rhenium desorbed may be due to pH increase at the electrode layer in the end of the desorption process.

Electrodesorption has some advantages as compared to usual desorption: it does not require complex reagents, large volumes of solutions or additional equipment. Desorption of ReO_4^- ions by means of polarization is of significance for application, i.e. for accumulation of ReO_4^- ions from dilute solutions with the subsequent charge desorption into a small volume. Behavior of ReO_4^- ions is similar to that other oxy-ions, such as Mo(VI) and V(V), in the process of their extraction from industrial sewages by means of adsorption and electrosorption at high-area carbon cloth.

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