

Hygienic Efficiency of Treatment Strongly Polluted Industrial Waste Water Using Fibrous Ion-Exchange Materials

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Abstract – The paper analyzes polymer fibrous ion-exchange materials on the basis of polyacrylonitrile matrix released as KN-1 cation exchanger and AS-1 and AN-1 anion exchangers. The purpose is to study the sorption properties of the specified materials in relation to multicomponent salt solutions of heavy metals. According to obtained results, the exchange processes are characterized by high speed, and materials – by high exchange capacity. The cascade filtration purifies heavily polluted industrial waste waters to the levels of 10^{-3} mg/l of Pb (II), Zn(II), Cd (II), Cu(II), Mo(VI), W(VI) thus fully satisfying hygienic requirements. The advantages of the studied materials include low flow resistance, a possibility of repeated regeneration (with acid and alkali) with desorption of valuable components and creation of waste-free or low-waste technologies on their basis.

Keywords – AN-1 anion exchanger; AS-1 anion exchanger; ions of heavy metals; KN-1 cation exchanger; industrial waste waters; sorption purification of waters.

I. INTRODUCTION

Production and processing of nonferrous metal ores are accompanied by the formation of large pits, mines and wells with further leaching reactions of non-ferrous metals under the influence of atmospheric precipitation or underground waters. Since industrial waste mine and pit waters are not usually exposed to purification, salts of toxic metals in concentrations exceeding the maximum permissible levels may get into open reservoirs in the areas of ore extraction [1, 2]. At present, modern industrial waste treatment technologies include several consecutive stages. The initial phase includes reactant treatment of polluted solutions by salts of calcium, iron or aluminum in alkaline environment. The formed slightly-soluble hydroxides of heavy metals deposit, and ions remained in the solution partially codeposit on the surface of amphoteric sludges of iron and aluminum [3]. The advantages of this processing method include the possibility of purifying large volumes and low cost excluding expensive reagents and equipment. The main disadvantage of this method is insufficient level of purification of solutions, in which the cleaned components can remain at the levels of hundreds milligrams per liter, which contradicts hygienic requirements. In this regard, chemical methods are combined with physical-chemical ones. Electric coagulation with ultrafiltration and electroosmosis are the most progressive of them [4]. The

advantages of such methods include deep purification, wide range of equipment available in the modern market, possibility of creating closed production cycles. The main restriction to their use is high cost of processes. The alternative to the specified methods of waste water detoxication are the sorption methods allowing removing pollutants from solutions to the values fully satisfying sanitary and hygienic requirements [5]. The advantages of chemical sorption methods include cost efficiency, availability of raw material base, high storage potential of new materials [6]. However, some sorbents described in scientific literature have essential disadvantages, such as the impossibility of regeneration, instability to hostile environment, difficulties of automation of waste water detoxication [7]. A significant restriction to a wide use of some highly effective sorbents is the form of production – granules or powder [8]. This may define insufficient working surface or high resistance to purified flow, respectively. In this regard nonwoven polymer ion-exchange fibers with developed surface and low hydraulic resistance are the most progressive.

Russia has mastered the production of polymer fibrous ion-exchange materials – weak-acid cation resin KN-1, strong base anion-exchange resin AS-1 and weak base anion-exchange resin AN-1 [9]. The specified materials are characterized by increased chemical resistance in wide pH ranges containing strong oxidizers and their ability to maintain the repeated cycles “sorption-regeneration” without losing initial absorbing and strength characteristics. The form of production of chemisorbents as nonwoven cloth ensures simple engineering solutions in terms of their assembly in the form of frame-type filter press installed on the way of a purified flow. The study of the main characteristics of new progressive sorption materials is relevant since it allows proving hygienic efficiency of their use to increase nature management safety and recommending sorbents for practical introduction.

II. METHODS AND MATERIALS

Sorption characteristics of ion-exchange materials were studied in laboratory conditions using synthetic solutions containing salts of heavy metals. The solutions were prepared from Sigma-Aldrich or Fluka reactants on distilled water. The required pH value was established through titration of 0.01 N HCl or NaOH solutions with terminal point control using a universal ionomer – Akvilon I510 (Russia). The sorption

processes were analyzed via atomic-absorption spectrometer with electrothermal atomization of sample using QUANT.Z-ETA device (Cortec Corp, Russia).

The sorption processes were studied in dynamic mode. For this purpose, the filtering sample weighing 1 g was placed in a glass funnel and the purified solution was passing through it with a speed of 100 ml/min. The temperature was maintained in the range of 20±1 °C throughout the entire process.

Fibrous polymer ion-exchange materials on the basis of polyacrylonitrile developed in NPO Khimvolokno (Mytishchi) were used as sorbents. They are produced as KN-1 cation exchanger and AS-1 and AN-1 anion exchangers (Fig. 1).

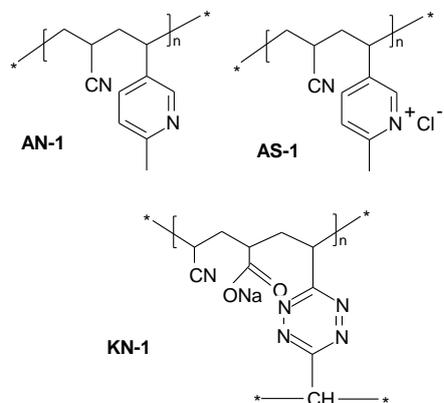


Fig. 1. Elementary links of polymer ion-exchange materials

Regeneration of KN-1 was carried out by dynamic washing with the small volume of 1-2% solution of mineral acid (salt), and then with 1-2% alkali solution (to restore initial properties). For AS-1 and AN-1 the sequence of washing was reverse (alkali, acid).

The study was conducted at technical facilities of the F.F. Erisman Federal Scientific Centre of Hygiene of the Federal Service for Consumer Rights and Human Welfare Protection (Mytishchi) and the North Ossetian State University named after K.L. Khetagurov (Vladikavkaz).

III. RESULTS

The study of sorption characteristics of polymer sorbents revealed their high efficiency in terms of purification of multicomponent heavily polluted water solutions (Table 1).

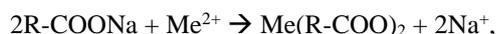
The studied sorbents have high storage potential in relation to salts of heavy metals being priority pollutants of industrial waste waters at non-ferrous smelters. Weak-acid cation resin KN-1 ensures the decrease of ions of lead, zinc, cadmium and copper by 55-73% after the first stage of purification. This sorbent showed the highest affinity to lead ions, which are defined as the main pollutants of industrial waste waters of plants processing sulphide polymetallic ores [10]. After the sixth stage of purification the metals reveal at the level of microconcentration thus satisfying hygienic requirements to waste waters discharged to open reservoirs.

The content of toxic metals in industrial waste water of tungsten-molybdenum industry varies widely [11, 12] causing high risks for human health in view of increased accumulative ability of elements in plants [13, 14]. The state of metals in the form of anions defines the efficiency of their use for sorption purification of anion exchangers. The use of strong base anion-exchange resin AS-1 decreases WO_4^{2-} and MoO_4^{2-} content to safe levels after the sixth stage of ion-exchange purification. In relation to the specified elements the weak base anion-exchange resin AH-1 was more efficient. The table shows that the first stage of filtration through AH-1 decreases tungsten by 76% and molybdenum by 63%. The possibility to reduce the content of metals to trace quantities is obvious upon the completion of the third stage of sorption.

TABLE I. CHARACTERISTICS OF WATER SOLUTION TREATMENT FROM TECHNOGENIC POLLUTANTS WITH POLYMER FIBROUS MATERIALS

Initial solution (mg/L)	Treatment phase (mg/L)						pH	Sorbent
	I	II	III	IV	V	VI		
Pb ²⁺ 200	110	49	11	2.4	0.9	0.001	6.0	KN-1
Zn ²⁺ 200	118	59	19	5.0	1.4	0.005		
Cu ²⁺ 200	130	62	21	6.1	1.6	0.004		
Cd ²⁺ 200	145	70	27	7.2	1.4	0.003		
WO ₄ ²⁻ 100	64	42	19	2.8	0.9	0.004	7.5	AS-1
MoO ₄ ²⁻ 100	69	44	17	2.9	0.8	0.005		
WO ₄ ²⁻ 100	24	1.7	0.92	0.001			3.0	AN-1
MoO ₄ ²⁻ 100	37	3.8	1.14	0.005				

The processes of ionic exchange of sodium of the carboxyl group by one of the heavy metals (Me²⁺) form the basis for sorption recovery of metals with KN-1 cation exchanger:



as well as donor-acceptor interaction of nitrogen atoms of the nitrile group and tetrazine ring. The transfer of free (lone) pair from nitrogen into d-vacant orbitals of transition metals ensures strong deduction of pollutants on a sorbent matrix, thus making the size of sorption exchange capacity exceeding

stoichiometric calculations for sodium atoms being part of a carboxyl radical.

The processes of transfer of electron pair from nitrogen forming the nitrile group and pyridine form the basis for ion-exchange mechanism of AH-1 and AS-1 anion exchangers, where the lack of shielding from chlorine ensures higher sorption capacity of AH-1 in comparison with AS-1.

The hygienic interest in heavy metals presented in the table is caused by the fact that the problem of environmental pollution is particularly important in certain regions of the

Russian Federation (in particular – in the Republic of North Ossetia with multiple enterprises of zinc-lead and tungsten-molybdenum industries) and in the world in general. It is caused both by physical and chemical properties of pollutants and their toxic effects on living organisms. Water pollution results in contamination of soil horizons where heavy metals can persist for several hundreds of years. This is defined by the lack of natural mechanisms of their biodegradation and high bioavailability for floral forms. The translocation of xenobiotics into plants and their subsequent migration along food chains causes high risks of food pollution. Continuous interest of the scientific community in the problem of pollution of natural and anthropogenically transformed landscapes by heavy metals is identified in biological media of a person [15]. Industrial enterprises and motor transport may be the sources of pollutants. Thus, in large cities the lead content in blood of children in some cases increases to 45 mkg/dl (at recommended acceptable levels of 5 mkg/dl) [16], which is the reason for mental pathologies and requires compulsory preventive antidotal procedures [17].

The bans on the use of ethylated lead as an additive to fuel decreases the volumes of its introduction into the habitat. However, the recirculation of toxicants in environmental objects subject to technogenic pollution defines the relevance of the problem and the need for its solution. In this respect high sorbing ability of studied materials – KN-1 cation exchanger – can be used to decrease toxic compounds of lead in industrial cities. The efficient measures include the installation of filtering ion-exchange cloths in places of melt, storm and drainage waters, mainly in areas with the maximum chemical risk of pollution. Repeated cycles of heavy metals detoxication from water objects will allow gradually reducing the content of pollutants in water and soil thus improving health and safety.

The example of lead illustrates the overall threat of thiol poison to human health. For certain regions the most relevant problem is pollution with cadmium compounds, which in the conditions of chronic intoxication of residents in Japan from the prefecture Toyama caused new nosologic unit – Itai-Itai disease characterized by osteomalacia, hypotrophy of muscular tissue, acute renal failure [18]. In case of chronic intoxication, tungsten salts increase the risks of leukemia, and the authors of article [19] make a conclusion, according to which long intake of low doses of an element by a human body poses bigger threat to human health than acute metal poisoning.

Despite the fact that zinc, copper and molybdenum are essential micronutrients, their presence in a human body in dosages exceeding daily requirement poses the threat of toxicosis caused by the inhibiting effect of metals on enzyme systems, activation of lipid peroxidation, disorder of the main organs and systems of an organism [20].

The advantage of the proposed solution to the hygienic problem of industrial waste water pollution with polymer chemisorbents is the possibility of reusing the filter-concentrated metals. For this purpose, there is a need to process the cation exchanger with 1-2% solution of mineral acid (salt or sulfuric) and anion exchanger – with 1-2% solution of alkali or soda. The variation of the volume of washing phase opens prospects of trace pollutant concentration to the values

satisfying the criteria of technological solutions. We studied the possibility of increasing the concentration of metals in washing solutions up to 10-40 g/l. This gives the possibility of using the received solutions at initial stages of technological processing, which forms the basis for waste-free (low-waste) technologies.

IV. CONCLUSION

The experimentally proved possibility of purifying multicomponent water solutions from priority pollutants of mining and processing enterprises to the levels satisfying hygienic requirements serves a scientific justification for recommendations on their introduction to nature protection practice thus decreasing pollution of environmental objects with heavy metals and enhancing the security of human health.

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