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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 $NH_2NH_2H_2O$ 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 ^{57}Co, ^{60}Co, ^{65}Zn, ^{89}Sr, ^{90}Sr, ^{134}Cs, ^{137}Cs 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-^{32}P, M-^{131}I, M-^{99}Mo+^{99m}Tc, M-^{14}C, 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: SO_2, SO_3, NH_3, H_2S, 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).10^4 m^2/kg, i.e. about 10^2 times greater than that of resin (10^2 m^2/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/m^3 [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 acrylonitrilic 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/m^2

and thickness of 10 mm was utilized as a raw material for making ion exchange sorbents. The mass of the polyacrylonitrilic layer on the fibers' surface was 15% of the total mass of the filter.

1-10% NaOH solutions and 0.5-5% polyethylenimine $(-NHCH_2CH_2-)_x[-(CH_2CH_2NH_2)CH_2CH_2-]_y$ solutions were used for the treatment of polyester fiber filters to make ion exchange sorbents.

The 0.001M $CuCl_2$ solution labeled by ^{64}Cu and the $K_2Cr_2O_7$ solution (pH 2) labeled by ^{51}Cr were used to find out the best technology of making cation and anion exchange sorbents, respectively. The radionuclides ^{64}Cu and ^{51}Cr were produced by irradiating $CuCl_2$ and $K_2Cr_2O_7$ 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}Cu (the half-life, $T_{1/2}$, is equal to 12.8 h, the energy of the γ-peak, E_γ, is equal to 0.511 MeV) and ^{51}Cr (the half-life, $T_{1/2}$, is equal to 27.72 d, the energy of the γ-peak, E_γ, 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.

Table 1. *Radionuclides used as labels.*

Elements	Radionuclides	$T_{1/2}$	E_γ, MeV
M-^{32}P	^{32}P	14.3 d	E_β=1.7
Cr(VI)	^{51}Cr	27.73 d	0.320
Co(II)	^{60}Co	5.27 y	1.17, 1.33
Ni(II)	^{65}Ni	2.5 h	1.480
Cu(II)	^{64}Cu	12.7 h	0.511
Zn(II)	^{65}Zn	244.1 d	1.115
Br(I)	^{82}Br	35.3 h	0.776
Sr(II)	^{89}Sr	50.5d	0.909
M-^{99}Mo+^{99m}Tc	^{99}Mo+^{99m}Tc	66 h (6.0 h)	0.140
Cd(II)	^{115}Cd	53.5 h	0.336
Sb(II)	^{124}Sb	60.2 d	1.691
M-^{131}I	^{131}I	8.04 d	0.364
Cs(I)	^{134}Cs	2.07 y	0.605

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

$$Q=(A_0 - A_e) / (A_0 - A_B)\ B / W \quad (1)$$

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 distribution coefficient K_d and the percent adsorption P were calculated by Equations (2), (3):

$$K_d=((A_0 - A_B) / (A_e - A_B) - 1)\ V / W \quad (2)$$

$$P=100\ (1 - (A_e - A_B) / (A_0 - A_B)) \quad (3)$$

where V is a total volume of the solution, ml.

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 filters 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 (Cu^{2+}) of the sorbents is 0.25 meq/g.

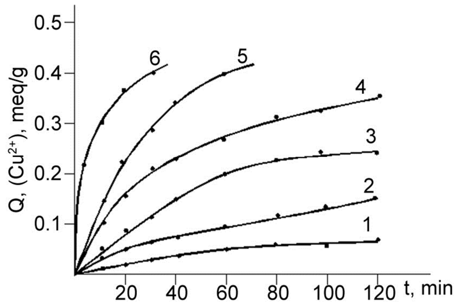

Figure 1. *Kinetics of saponification of the fibers in a 5% NaOH solution at 25°C (1), 30°C (2), 40°C (3), 50°C (4), 70°C (5) and 90°C (6).*

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^{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-^{32}P, M-^{131}I, M-^{99}Mo+^{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.

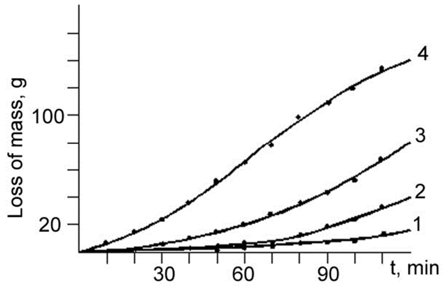

Figure 2. *Change in linkage quality between polyester fibers and the polyacrylonitrile layer after chemical treatment during t minutes at 30°C (1), 50°C (2), 60°C (3) and 70°C (4).*

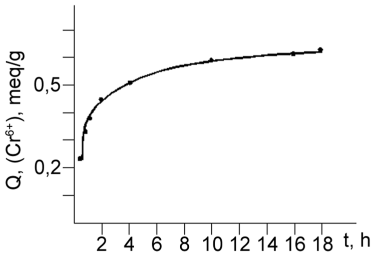

Figure 3. *Kinetics of anion exchange groups' formation at 40°C in a 1% polyethylenimine solution.*

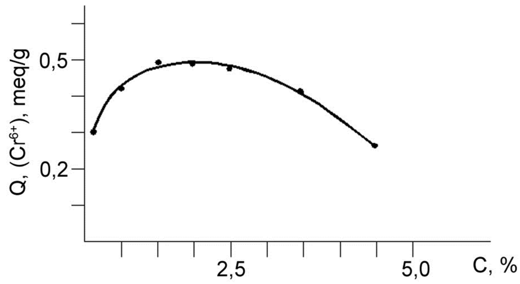

Figure 4. *Dependence of exchange capacities on the concentration of polyethylenimine at 40°C.*

Table 2. *The distribution coefficient K_d (mL/g) for different ions and organic substances (C_0=10 mg/L, V=50 mL, W=0.5 g).*

Elements	Exchanger	pH of solutions									
		1	2	3	4	5	6	7	8	9	10
Co(II)	Cationic	3000	2600	2300	2000	1700	1000	126	138	150	160
Ni(II)		125	600	870	920	990	750	430	510	780	1000
Cu(II)		140	400	600	480	400	560	650	560	460	340
Zn(II)		230	2000	4000	5000	4000	1900	1700	1400	900	800
Sr(II)		11	25	45	100	300	1000	1900	8000	6000	900
Cd(II)		980	830	680	520	380	240	97	75	46	17
Sb(II)		260	190	150	130	120	120	115	90	70	35
Cs(I)			100	200	900	1900	3200	4000	4000	1500	11
Cr(VI)	Anionic	200	150	100							
M- ^{32}P			3200	3000	2700	2500	1900	1100	300	150	
M-^{131}I			3100	2800	2600	2300	2100	1900	500	150	
^{99}Mo+^{99m}Tc				2900	2800	2400	2300	2000	500	140	

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^+ and K^+ on the adsorption of different metals at pH=7 is presented in Table 3.

Table 3. *The influence of additional foreign cations Na^+ and K^+ on the distribution coefficient K_d (mL/g) of different ions at pH=7.*

Elements	Na^+		K^+		$Na^+ + K^+$
	10 mg/L	100 mg/L	10 mg/L	100 mg/L	100+100 mg/L
Co(II)	130	140	130	140	140
Ni(II)	510	300	520	420	500
Cu(II)	600	460	550	530	530
Zn(II)	1700	800	1700	800	800
Cd(II)	38	34	50	32	20
Sb(II)	115	115	115	115	115

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 ΔQ % against a number N of regenerations was studied. Test results are given in Figure 6.

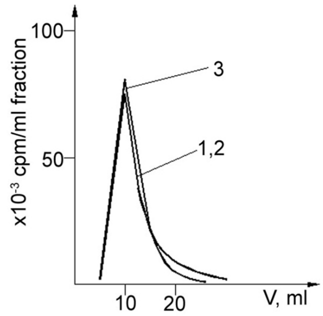

Figure 5. *Elution profiles of copper, cobalt and cadmium against the volume of eluent.*

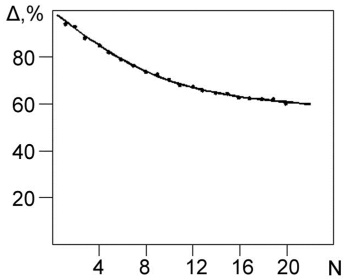

Figure 6. *The capacity ΔQ decrease against a number N of regenerations.*

Nonwoven cloth weighing 1 kg/m^2 made of analogous fibers is widely used in filters with an output of 3,000 to 25,000 m^3/h for removal of SO_2, SO_3, HF, HCl, Cl_2, NH_3, H_2S, NH_2-NH_2 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-^{32}P, M-^{131}I, M-^{99}Mo+^{99m}Tc, etc.) from wastewater. The cation exchange sorbents' capacity is 0.25 meq/g (Cu^{2+}) while the anion exchange sorbents' capacity is 0.45 meq/g (Cr^{6+}).

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