The Application of Fiber Ion Exchange Sorbents for Wastewater Treatment and Purification of Gas Mixtures

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Abstract: We developed a method of modifying the polyester material to produce ion exchange fiber sorbents. The production of cation exchange sorbents involved the treatment of polyester fibers with a 20–25% solution of NH2NH2H2O at 70–90°C and a 5% solution of NaOH at 40°C. Anion exchange sorbents were prepared by the treatment of cation exchange sorbents with a 1–5% solution of polyethylenimine at ambient temperature. These new types of sorbents can be used to remove radionuclides, heavy metal ions and organic contaminants from wastewater and drinking water. We studied main properties of these sorbents and their ability to remove 57Co, 60Co, 65Zn, 89Sr, 90Sr, 134Cs, 137Cs and other radionuclides, heavy metal ions (Zn, Ni, Cu, Sb, Pb, Cd, Cr, U, etc.), organic molecules M (pesticides, phenols, dioxins, benzene, toluene, etc.), radio-labeled organic molecules M-32P, M-131I, M-99Mo-99mTc, M-14C, etc. The static exchange capacity is 1–2 meq/g for cationic sorbents and 0.5–1 meq/g for anionic sorbents. The developed sorbents have been effective in removing low concentrations of contaminants from water (lower than 100–200 mg/L) as well as in purifying the gas mixtures from toxic and aggressive gases: SO2, SO3, NH3, H2S, etc.

Keywords: Polyester, Cation Exchange, Anion Exchange, Fiber Sorbent, Wastewater Treatment

1. Introduction

Drinking water and wastewater purification from radionuclides, heavy metal ions and organic contaminants is one of the most important problems of the modern world. To solve it, the ion exchange method utilizing different types of resins and fiber sorbents [1] is widely used.

The advantage of fiber ion-exchange sorbents over resin is their high sorption rate, effective regeneration and a low pressure drop value of the sorbent layer for purified water [2-4]. The specific surface of fiber sorbents is (2–3).104 m2/kg, i.e. about 102 times greater than that of resin (102 m2/kg). Due to that, fiber sorbents have a much higher sorption rate than resin.

The main drawback of fiber sorbents is their very low specific weight which is 50–200 kg/m3 [5-8]. There are many fiber filters produced in various plants, but most of them are intended only for air purification from dust and aerosols, and they do not have ion-exchange properties. The purpose of this work is to develop a technology for producing dust fiber filters with ion exchange properties. In many cases, this approach is economically more effective because it does not require construction of new plants. One of the most produced dust filters is a polyester fiber filter. Its production process includes acrylonitrile emulsion treatment to improve mechanical characteristics. This feature can be used in the technology for producing cation and anion exchange sorbents.

2. Materials and Methods

A polyester fiber filter with surface density of 0.270 kg/m2
and thickness of 10 mm was utilized as a raw material for making ion exchange sorbents. The mass of the polyacrylonitrile layer on the fibers’ surface was 15% of the total mass of the filter.

1-10% NaOH solutions and 0.5-5% polyethylenimine (\(-\text{NHCH}_2\text{CH}_2-)\), [\text{CH}_2\text{CH}_2\text{NH}_2\text{CH}_2\text{CH}_2-\)], solutions were used for the treatment of polyester fiber filters to make ion exchange sorbents.

The 0.001M CuCl\(_2\) solution labeled by \(^{64}\text{Cu}\) and the \(\text{K}_2\text{Cr}_2\text{O}_7\) solution (pH 2) labeled by \(^{51}\text{Cr}\) were used to find out the best technology of making cation and anion exchange sorbents, respectively. The radionuclides \(^{64}\text{Cu}\) and \(^{51}\text{Cr}\) were produced by irradiating CuCl\(_2\) and \(\text{K}_2\text{Cr}_2\text{O}_7\) in the nuclear reactor of the Institute of Nuclear Physics (Tashkent, Uzbekistan). A Ge(Li) detector with a resolution of about 1.9 keV at 1.33 MeV and a 4096-channel multichannel analyzer were used to detect a γ-quantum from radionuclides. Areas under γ-peaks of radionuclides \(^{64}\text{Cu}\) (the half-life, \(T_{1/2}\), is equal to 12.8 h, the energy of the γ-peaks, \(E_\gamma\), is equal to 0.511 MeV) and \(^{51}\text{Cr}\) (the half-life, \(T_{1/2}\), is equal to 27.72 d, the energy of the γ-peaks, \(E_\gamma\), is equal to 0.320 MeV) were measured to calculate the amount of Cu and Cr, respectively.

Other radionuclides used in investigations of sorbents’ characteristics as labels of ions and organic substances are given in Table 1.

| Elements | Radionuclides | \(T_{1/2}\) | \(E_\gamma\) MeV |
|----------|--------------|-------------|----------------|
| \(\text{M}^{3+}\) | \(^{32}\text{P}\) | 14.3 d | 1.7 |
| \(\text{Cr}^{6+}\) | \(^{51}\text{Cr}\) | 27.73 d | 0.320 |
| \(\text{Co}^{2+}\) | \(^{60}\text{Co}\) | 5.27 y | 1.17, 1.33 |
| \(\text{Ni}^{2+}\) | \(^{60}\text{Ni}\) | 2.5 h | 1.480 |
| \(\text{Cu}^{2+}\) | \(^{64}\text{Cu}\) | 12.7 h | 0.511 |
| \(\text{Zn}^{2+}\) | \(^{87}\text{Zn}\) | 244.1 d | 1.115 |
| \(\text{Br}^{-}\) | \(^{85}\text{Br}\) | 35.3 h | 0.776 |
| \(\text{Sr}^{2+}\) | \(^{85}\text{Sr}\) | 50.5d | 0.909 |
| \(\text{Mo}^{99-100}\text{Te}^{99m}\) | \(^{99m}\text{Mo}\) | 66 h (6.0 h) | 0.140 |
| \(\text{Cd}^{110}\) | \(^{110}\text{Cd}\) | 53.5 h | 0.336 |
| \(\text{Sb}^{122}\) | \(^{122}\text{Sb}\) | 60.2 d | 1.691 |
| \(\text{M}^{1-131}\) | \(^{131}\text{I}\) | 8.04 d | 0.364 |
| \(\text{Cu}^{2+}\) | \(^{133}\text{Cs}\) | 2.07 y | 0.605 |

The exchange capacity \(Q\), meq/g, was calculated by Equation (1):

\[
Q = \frac{(A_0 - A_e)}{(A_0 - A_B)} B / W \quad (1)
\]

where \(B\) is the carrier amount, meq; \(W\) is the exchanger weight, g; \(A_0\) is a count rate of the original solution; \(A_e\) is a count rate of the solution at equilibrium; \(A_B\) is a background count.

The exchange capacity \((\text{Cu}^{2+})\) of the sorbents is 0.25 meq/g.

The sorption processes of ions from water in dynamic conditions were studied by using columns with a diameter of 12 mm; the weight of sorbents was 1 g.

3. Results and Discussion

The kinetics of saponification of the fibers and the alteration of linkage quality between the polyester fiber and the polyacrylonitrile layer after chemical treatment of fibers were studied in the range of NaOH solution concentration from 1 to 10%. For example, the results for concentration of 5% are given in Figures 1 and 2.

An increase in solution treatment temperature and treatment duration causes filter capacity increase, but linkage between the polyester fiber and the polyacrylonitrile layer is attenuated and the layer begins scattering. Thus, the treatment with a 5% solution of NaOH at 45-50°C for 1 hour was selected as the optimal condition for cation exchange sorbents production. The exchange capacity \((\text{Cu}^{2+})\) of the sorbents is 0.25 meq/g.

Anion exchange sorbents are made by treatment of cation exchange filters in an H-form with a water solution of polyethylenimine. Amine groups attach to carboxy groups by electrostatic forces. The kinetics of anion exchange groups’ formation at concentrations of polyethylenimine from 0.5 to 5% and temperature from 20°C to 70°C were studied. Figure 3 demonstrates a kinetics curve at 40°C and a 1% concentration of polyethylenimine. Figure 4 shows dependence of exchange capacities on the concentration of polyethylenimine at 40°C and the treatment time of 8 hours.

The treatment of the cation exchange sorbents with a 1% solution of polyethylenimine at 40°C for 8-10 hours was...
selected as the optimal condition for the anion exchange sorbents’ production. The sorbents’ capacity (Cr\textsuperscript{6+}) is 0.45 meq/g.

Removing heavy metal ions (Zn, Ni, Cu, Sb, Co, Cd, Cr, etc.) and organic molecules labeled by radionuclides (M\textsuperscript{32}P, M\textsuperscript{131}I, M\textsuperscript{99}Mo\textsuperscript{99m}Tc, etc.) from water was studied. Dependence of the distribution coefficient \(K_d\) for different ions and organic substances on the solutions’ pH is presented in Table 2.

The specific behavior of the \(K_d\) of Co(II), Ni(II) and Cu(II) is explained by the dependence of the relation between the \(M^{n+}\) form and hydrolyzed forms in the solution on pH \([9]\). The influence of additional foreign cations Na\textsuperscript{+} and K\textsuperscript{+} on the adsorption of different metals at pH=7 is presented in Table 3.

Adsorbed ions were eluted with a 1M HCl solution at a flow rate of 2 mL per minute, and 1 mL fractions were collected each time for radiometric measurements. As an example, Figure 5 shows elution profiles of copper, cobalt and cadmium: activity in count per minute (CPM) per fraction is plotted against the volume of eluant. About 95% of adsorbed ions were recovered by elution with a 30 mL HCl solution. The capacity decrease \(\Delta Q\) % against a number \(N\) of regenerations was studied. Test results are given in Figure 6.
Figure 5. Elution profiles of copper, cobalt and cadmium against the volume of eluent.

Figure 6. The capacity $\Delta Q$ decrease against a number $N$ of regenerations.

Nonwoven cloth weighing 1 kg/m² made of analogous fibers is widely used in filters with an output of 3,000 to 25,000 m³/h for removal of SO₂, SO₃, HF, HCl, Cl₂, NH₃, H₂S, NH₂-NH₂ and other gases and liquid aerosols, the most common atmospheric pollutants [10-15].

4. Conclusion

The above described results of investigations show that chemically modified polyester fiber filters have satisfactory adsorption characteristics. These cation and anion exchange filters can be used for removing metal ions (Zn, Ni, Cu, Sb, Co, Cd, Cr, etc.) and organic compounds (M⁻³²P, M⁻¹³¹I, M⁻⁹⁹Mo⁺±⁹⁹mTc, etc.) from wastewater. The cation exchange sorbents’ capacity is 0.25 meq/g (Cu²⁺) while the anion exchange sorbents’ capacity is 0.45 meq/g (Cr⁶⁺).

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