

STUDY OF APPLICATION OF HYDROPHOBIC FIBROUS SORBENTS FOR WATER PURIFICATION FROM METAL IONS

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Sorption properties of hydrophobic fibrous sorbents on the basis of polypropylene and polyethylene terephthalate produced from thermoplastic polymer wastes to metal ion series in aqueous media has been studied. Based on the experimental data of extraction degree dependencies on fibre laying density, dispersity, presence of air in sorbent, volume of pass solution the mechanism of metal ion sorption from aqueous media with hydrophobic fibrous materials is suggested.

Introduction

At present quality of water in natural sources is considerably deteriorated. Metals, majority of which are very toxic, form a specific group of hydrosphere contaminants. Drinking water pollution with these metals occurs both as a result of sedimentation in natural basins and at transportation by service lines. Therefore, there is the necessity in medium-priced packaged units. Filter materials entering into their composition should possess good sorption properties as well as efficiency.

In the University of Architecture and Building the technology in nonwoven fibrous materials production from the wastes of thermoplastic polymers by untraditional filter-free way has been developed [1]. This technology allows for solving the tasks of water and air purification and polymer wastes utilization. New fibrous sorbents, being cheap and available, possess, at the same time, good filtering properties, high chemical stability, strength, wear resistance, low density. Polypropylene fiber, obtained from thermoplastic wastes, seemed to be well for oil and petroleum products collection of water surface, iron ions (III) from waste water, and also as filtration materials for gas mixtures purification [2–5]. In this case, tap water, passed along them, meets requirements of SanPiN in sanitary and bacteriological indices. It is obvious, that the investigation on perspectives in use of new fibrous materials in practice of economic-domestic water supply is very urgent.

Sorption property of polypropylene fiber relative to a number of metal ions was investigated earlier [6]. It is showed that the elements, forming stable hydro complexes in mediums close to the neutral ones, are extracted most efficiently from water.

In the given paper the range of investigated fibrous materials, varying in polymer nature, fiber dispersity, degree of their hydrophobic property is expended.

Methods of investigation

Synthetic fibrous materials, made from wastes of polypropylene – PP (crushed disposable syringes, films, coils) and polyethylene terephthalate – PETP (packages, drink containers etc.) were used for investigation. The first sorbent refers to carbon-chain, and the second one refers to heterochain polymers according to their chain

structure. But both of them have hydrophobic surface. Besides, PP fiber was presented by the samples of various dispersity: with fiber of 10...50 and 1...10 mkm thick. The great bulk of the first sample had fiber of 30 mkm thick, but there were some fibers of larger size to 50 mkm. Fibers of the second sample are mainly of 3 mkm.

The degree of metal ions extraction from aqueous mediums was investigated by the «introduced-found» method at model solutions, which had been prepared by aliquot evaporation of state standard samples of metal solutions in fluoroplastic glasses under IR-lamp at 60...80 °C dry with further dissolution of a solid residual in 10 ml of bidistilled water. Their acidity was controlled by a pH-tester and regulated by 1 M NH₄OH addition. Sorption was carried out in dynamic conditions: fibrous polymer was placed in a column and model solution with constant velocity was passed through it by means of peristaltic pump. Metal impurities content was controlled in the input and output solutions by atomic emission method. For this purpose, before sorption and after passing through the sorbent 1ml of every solution was evaporated at graphite collector with 0,1 g weight containing 3 % sodium in the form of chloride. Quantitative analysis was carried out at spectrograph ISP-30 with raster-condenser lighting system by the method of calibration curve.

The influence of different factors on fibrous material sorption property was studied by the example of iron ions. The choice of this element is stipulated by its considerable content in all natural and drinking waters. Fe (III) determination was carried out in the input and output solutions by spectrophotometric method (SP) with sulfosalicylic (2-oxide-5-sulfobenzonic) acid in the form of iron disulfosalicylate [7].

Degree of elements extraction is calculated according to the formula:

$$X = (1 - C/C_0) \cdot 100,$$

where: C_0 and C is metal concentration in solution before and after sorption, wt. %; X is the degree of extraction, %.

To determine total exchange capacity (TEC) air-dry sorbents of 5 g weight were placed into beakers of 100 ml volume, filled up with 50 ml 0,1 M of aqueous-alcoholic (1:1) solution of NaOH (to determine the capacity of cation exchanger) or with the same quantity of aqueous-alcohol solution of HCl (to determine the capacity

of anion exchanger). The obtained systems were left for a day to establish the equilibrium. After sorbent extraction from the solution, the latter was titrated with 0,1 M solution of HCl or with 0,1 M solution of NaOH in the presence of indicators of methyl orange or phenolphthalein, respectively.

The investigation of fibrous material structure was carried out by the method of IR-spectroscopy after their milling and comminution in a mortar with further pressing in tablets with KBr. Spectra were registered by the device IR-Fourier, spectrophotometer of «Nicolet 5700 FT-LR» type and «TRASSISSIONS» attachment.

Results and discussion

The investigation of extraction degree of metals ions from aqueous mediums of PP and PETP with sorbents showed (Table 1) that both fibrous materials possess approximately the same sorption property, which does not depend on polymer nature but defined by individual properties of the elements. It is seen that Al, Cr, Fe, Pb, Be are more completely extracted from the solution, i. e. those elements, which are capable of forming strong hydro complexes or slightly soluble hydroxides. They are multiply charged, as a rule, and possess higher polarization. The degree of metal ions extraction depends on stability constants of hydro complexes (Fig. 1).

Table 1. The degree of metal ions extraction from aqueous mediums with fibrous sorbents ($C_{intr.}=1 \cdot 10^{-3}$ wt. %; $n=3$; $P=0,95$)

Element	Hydro complexes content	lg K	Sorbent					
			PETP		PP with transverse diameter of fibers, mkm			
			Solved 10^4 , mac. %	X, %	Solved 10^4 , mac. %	X, %	Solved 10^4 , mac. %	X, %
Be	[BeOH] ⁺	7,5	2,0±0,2	80	3,2±0,5	68	0,80±0,09	92
Ca	[CaOH] ⁺	1,5	8,0±1,6	20	7,0±1,4	30	7,0±1,4	31
Mg	[MgOH] ⁺	2,6	7,6±1,2	24	7,5±1,4	25	7,0±2,0	30
Cu	[CuOH] ⁺	6,0	2,0±0,2	80	1,3±0,2	87	0	100
Zn	[ZnOH] ⁺	6,3	3,2±0,5	68	3,0±0,5	70	2,5±0,4	75
Cr	[CrOH] ²⁺	10,1	0	100	0	100	0	100
Co	[CoOH] ⁺	4,4	5,1±0,6	49	7,0±0,9	30	6,0±0,7	40
Fe	[FeOH] ²⁺	11,9	0,20±0,02	98	0	100	0	100
Ni	[NiOH] ⁺	5,0	3,2±0,5	68	2,5±0,5	75	1,5±0,3	85
Al	[AlOH] ²⁺	9,0	1,5±0,3	85	1,0±0,2	90	0,50±0,06	95
Pb	[PbOH] ⁺	7,5	2,7±0,4	73	2,5±0,5	75	2,0±0,3	80
V	[VO(OH)] ⁺	9,2	0,20±0,02	98	0,20±0,02	98	0	100

n is the number of parallel measurements; lgK is the logarithm of stability constant of hydro complexes, P is the confidence probability

In conformity with interaction type of adsorbate with adsorbent there are physical adsorption, chemical adsorption and ion exchange. In this case the ion-exchange mechanism of metal ions sorption is not excluded due to the presence in polymers carbonyl-containing groups of various types, including carboxyl ones, formed in the process of their thermal-oxidative degradation. But in this case, the materials should possess a certain exchange capacity. Determination of sorbents total exchange capacity showed that they possess insignificant capacity as cation exchangers (for PP it is

0,010 mmole-equ/g, for PETP it is 0,025 mmole-equ/g) which is obviously deficient to result in such a high polymers sorption property.

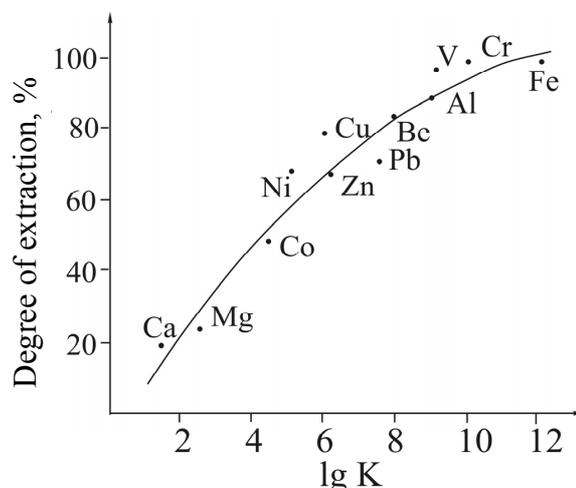


Fig. 1. Dependence of degree of metal extraction with fibrous sorbents from logarithm of their hydro complexes stability constant

Thermochemical modification of PP fiber was carried out in the paper to attach them hydrophilic properties and increase sorption property. Thermochemical oxidation was carried out with saturated solution of potassium permanganate in acid medium. Fiber modified in this way became more hydrophilic. It follows from the analysis of IR-spectra that any considerable changes have not occurred in structure of polypropylene fiber after its chemical treatment. Ketonic bunchings (1720 cm^{-1}) are still dominant and absorption in the field of valence vibrations of oxygen-containing groups (1707 cm^{-1}) increased slightly. However sorption property of modified sorbent (Table 2) decreased. It allows us to suppose that it is the presence of hydrophobic surface that plays the determining part in sorption process.

Table 2. Influence of PP fiber chemical modification on the degree of extraction of metal ions from aqueous mediums ($C_{intr.}=1 \cdot 10^{-3}$ wt. %; $n=3$; $P=0,95$)

Element	Polypropylene fiber			
	Unmodified		Modified	
	Solved, 10^4 mac. %	X, %	Solved, 10^4 mac. %	X, %
Cu	1,3±0,2	87	2,5±0,5	75
Zn	3,0±0,3	70	4,2±0,7	58
Cr	0	100	2,2±0,3	78
Co	7,0±0,8	30	8,0±0,9	20
Fe	0	100	1,3±0,2	87
Ni	2,5±0,5	75	4,2±0,7	58
Al	1,0±0,2	90	1,4±0,3	86
Pb	2,5±0,5	75	3,0±0,5	70
V	0,20±0,02	98	1,0±0,1	90

It should be noted that after transmission of solution containing metal ions through the column, filled up with the sorbent, coarsely dispersed sediment of poorly soluble salts is observed on the surface of polymer fibers. It is obvious that sedimentation occurs in sorption pro-

cess in spite of the fact that initial solutions are rather diluted. In the process of solution filtration through the hydrophobic fibrous material the complex system consisting of three phases: hydrophobic polymer, air, adsorbed on its surface and solution is realized. Probably, concentration of aquated metal ions inside sorbent porous system decreases near the phase boundaries «solution-hydrophobic element» and «solution-gas» owing to negative adsorption. Therefore, supersaturation occurs in the volume of solution and formation of nuclei of their poorly soluble compounds starts. Mature particles of new phase are adsorbed on polymer surface colliding with pores walls. In this case, ions concentration in the solution, passed through the sorbent, decreases. The decrease in degree of metal ions extraction with modified sorbent is the verification of proposed mechanism. Strengthening of hydrophilic properties due to the modification results in fibrous material depletion with air bubbles, decrease of concentration gradient on the boundary «solution-gas». In this connection, the probability of forming and further growth of critical nuclei decreases.

Air may influence sorption process as it is usually adsorbed on the surface of hydrophobic polymer. The investigation of PP fiber sorption property in vacuum environment (~1 Pa) and at air pressure (after system depressurization) was carried out with model solution of Fe(III), the content of which was determined in the input and output solutions by spectrophotometric method with sulfosalicylic acid (Fig. 2).

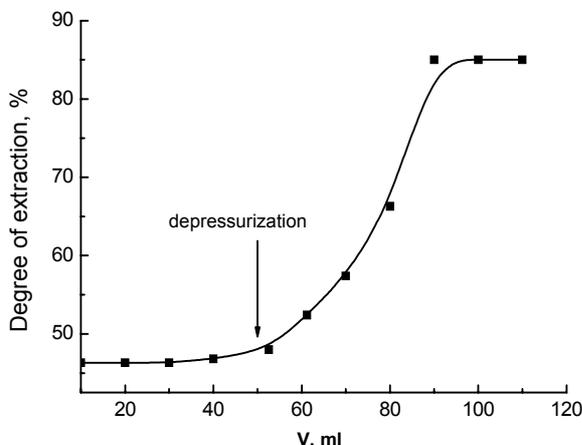


Fig. 2. The degree of Fe (III) ions extraction at pH 7,5 after column evacuation with sorbent and system depressurization

It is seen that in the case of column evacuation the degree of Fe (III) extraction decreases twice and at air introduction it increases and achieves maximum. Probably, weak dispersion interactions between metal ions and polymer, promoting the decrease of thickness of solution layer, depleted by ions, are nevertheless probable on the boundary surface «liquid-hydrophobic polymer». On the interface «solution-gas» there are no such interactions, and the size of the layer depleted by ions equals to the size of ion hydrate shell. Therefore, the solution is more supersaturated far from boundary surface in air presence that promotes forming critical nuclei.

Pores of different sizes and shapes are formed at laying fibrous material into a column. It defines the quantity of air, adsorbed with polymer, influencing the degree of metal ions interaction. The influence of sorbent laying density on its sorption property, which was investigated at model solution Fe (III), is presented in Fig. 3. The density of ? sorbent laying, occupying different volume at its equal weight, was determined by the formula:

$$\rho = m/V = m/\pi R^2 h,$$

where m is the sorbent weight, g; R is the column radius, sm; h is the height of sorbent layer, sm.

At sorbent free location in the column pores are too large, and formed particles of the new phase are not only adsorbed on its surface but pass partially to the filtrate. In this case the degree of extraction is not high. When sorbent is densified the size of pores decreases that is favorable for the occurrence of dispersion interaction between particles and polymer. The extraction degree increases, achieving maximum. Further densifying results in fibrous material air depletion that promotes decreasing concentration gradient on the interface «liquid-gas», and sorption property reduces.

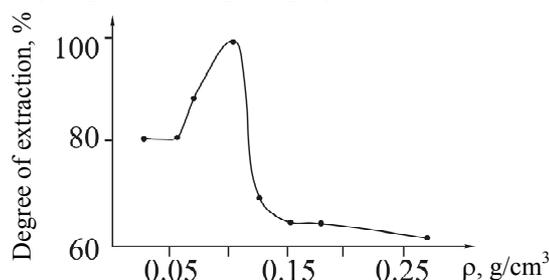


Fig. 3. Dependence of Fe (III) extraction degree on ? laying density of PP sorbent

The obtained experimental data indicate physical sorption mechanism. It should be expected that highly dispersed sorbent should possess higher sorption property. The data in Table 1 indicates this. It is seen that at decreased fiber thickness from 30 to 3 mkm more complete extraction of Ca, V, Zn, Pb, Ni ions is observed, and sorption of Be, Mg, Co ions increases.

Conclusion

Sorption property of metal ions from aqueous media with fibrous polymeric sorbents, made of thermoplastic material wastes, is studied by the methods of atomic emission spectroscopy and spectrophotometry. It is stated that in the presence of carbonyl containing groups of various type, including carboxyl ones, forming in the process of thermal-oxidative degradation, total exchange capacity of sorbents is small. Dependence behavior of extraction degree of metal ions from aqueous media (pH 6,5...7,5) on their hydro complexes stability, dispersity and density of fibers laying, degree of hydrophobic property, air presence in a sorbent indicate primary physical sorption mechanism. At contact of solution with polymer hydrophobic surface, where air is adsorbed, the occurring concentrations gradient on the interfaces «solution-gas» and «solution-polymer» pro-

motes forming and further rising of solid phase. As a result, the coarsely dispersed deposit of poorly soluble salts is extracted on the surface of polymer fibers, and ions concentration in the solution, passed through the sor-

bent, decreases. Due to this fact the hydrophobic fibrous polymeric materials may be used for water and drains purification from metal ions. They are cheap, available, and capable of regeneration and may be easily utilized.

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TECHNOLOGICAL AND HYGIENE-SANITARY ASPECTS OF USING BIOLOGICALLY PURE PROCESS WASTE WATER IN THE SYSTEMS OF TECHNICAL WATER SUPPLY

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According to sanitary-toxicological factors biologically purified waste water of chemical enterprise are referred to low-toxic substances, are not allergens, do not possess irritant action on mucous tunics and skin and are suitable for recycling water system makeup. Crucial factors of reusing these waters are their corrosive activity, susceptibility to mineral salt accumulation and bioaccretion.

The systems of industrial water supply and water draining of industrial enterprises influence negatively both directly and indirectly the environment. It concerns both water diversion capacity from natural water sources and their contamination with sewage water. Therefore, such systems should operate according to the requirements of environmental control [1]. Measures in environmental control, water resources conservation [2] and environmental safety support should be provided. Industrial water supply should stipulate maximal rotation of process sewage water for water losses compensation [3]. Biologically purified sewage water (BPSW) is one of the sources of water compensation in the systems of industrial water supply at chemical and by-product coke enterprises [4, 5]. The possibility of BPSW using is based on the conformity principle of used water quality to the conditions of its further application. This principle demands the choice of industrial water supply system, where BPSW will be used, and the range of factors both of technological and hygiene and sanitary character should be taken into account.

Service water systems may be direct-flow and reverse according to the mode of water use. The direct-flow

systems propose single water use with further purification of contaminated sewage water before its discharge into municipal sewage or surface reservoirs. Such technology of using water, quite often high-quality drinking one, is not only wasteful, but also potentially harmful for the most part of population. The direct-flow water use for industrial water supply is permitted only at justification of unreasonableness of reverse water supply systems or impossibility of their creation.

The reverse systems are divided into local, centralized and mixed. At local systems water is used after reduction (regeneration) in one or several technological processes. At centralized water supply water passes the purification in a single flow and returns to the production after being used for different purposes. At mixed water supply water of one reverse system is used in another one (water of cooling system is used in technological one; water of technological system is used in transporting one etc.).

There are technological, transporting and cooling service water systems according to the character of water use in the technological processes. At technological system operation, and in some cases at transporting system