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Physico-chemical effects of ion-exchange fibers on electrokinetic transportation of metal ions

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ABSTRACT

Ion-exchange textiles can be used in electroremediation of heavy metal contaminated liquid effluents. In this work, the behavior of FIBAN ion-exchange textiles was tested for the transportation of two heavy metals: lead and zinc, under the effect of a constant direct electric current. Detailed characterization of fibers has been carried out in order to determine the effect of their structure on the retention of heavy metal during their electrokinetic transport. Ion-exchange fibers structure was studied by electronic scan microscopy, X-ray fluorescence, spectrogammametric analysis and Fourier Transformed Infrared Spectroscopy/Attenuated Total Reflectance. Hittorf method was used to determine the transport number of Pb^{2+} and Zn^{2+} during the electrokinetic treatment.

1. Introduction

Ion-exchange textiles have been recently reported to be successful in several environmental applications such as: water treatment, hydrogen sulfide removal from gases, solvent extraction and heavy metal removal from effluents and soils [24,25,26]. Ion-exchange textiles are made of fibers, which are based on polymer matrices which provides to the material hydrophilic properties and a good mechanical resistance. This kind of textiles has been firstly used as a suppressor of the packed material in columns for ion-exchange chromatography, improving the baseline stability and decreasing ion-exclusion effects and chemical reactions [33]. The use of textiles was favored by their high separation capacity, fast ion-exchange rates and good electrical conductivity [5]. Applications of textiles are now extended and include the separation of rare earth elements [1], the enrichment of uranium from seawater [28], purification of air by the removal of alkaline or acidic impurities [22] and chromatographic separation methods [30,6,11]. Recently, it was also proposed to use the ion-exchange textiles in medical and pharmaceutical applications [32,10].

Polluting elements such as heavy metals are very difficult to eliminate completely from the contaminated industrial effluents, and usually, low metal concentration remains in the effluents. Electrokinetic remediation is one of *in situ* processes that have been developed for metal removal. Depending on the nature and the concentration of heavy metals, different strategies were reported to improve the efficiency of the electrokinetic treatment [20]. To improve the removal of heavy metals, other alternative materials can be tested such as ion-exchange textiles.

Ion exchange textiles shows good mechanical properties and have a high ion-exchange capacity with the particular characteristic of being hydrophilic materials [9,2,29,27]. Basta et al. [2] noted that the hydrophilic and macroporous structure of the textiles permits the mobility of ions inside and through them, and the ionic mobility is comparable to that in aqueous solutions. Soulier et al. [29] confirmed the hydrophilic nature of ion-exchange fibers. Ezzahar et al. [9] found that ion-exchange fibers are fibrous non-woven grafted under irradiation. They also proved that the macromolecular chains of ion-exchange fibers are hydrophilic and non-crosslinked.

In this work, the electrokinetic transportation two heavy metals: lead and zinc, in aqueous solution through ion-exchange textiles is studied, and the textile structure is examined in order to explain the ionic transportation through the textiles.

2. Materials and methods

2.1. Ion-exchange textiles

Ion-exchange textiles were supplied by the Institute of the organic chemistry and physics of the Belarus National Academy of Sciences. Textile fibers were manufactured with two types of

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polymer matrices. The first group of fibers was made of polypropylene (PP) modified by radiochemical grafting of polystyrene (ST), using as co-polymer divinyl-benzene (DVB) [27]. PP-ST-DVB matrices were used as a structural base for the preparation of a fiber with a wide range of ion-exchange functional groups such as: sulfonic, carboxylic and phosphoric. All of these functional groups can be negatively ionized and therefore, they can be used for the preparation of cation (i.e. heavy metals) exchange fibers. The presence of such a variety of functional groups gives to the fiber unique cation-exchange properties [27]. In this work, two fibers of this group were tested: FIBAN K-1 which is a strong acid cation-exchange fiber that contains sulfonic groups; and FIBAN K-4 which is a weak cation-exchange fiber with carboxylic groups.

The second group of ion-exchange fibers used in this work is an anion-exchange fiber. The FIBAN A-6 fiber was selected in this study. This fiber contains the amine group. This is a basic fiber with a polymeric matrix of industrial polyacrylonitrile NITRO D.

2.2. Experimental setup

The experimental setup is depicted in Fig. 1. The electrokinetic cell made of Plexiglas is divided in three compartments of the same volume (0.1 L each compartment). Ion-exchange textiles are installed between compartments, the anionic-exchange textile on the cathode side and one of the cathodic-exchange textiles on the anode side. The main electrodes, anode and cathode, are located on both ends of the cell. Graphite sheet was used for both anode and cathode for its low cost and good electric conductivity. Moreover, the graphite sheet allows a good contact with the electrolyte solution and therefor, a good electrical conductivity between the electrode and the solutions. The distance between the main electrodes is 20 cm and the surface area is 3.14 cm^2.

2.3. Experimental procedure

The cell compartments were filled with lead(II) or zinc(II) nitrate solution at the concentration of 10^{-3} or 10^{-4} M. A power supply was used to apply a constant DC electric current in each experiment for 4 h. The selected values were: 10, 20, 30 and 40 mA. Experiments were carried out at room temperature which is around 298 K.

After 4 h of treatment, the electric current is shut down and samples from the three cell compartments were taken immediately to avoid any change in ion concentration by back-migration due to concentration gradients between compartments. The volume of liquid in the cell compartments was constant because electro-osmotic flow was negligible. Ion concentration in solution

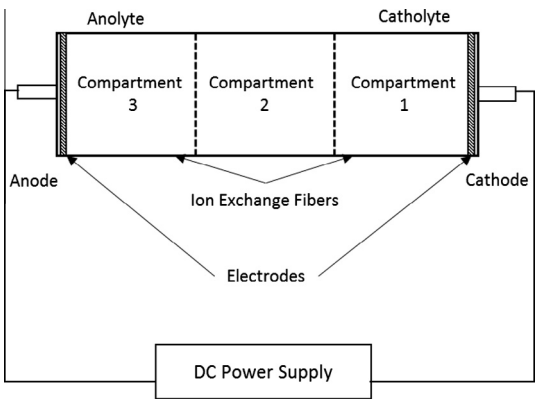

Fig. 1. Experimental setup for the determination of the transport number by the method of Hittorf.

was determined by a Unicam 929 Atomic Absorption Spectrophotometer, [12,13,7,34].

2.4. Transport number

Transport number for the selected ions in each experiment was determined using the three FIBAN ion-exchange textiles: K-1, K-4 and A-6. The anionic textile, FIBAN A-6, was used on the cathode side, and one of the cationic textiles, K-1 or K-4, was used on the anode side in each experiment. The migration of each ion/counter-ion through each textile was determined. Then, the transference number was calculated using the method of Hittorf [19,17,35].

The method of Hittorf is directly based on the definition of the ion transference number. Transference number is defined as the fraction of the electric current transported by ions and counter-ions (Eq. (1)):

$$t_i = F\frac{J_i}{I} \tag{1}$$

where t_i is the transport number (dimensionless), F is the Faraday constant, 96,480 C/mol, J_i is the flow of the ion/counter-ion i (mol/m^2 s), and I is the current density through the textile (A/m^2).

After a predefined treatment time t, ion concentration in each compartment solution is measured. The amount of each ionic species that migrate from one compartment to the other can be calculated considering the initial and final concentration of each species in each compartment. The transport number for the species i is then calculated with the Eq. (2):

$$t_i = F\frac{V\Delta C}{ISt} \tag{2}$$

where ΔC is the variation of concentration of the species i in a compartment of the cell (mol/m^3), V is the volume of each cell compartment (m^3), S is the surface area of the ion-exchange textile (m^2), and t is the treatment time (s).

2.5. Water uptake of textiles

Ion-exchange textiles were dried and then weighted. Textiles were immersed in distilled water at room temperature (298 K). Every 10 min, textiles were taken out and placed on a filter mesh to remove the excess of water by gravity. The amount of water absorbed by a textile was determined by weighting. Experiments were done in quadruplicate for each textile. Results reported are the average value for the 4 experiments.

The absorption of water in the textiles can be followed by weight variation. The swelling ratio can be expressed with Eq. (3) [3,4]:

$$T_g = \frac{m_H - m_E}{m_H}100 \tag{3}$$

where T_g is the moisture content of the textile (%), m_H is the wet mass of the textile (kg), and m_E is the dry mass of the textile (kg).

2.6. Analyses

Scanning electron microscopy (SEM) using secondary electron mode allows obtaining surface images of the microscopic structure of the ion-exchange textile. Those images permit the determination of the microscopic structure of fibers. X ray fluorescence Spectrometry (XRF) was used for the quantification of elemental composition. XRF was carried out using Oxford ED2000 equipment. The acquisition time of the FIBAN K-4 spectrum obtained with Cd-109 is 40,000 s, while for the FIBAN K-1 and A-6 is 900 s.