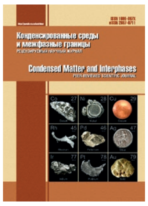

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The influence of acid activation of bentonite in the composition of a bipolar membrane on the characteristics of the electrodialysis conversion of sodium sulphate

S. I. Niftaliev[1], O. A. Kozaderova[1], K. B. Kim[1✉], P. E. Belousov[2], V. V. Krupskaya [2], A. V. Timkova[1]

*[1]Voronezh State University of Engineering Technologies,
19 Revolutsii pr., Voronezh 394036, Russian Federation*

*[2]Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry of the Russian Academy of Sciences,
35 Staromonetny per., Moscow 119017, Russian Federation*

Abstract

The effect on the characteristics of the electrodialysis process of the acid activation of bentonite included in the cation-exchange layer of an experimental bipolar membrane obtained by applying a liquid LF-4SK cation-exchange layer containing bentonite particles onto an anion-exchange membrane-substrate MA-41 was studied.

Acid activation of bentonite was carried out with nitric acid (C = 1 and 4 mol/dm^3) for 6 hours at temperatures of 20 and 90 °C. The conversion of sodium sulphate (C = 0.5 mol/dm^3) was carried out in a six-section electrodialysis apparatus with experimental bipolar membranes containing bentonite in its original form and after acid activation. It has been shown that the addition of bentonite treated with nitric acid (C = 4 mol/dm^3, t = 90 °C, τ = 6 h) to the cation-exchange layer of a bipolar membrane leads to an increase in productivity, current efficiency and a decrease in energy costs compared to a membrane containing bentonite in its original form.

Experimental bipolar membranes made on the basis of MA-41 and a liquid sulphonic cation exchanger containing acid-activated bentonite clays make it possible to obtain an acid and alkali performance comparable to that of the MB-3 bipolar membrane.

Keywords: Electrodialysis, Bipolar membrane, Acid activation, Bentonite, Sodium sulphate, Acid, Alkali

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✉ Ksenia B. Kim , e-mail: kmkseniya@yandex.ru

1. Introduction

Electrodialysis with bipolar membranes is a technology for the production of acids and bases without the formation of secondary by-products and the use of additional chemicals [1-4]. The efficiency of the electrodialysis process is largely determined by the electrochemical characteristics of the used bipolar membranes [5–7]. Catalytic additives of various nature are introduced into the bipolar region of the membrane, which affect the dissociation of water molecules for the improvement of their properties [8–16]. There are data that silicate and hydroxyl groups are effective catalysts for water dissociation in the bipolar region [17–18]. The addition of particles of clay material to a bipolar ion-exchange membrane allows obtaining a nanocomposite with improved characteristics [19–21], due to the peculiarity of the structure and composition of clay, as well as the presence of such properties as hydrophilicity and the ability to ion exchange. The chemical activation of clay is carried out for the improvement of the properties, for example, treatment with sodium or calcium salts [22], as well as thermal activation [23]. Among various methods, acid treatment is the most effective way to activate the surface and increase its specific area, which occurs as a result of the modification of the components of bentonite clays, primarily montmorillonite and other clay minerals [24–26].

The aim of this study was the investigation of the effect of acid activation of bentonite in the composition of an experimental bipolar membrane on the characteristics of the electrodialysis conversion of sodium sulphate.

2. Experimental

An experimental ion-exchange bipolar membrane was obtained by applying a liquid sulphopolymer LF-4SK layer containing bentonite particles onto an MA-41 anion-exchange membrane according to a well-known method [27]. In this study, bentonite from the Trebia deposit (Morocco) was added to the cation-exchange layer of the membrane (Fig. 1). The sample of natural bentonite consists of 76% smectite and the following impurities: 5% illite, 5% quartz, 21% feldspar, 2% calcite [26]. Smectite is represented by alkaline montmorillonite with a predominance of sodium cations in the interlayer, the main charge is localized in the octahedral layer.

For acid treatment of bentonite, nitric acid of various concentrations was used (1 and 4 mol/dm^3), the process was carried out with constant stirring at temperatures of 20 and 90 °C. Next, the solid phase was washed with distilled water to a neutral pH value and dried at 60 °C to constant weight.

The study considers four types of experimental bipolar membranes, in the cation-exchange layer of which bentonite (3% by mass) is added:

– $MB_{MAR.\ ORIG}$ – original bentonite;

– MB_{MAR1} - bentonite processed under the following conditions: $C(HNO_3)$ = 1 mol/dm^3, t = 20°C, τ = 6 h;

– MB_{MAR2} -$C(HNO_3)$ = 1 mol/dm^3, t = 90 °C, τ = 6 h;

– MB_{MAR2} - $C(HNO_3)$ = 4 mol/dm^3, t = 90 °C, τ = 6 h.

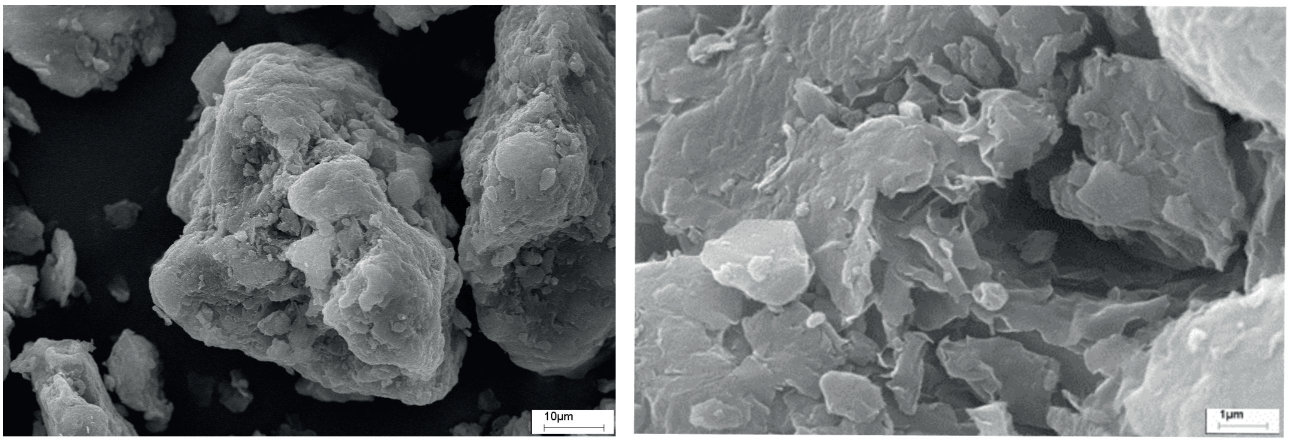


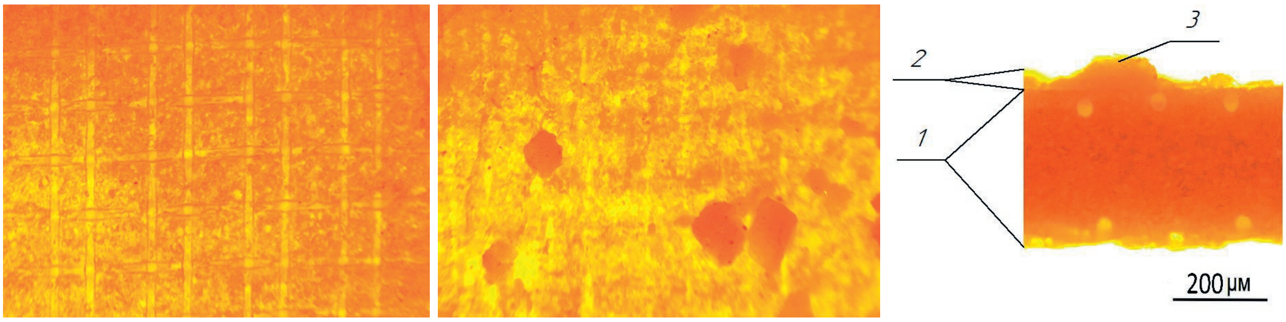
Fig. 1. Images of the surface of an air-dry sample of bentonite (Trebia deposit, Morocco), obtained by scanning electron microscopy (LEO 1450VPCarlZeiss) at different magnifications

Images of the surface and section of the experimental bipolar membrane with bentonite particles were obtained using a Levenhuk 625 optical microscope (Fig. 2).

The properties of experimental ion-exchange membranes were studied during the electrodialysis of sodium sulphate solution (0.5 mol/dm^3) and compared with the best domestic bipolar membrane MB-3 (UCC Shchekinoazot), with the lowest electrical resistance during operation [28].

The studies were carried out in a six-section flow type electrodialysis cell (Fig. 3) consisting of the studied bipolar membrane, heterogeneous cation- (RalexCMH-PP) and anion-exchange (Ralex AMH-PP) membranes manufactured by MEGA (Czech Republic) [29].

The concentration of acid and alkali obtained during the conversion of sodium sulphate was determined by acid-base titration. The efficiency of the electrodialysis process (fluxes of hydrogen and hydroxyl ions generated inside the bipolar membrane, J, mol/(cm^2·s); current efficiency η, %; specific energy consumption for the production



a b c

Fig. 2. Photographs of membranes (optical microscope Levenhuk 625): a – surface of the anionic membrane of the MA-41 substrate; b – surface of the cation-exchange layer with bentonite particles; c – experimental bipolar membrane (1 – membrane-substrate, 2 – cation-exchange layer, 3 – particle of bentonite clay on the surface of the cation-exchange layer)

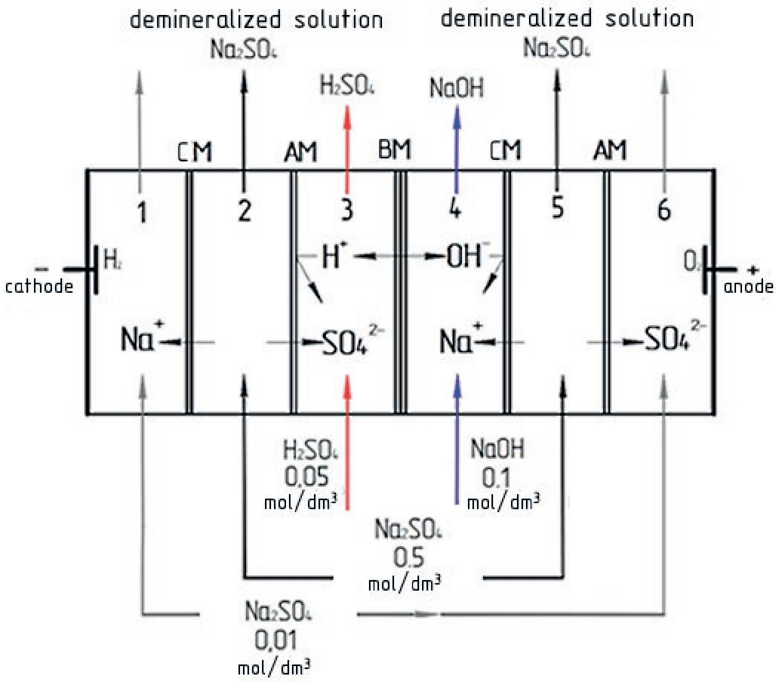


Fig. 3. Scheme of the flow of ions in the chambers of the electrodialysis cell during the conversion of sodium sulphate (C = 0.5 mol/dm^3): CM – a cation exchange membrane, AM – an anion exchange membrane, BM – a bipolar membrane

of the target product W, kWh/kg) was calculated using the following formulas:

$$J_i = \frac{(C_0 - C_i)\cdot V}{\tau \cdot S}, \tag{1}$$

$$\eta = \frac{\left(C_0 - C_i\right)\cdot V \cdot F}{\tau \cdot I}\cdot 100, \tag{2}$$

$$W = \frac{I \cdot U \cdot \tau}{m}, \tag{3}$$

where C_0 is initial concentration of the solution, mol/dm³; C_i is concentration of ions in the studied section, mol/dm³; V is solution volume, dm³; F is Faraday number A·s/mol; τ is time, s; I is current, A; U is voltage, V; m is the mass of the product, kg.

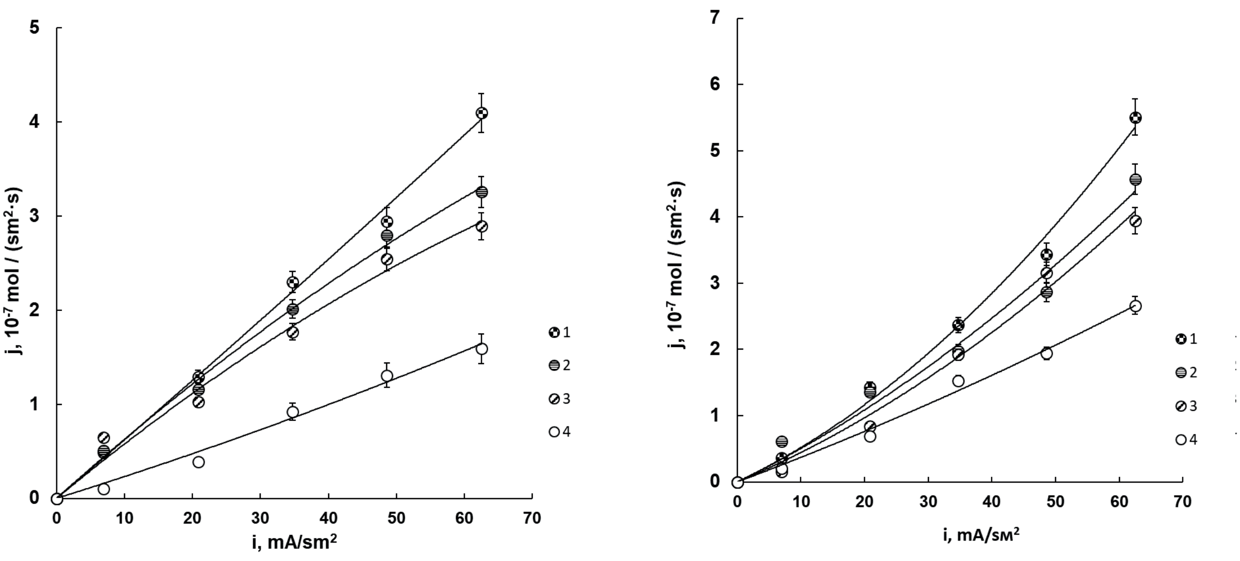
3. Results and discussion

The obtained experimental results (Fig. 4) allow us to conclude that the acid activation of bentonite introduced into the bipolar membrane led to an increase in the flux of H^+ ions by 2.5 times, and the flux of OH^- ions increased by 2.1 times.

The addition of acid-treated bentonite to the cation-exchange layer of the bipolar membrane also led to a reduction in energy costs (Fig. 5).

Bipolar ion exchange membranes containing acid-activated bentonite (MB_{MAR3}), in terms of performance and current efficiency are not inferior to industrial MB-3 samples [3] (Table 1).

The obtained results can be explained by the significant changes in the composition and structure of montmorillonite which occur



a b

Fig. 4. Dependence of the fluxes of H^+ (a) and OH^- (b) ions generated in a bipolar membrane on the current density for experimental samples: *1* – MB_{MAR3}, *2* – MB_{MAR2}, *3* – MB_{MAR1}, *4* – $MB_{MAR.ORIG}$

Table 1. Characteristics of the process of sodium sulfate conversion during electrodialysis with MB-3 and experimental membranes (at current density i = 60 mA/cm²)

	H_2SO_4		NaOH	
	P, mol /m²·h	η, %	P, mol /m²·h	η, %
$MB_{MAR.ORIG}$	2.91±0.29	25.01	9.58±0.96	41.11
MB_{MAR1}	5.24±0.52	44.70	16.46±1.65	60.89
MB_{MAR2}	5.90±0.59	50.30	14.19±1.42	70.58
MB_{MAR3}	7.43±0.74	63.10	19.82±1.98	85.02
MB-3[3]	6.93±0.69	59.21	18.10±1.81	77.10

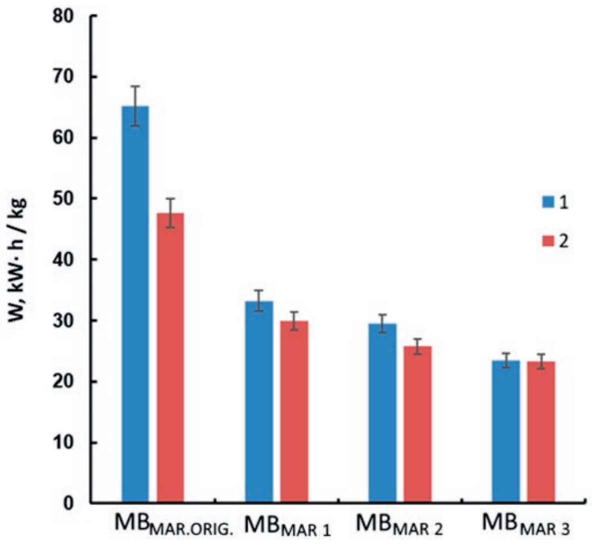


Fig. 5. Energy costs for obtaining the target product (at current density i = 60 mA/cm^2): *1* – H_2SO_4, *2* –NaOH

during acid activation. The content of alumina in the sample decreased from 23.3 to 7.6%, the content of magnesium oxide decreased from 2.4 to 0.5%, and the content of silica increased from 59.5 to 80.22% [26]. This was due to the replacement of interlayer cations by oxonium ions, leaching of octahedral cations, and partial resolution of layer 2:1 and, as a consequence, the formation of amorphous silica [26]. Also, after acid treatment, the average size of aggregates of clay particles decreased from 270 to 150 nm [26]. The specific surface area increased from 26 to 78 m^2/g, on the one hand, due to an increase in the proportion of amorphous silica, on the other hand, due to surface modification and an increase in microporosity (the total pore volume increased from 0.431 to 4.397 cm^3/d) [30]. Thus, the improvement in the characteristics of electrodialysis using bipolar membranes containing acid-activated bentonite is associated with an increase in bentonite catalytically active with respect to the water dissociation reaction of silicon groups and, possibly, an improvement in the dispersion of bentonite clay particles in a liquid sulphopolymer.

4. Conclusions

The conducted studies have shown that the addition of acid-activated bentonite to the cation-exchange layer of a bipolar membrane increases the dissociation of water molecules. Activation with nitric acid (C = 4 mol/dm^3, t = 90 °C, t = 6 h) of bentonite, which is the part of the experimental bipolar membrane, improves the characteristics of the electrodialysis conversion of sodium sulphate compared to the membrane containing bentonite in its original form (for H^+ productivity and current efficiency increase by 2.5 times, energy costs for obtaining the target product decrease by 2.7 times; for OH^- productivity and current efficiency increase by 2.1 times, energy costs for obtaining the target product decrease by 2 times). This is due to the fact that acid activation increases the content of silicon groups in bentonite, which accelerates the dissociation of water molecules, and hence the rate of generation of H^+ and OH^- in the bipolar region of the membrane increases significantly. Also, when bentonite is treated with nitric acid, a decrease in the particle size and an increase in the specific surface area and microporosity were observed, which probably improves the dispersion of bentonite particles in the liquid polymer LF-4SK.

The use of a bipolar membrane with acid-activated bentonite allows obtaining fluxes of H^+/OH^--ions during the conversion of sodium sulphate, comparable to the fluxes of these ions obtained using bipolar membrane MB-3 (the best domestic sample).

Author contributions

All authors made an equivalent contribution to the preparation of the publication.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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Information about the authors

Sabukhi I. Niftaliev, Dr. Sci. (Chem.), Professor, Head of Department of Inorganic Chemistry and Chemical Technology, Voronezh State University of Engineering Technologies (Voronezh, Russian Federation).

https://orcid.org/0000-0001-7887-3061
sabukhi@gmail.com

Olga A. Kozaderova, Dr. Sci. (Chem.), Professor at the Department of Inorganic Chemistry and Chemical Technology, Voronezh State University of Engineering Technologies (Voronezh, Russian Federation).

https://orcid.org/0000-0002-8135-5801
kozaderova-olga@mail.ru

Ksenia B. Kim, Cand. Sci. (Chem.), Associate Professor at the Department of Inorganic Chemistry and Chemical Technology, Voronezh State University of Engineering Technologies (Voronezh, Russian Federation).

https://orcid.org/0000-0001-5564-8267
kmkseniya@yandex.ru

Petr E. Belousov, Cand. Sci. (Geology and Mineralogy), Senior Researcher, Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry of the Russian Academy of Sciences (Moscow, Russian Federation).

https://orcid.org/0000-0002-2657-5828
pitbl@mail.ru

Victoria V. Krupskaya, Cand. Sci. (Geology and Mineralogy), Senior Researcher, Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry of the Russian Academy of Sciences (Moscow, Russian Federation).

https://orcid.org/0000-0002-6127-748X
krupskaya@ruclay.com

Anna V. Timkova, postgraduate student, Department of Inorganic Chemistry and Chemical Technology, Voronezh State University of Engineering Technologies (Voronezh, Russian Federation).

https://orcid.org/0000-0003-0630-2993
timkova.anna@mail.ru

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