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Synthesis of Anion Exchange Materials based on Acrylonitrile

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Abstract: Synthetic polymeric sorbents are characterized by high physical and chemical stability and heat resistance; they are relatively inert and hydrophobic which makes them highly sought in water treatment and hydrometallurgy. However, this substance is costly. Therefore, it is necessary to develop the main stages of industrial synthesis of high-capacity low-basic anion exchangers based on acrylonitrile which is the purpose of this study. The study investigates the synthesis and properties of anion exchangers based on acrylonitrile for use in water treatment and the conditions of the copolymerization reaction which increases the yield and quality of the conditioned copolymer. Samples of anion exchangers with high capacity and osmotic stability characteristics were obtained by aminolysis of nitrile groups in the synthesized copolymers. The study developed regimes of anion exchangers with better quality characteristics than those of similar sorbents.

Key words: Ion exchangers, anion exchangers, ion exchange, water treatment, similar sorbents, hydrophobic

INTRODUCTION

Over the past decade, the global range of ion exchangers has been significantly updated by the production of high-capacity low-basic anion exchangers and carboxylic cation exchangers with a homogenous grain size composition (Nachod and Schubert, 2013; Rieman and Walton, 2013; Liguori *et al*., 2015). Ion exchangers are widely used in the power industry in the treatment of heat transfer agents and other water media (Bulata *et al*., 2016; Cheng *et al*., 2017; Tanaka, 2015). A significant part (about 18%) of the modern range of such materials comprises of sorbents based on derivatives of acrylic and methyl-acrylic acid with high capacity and osmotic stability characteristics (IERM, 2014; TGAF, 2015). They can be applied for sorption in static and dynamic conditions, regenerated and reused. In addition, polymeric sorbents are generally characterized by high sorption capacity in respect to various classes of compounds (Vlakh *et al*., 2013; Tao and Fletcher, 2013; Vidal *et al*., 2015). The main manufacturers such as Dow Chemical, Rohm and Haas, Lanxess, etc., supply products that are characterized by high prices and quota allocation to the Russian market which necessitates the development of a Russian counterpart with similarly good characteristics that would also be more cost-efficient. The demand of the Russian industry for synthetic polymeric sorbents used in water treatment and hydrometallurgy necessitate the design of new efficient ion exchange materials and the organization of their mass production on a modern industrial basis.

Aim of the study: This study aims to develop the main stages of industrial synthesis of high-capacity low-basic anion exchangers based on acrylonitrile which have become widely used in water treatment and hydrometallurgy involving nonferrous and rare metals.

MATERIALS AND METHODS

In order to achieve the set aim, we studied the synthesis of high-capacity low-basic anion exchangers based on acrylonitrile copolymers with DVB and MMA with simultaneous determination of the main properties of synthesized anion exchangers.

The copolymer was synthesized according to the known method (EPO, 2008, 2010, 2013) in a Scheidt globe equipped with a stirrer, thermometer and backflow

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Table 1: Synthesis conditions and properties of low-basic anion exchanger samples

	Sample number								
Index	1	2	3	4	5	6	7	8	9
Copolymerization mixture composition in mass (%):									
Divinylbenzene acrylonitrile methyl	15.0	15.0	15.0	20.0	20.0	20.0	20.0	20.0	20.0
methacrylate	80.0	80.0	80.0	75.0	75.0	75.0	75.0	75.0	75.0
	5.00	5.00	5.0	5.00	5.00	5.00	5.00	5.00	5.00
Blowing agent content in mass (%):	IO 15	PB-3, 15	PB-3, 20	IO 15	PB-3, 10	PB-3, 15	IO 20	PB-3, 20	PB-3 20
Amination reagent; Di Ethylene Tri Amine (DETA)									
Static Exchange Capacity (SEC) (mg eq/cm^3)	3.30	3.45	3.65	2.90	2.85	3.05	3.20	3.30	3.25
Dynamic exchange capacity (DEC) (mg eq/cm^3)	1850	1975	2010	1860	1980	2160	2295	2330	2300
Osmotic stability (%)	99.0	99.0	99.0	99.0	99.0	99.0	99.0	99.0	99.0
Swelling ratio	1.55	1.50	1.55	1.40	1.40	1.45	1.40	1.45	1.40
Mechanical strength (%)	98.0	99.0	99.0	98.0	98.0	99.0	98.0	99.5	99.0

condenser. The content of acrylonitrile was 75-80 mass%, DVB-15-20.0 mass(%), methyl methacrylate not more than 5.0 mass(%). The compositions of polymeric mixtures used in the experiments are indicated in Table 1. The initial content of divinylbenzene in the crude product was 56.8 mass%. About 4 mass(%) of benzoperoxide was used to initiate radical reactions. The blowing agent was Iso Octane (IO) and the PB-3 solvent (Leading Research and Development Institute for Chemical Technologies JSC, Moscow). The organic to aqueous stage ratio during copolymerization (O:A) was 1:3. The reaction was conducted with constant stirring and at a temperature of 85°C for 10 h including the stages of stage heating and cooling of the stock.

RESULTS

Acrylonitrile was chosen as the main monomer for obtaining a polymeric matrix because several companies that produce it are located in Russia and Belarus on the one hand and due to the high technical parameters of sorbents based on copolymers of Acrylo Nitrile (AN) with Di Vinyl Benzene (DVB) and Methyl Meth Acrylate (MMA) on the other hand.

The synthesis of a high-quality product with high yield and competitive technical characteristics is only possible during the intermediate stage of the respective polymeric matrix. Therefore, the first design stage of anion exchangers based on acrylonitrile involved tests of copolymerization regimes for AN, DVB and MMA in the presence of benzoyl peroxide and various blowing agents. These results were syntheses of a series of porous cross-linked copolymers after their aminolysis with Di Ethylene Tri Amine (DETA), samples of final anion exchangers were obtained and their sorption and strength properties were determined.

The synthesis of the end anion exchanger was conducted based on the amination reaction of copolymers with Di Ethylene Tri Amine (DETA) in the presence of elementary sulfur as the catalyst for 10 h at a temperature of 120-140°C. The isolated product was analyzed according to known methods (GOST 20301-74, GOST 20255.1-89, Industrial Standard 95.291-86 and All-Russian Thermal Engineering Institute Organization Standard 37.002-2005) to determine its technical characteristics. The obtained results are presented in Table 1.

The study found that the best result of copolymer synthesis was achieved when using a dispersion medium based on Modified Carboxy Methyl Cellulose (MCMC), brand name PB-3 and a 20% ammonium chloride solution. Aggregations did not form in any cases when this dispersion medium was used. The use of starch, Carboxy Methyl Cellulose (CMC) and Methyl Hydroxy Ethyl Cellulose (MHEC) did not allow obtaining the required copolymer with stable quality parameters.

DISCUSSION

The key's conditions for the synthesis of a high-quality AN-DVB copolymer are the choice of the dispersion medium, composition of the copolymerization mixture and the choice of the blowing agent. One of the reasons behind the obtainment of substandard copolymers is the formation of coalescent copolymer grains (aggregates). Due to the high water solubility of AN, part of it transitions from the reaction zone to the aqueous phase and polymerizes therein with a formation of a polyacrylonitrile homopolymer. At that, the share of substandard product (aggregates) obtained during the reaction increases in proportion to the amount of polyacrylonitrile formed. In order to counteract this phenomenon, it is necessary to block the transition of acrylonitrile to the aqueous stage by reducing its solubility in an aqueous dispersion medium. The criterion for assessing the effectiveness of the dispersion medium

(a)

(b)

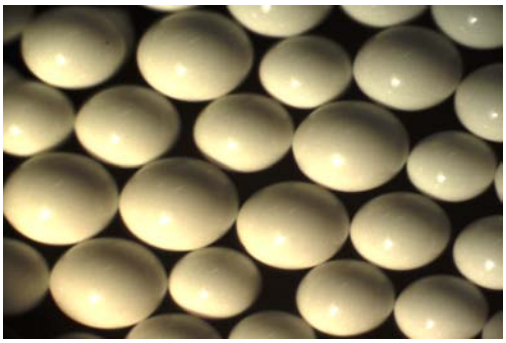

Fig. 1: Grains of the copolymer of acrylonitrile divinylbenzene: a) the anion exchanger based thereon and b) when using a dispersion medium based on an aqueous solution of ammonium chloride and modified carboxymethyl cellulose

for the copolymerization reaction of AN and DVB was the maximum possible yield of the copolymer with grains of regular spherical form.

The obtained copolymer consisted of even white spherical grains without aggregates (Fig. 1). A series of nine experiments showed good repeatability of the results.

Thus, the optimal emulsion stabilizer during the copolymerization of acrylonitrile and divinylbenzene is MCMC. Using it in combination with an aqueous salt solution of ammonium chloride enabled achieving a high yield of a high-quality copolymer without any aggregation whatsoever.

After washing and removal of the blowing agent, the copolymer samples were subjected to an amination reaction with DETA in accordance with the abovementioned method. This produced 9 samples of high-capacity low-basic anion exchangers based on copolymers of AN with DVB and MMA. Experimentally measured characteristics of obtained anion exchangers which were presented in Table 1, showed that the conduction of a follow-up amination reaction enabled

Table 2: Technical characteristics of low-basic anion exchangers based on acrylic matrices

Anion exchanger brand (manufacturer)	DEC (mg eq/cm^3)	Osmotic stability (%)
Purolite A 830 and A 830 W (Purolite USA)	1450-1690	99.0-100.0
Relite MG-1 (Resindion S.P.L Italy)	2470-2500	99.8-100.0
Amberlite IRA 67 (Rohm and Haas USA)	1450-1500	99.0-100.0
Synthesized anion exchanger samples No. 7-9	2290-2330	99.0-99.50

synthesizing samples of low-basic anion exchangers with indices of Dynamic Exchange Capacity (DEC) of 2300-2330 mg eq/cm^3 and osmotic stability and mechanical strength of at least 99.0%.

The comparative analysis of the technical characteristics of synthesized anion exchanger samples and the most widely used industrial anion exchangers made by various foreign manufacturers (Table 2) showed that the technical characteristics of obtained anion exchange sorbents exceeded those of foreign counterparts while being inferior only to the record capacity indices of the Relite MG-1 anion exchanger (Resindion SPL, Italy).

CONCLUSION

This study developed conditions for the synthesis of copolymers AN with DVB and MMA in the presence of a blowing agent based on MCMC-PB-3 which are an initial matrix for further synthesis, based on the aminolysis reaction with DETA of high-capacity low-basic anion exchangers based on the derivatives of acrylic and methyl-acrylic acids. The developed anion exchanger synthesis regimes are a basis for the creation of the Russian industrial technology of efficient anion exchanger synthesis technology for water treatment and hydrometallurgy of nonferrous and rare metals. In terms of their sorption and strength characteristics, the synthesized samples surpass the sorbents of most leading foreign manufacturers.

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