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ANALYSIS OF SULFOCATIONITE BASED ON PYROLYSIS OIL FOR WASTEWATER TREATMENT

Ergasheva Yulduzoy [1]***, Beknazarov Hasan*** [1]***, Yigitaliyev Sardorbek*** [1]

[1] Department of General Medicine, Faculty of Treatment, Angren University

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Abstract

This study describes the results of investigating the products of the sulfonation reaction between pyrolysis oil and sulfuric acid at various temperatures and time intervals. The highest sulfur content in sulfonated cation exchangers was observed at sulfonation temperatures of 100 and 120 °C for the pyrolysis oil with a reaction time of 2 hours. The resulting product is widely used as a dispersant for coatings and paints, a plasticizer for cement, and for other purposes. It is a synthetic polymer consisting of a network of interconnected sulfonic acid functional groups, which makes it highly charged and highly selective.

Keywords: *Pyrolysis oil, sulfonation, structural group analysis, sulfonic cation exchangers, water softening, polycondensation, ion-exchange resin, acidity*

The production of sulfonic cation exchangers through sulfonation of industrially manufactured polymers and oligomers, as well as their application, is widespread. However, considering that this type of macromolecular compound has certain limitations, numerous scientific studies confirm that superior results are achieved when using ion exchangers (anion or cation exchangers) obtained by preliminary modification with various organic compounds followed by sulfonation for diverse purposes. Ion exchangers contain multiple functional groups, including hydroxyl, primary, secondary, tertiary amino groups, carboxyl, and other groups. As polyfunctional compounds, their applications are diverse. Currently, the chemical industry is transitioning from raw materials to finished products through the production of semi-finished products, including those using organic synthesis and nanotechnology, while effectively utilizing local raw materials. At the same time, one of the urgent tasks is the gradual reduction of raw material exports (natural gas, industrial salts, etc.) and the organization of their processing within the republic. For this purpose, a cation exchanger was synthesized using secondary products by processing the by-product “pyrolysis oil” from the Ustyurt Gas Chemical Complex, owned by Uz-KorGaz Chemical LLC.

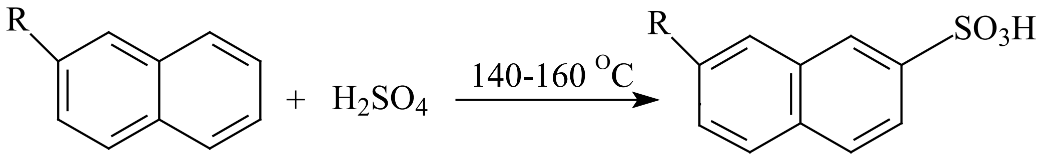
In general, sulphocation exchangers are universal and highly selective ion exchangers. These compounds are recognized as one of the vital substances for life processes and are used in various industrial processes (Pat.2241665.

RF. 2004). In the process of obtaining sulfonic cation exchangers from heavy oil residues, the waste generated during oil refining was treated with solid sulfuric acid under constant stirring conditions. The ionic modifier, which is the target product, is washed with water, purified from unreacted sulfuric acid, and dried to a neutral medium (pH=7), then brought to a constant mass. This method allows for obtaining a sulfocationite based on heavy oil residues in a short time at room temperature. It was established that the main characteristics of the sulfocationite obtained by this method are superior. The production of this ion exchanger can be considered environmentally safe, as oil refining waste was used as the raw material for its production (Pat. 2623574C1. RF. 2016). In accordance with classical theory, the patterns of absorption and swelling of new ion exchangers were studied. The obtained results enable the creation of ion exchangers with optimal properties for the purification of industrial wastewater (Rakhimova L. S., Abdutalipova N. M., Nazirova R. A., Tursunov T. T., Berdieva M. I., Mutalov Sh.A., 2014). The use of polymeric ion-exchange oligomerionites has been known for many years. The application of oligomeric-type catalysts is due to the wide selection of oligomeric matrices and the possibility of incorporating cationic and anionic catalytic centers within them. One of the main advantages of using ion-exchange oligomers is the ease of separating them from the reaction mixture. This facilitates the isolation and washing of catalysts, prevents the formation of stable emulsions, and avoids the accumulation of large volumes of wastewater. The absence of wastewater simplifies the technological scheme of production processes. Another advantage of ionites is their ability to be stably reused multiple times and applied for long periods in continuous processes (Yaroslavtsev A. B., Nikenenko V. V., Zabolotskiy V. I., 2003). β-Naphthalenesulfonic acid was obtained from industrial naphthalene through high-temperature sulfonation, after which a small amount of α-naphthalenesulfonic acid isomer was isolated by hydrolysis. The condensation reaction between β-naphthalenesulfonic acid and formaldehyde was conducted in an acidic medium. The condensate of naphthalenesulfonic acid and formaldehyde was then produced by neutralization with an alkali (Wang, T. H., 2004). Highly mineralized water is also characterized by a lower capacity to retain heavy metal ions and hardness ions compared to organic and inorganic ions (Vaaramaa, K., 2003). The application of the acidic form of weakly acidic cation exchangers in water pre-treatment provides effective decarbonization, despite the low efficiency of water softening (Makarenko, I., 2012). The application of weakly acidic cation exchangers in their acid form under conditions of low alkalinity and high water mineralization cannot provide effective water softening (Makarenko, I., 2014). Overall, despite the widespread use of ion exchange in water purification, the application of this method for stabilizing saline natural waters and wastewater is ineffective (Alexandratos, S. D., 2009). One of the drawbacks of using weakly acidic cation exchangers for water softening is their extremely low regeneration efficiency. However, it is precisely for this reason that their use is advisable for softening saline waters with high sodium ion content (Gomelja, N., 2004).

Methodology

For the synthesis of sulphocationic exchange resin, the following processes are carried out: Pyrolysis oil is sulfonated with concentrated sulfuric acid (molar ratio 1:1.5) at 160–165 °C for 3–4 hours, resulting in a dark black sulfomass; the sulfomass, placed in a pressure vessel, is diluted with distilled water and subjected to polycondensation with 38% formaldehyde (initial molar ratio of naphthalene to formaldehyde 1:2) at 110–120 °C and a pressure of 2–4 MPa; the water-insoluble solid polycondensate is mechanically ground and heated at 90–95 °C for 12 hours to complete polycondensation.

Synthesis of naphthalene sulfonic acid. Pyrolysis oil is sulfonated with concentrated H2SO4 to produce β-naphthalene sulfonic acid. The pyrolysis oil is mixed with sulfuric acid at 70 °C and boiled for 1 hour. According to equation 1, to achieve complete conversion, the reaction water formed during the sulfonation process is distilled off using an azeotropic method. During the reaction, along with β-naphthalene sulfonic acid, naphthalene disulfonic acids or dinaphthyl sulfones with a double naphthalene ring may also be formed.

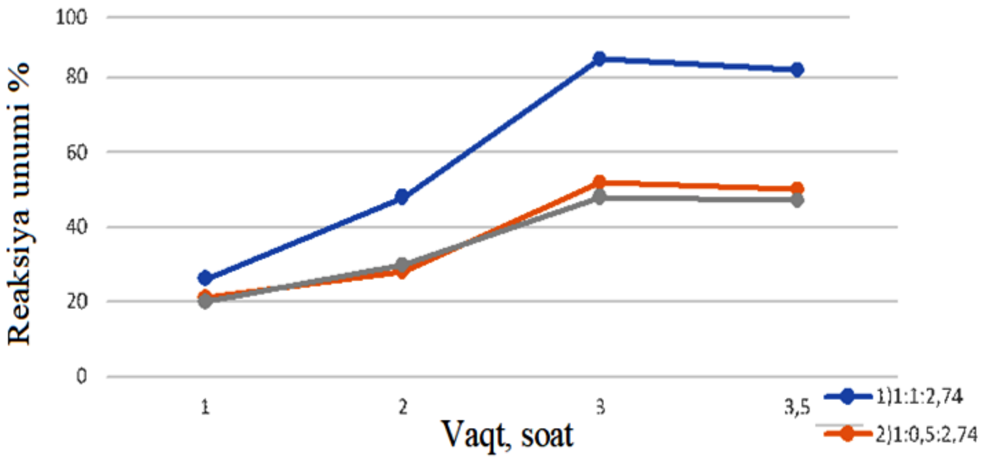


Naphtali

β-naphthalenesulfonic acid

The graph illustrating the influence of various factors on the yield of sulfocation exchanger derived from pyrolysis oil, specifically time and molar ratios of the starting materials, is presented below in Figure 1.

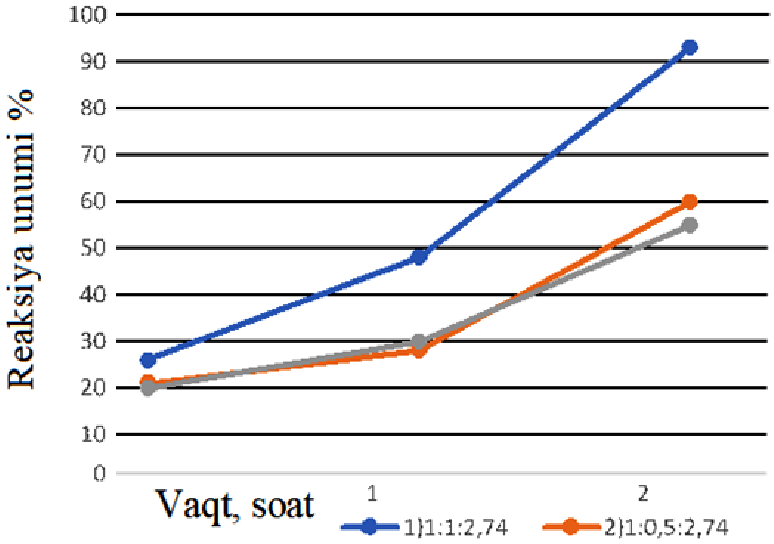
Figure 1. *Time-dependent yield of sulfocationite derived from pyrolysis oil*



Molar ratio of pyrolysis oil and sulfuric acid: 1–(1:1,5); 2–(1:0.5);

The relationship between the yield of sulphocatonite obtained from pyrolysis oil and time is presented in Figure 1. As shown in Figure 1, the highest efficiency compared to other variants is achieved with a pyrolysis oil to sulfuric acid ratio of 1:1.5. The synthesis process lasts for 3 hours. In an experiment conducted over 3.5 hours, the yield of sulphocatonite gradually decreases. This can be explained by the fact that the substances used as raw materials exist in various states of aggregation for 3 hours or more.

Figure 2. *Relationship between the yield of sulphocationite produced from pyrolysis oil and the molar ratio of pyrolysis oil to sulfuric acid*



Pyrolysis oil, molar ratio of sulfuric acid 1-(1:1,5); 2-(1:0,5);

The presence of interacting substances in two different states of aggregation reduces the effectiveness of their interaction. The dependence of the synthesized sulphocatonite yield on temperature can be seen in Figure 2.

As shown in Figure 2, the optimal component ratio for sulfocatonite production is 1:1.5, with the profitability of sulfocatonite reaching 79.8%. The highest dry residue is obtained at a ratio of initial products of 1:0.5; however, the plasticizing effect of the resulting sulfocatonites is low in this case. Based on these findings, the optimal temperature of 160 °C was chosen for sulfocatonite production. Reaction time also plays a significant role in the production of sulfocatonites. To determine the optimal reaction yield temperature, all three ratios of initial products were tested. The figure below illustrates the dependence of sulfocatonite yield on reaction time at a temperature of 160 °C. As evident from the figure, when the reaction is carried out for 180 minutes under optimal conditions, the sulfocatonite yield is 79.8%. Under these conditions, prolonging the reaction further leads to a decrease in product yield. As shown in the figure, when the reaction is conducted for 180 minutes under optimal conditions, the yield of sulfocatonite is 79.8%.

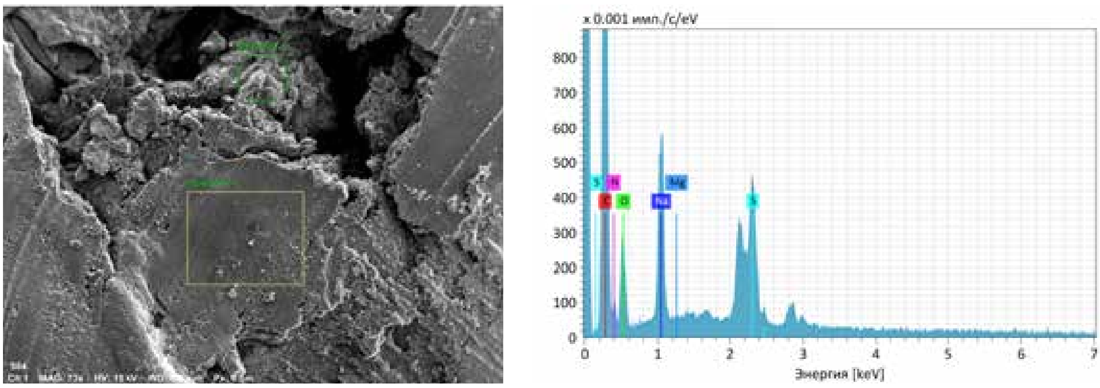
Results and analysis. Our research investigated the effects of temperature, time, and molar ratios of substances on the product yield in the production of a sulfocation exchanger using pyrolysis oil and sulfuric acid. The obtained results are presented in Table 1 below.

Table 1. *Influence of molar ratios of substances and reaction time on product yield*

№	Molar ratios	Time, hour	Yield, %	№	Molar ratios	Time, hour	Yield, %
1.	1:0,5	1	26,2	11	1:0,5	**3**	49,4
2.	1:0,8		37,3	12	1:0,8		65,8
3.	1:1,2		47,4	13	1:1,2		72,5
4.	1:1,3		54,3	14	1:1,3		78,7
5.	1:1,5		56,5	**15**	1:1,5		**79.8**

Table 1 reflects the influence of various factors on the yield of sulfokationite: time and the molar ratios of the initial substances. As can be seen from Figure 2, the highest yield compared to other variants is achieved when the ratio of pyrolysis oil to sulfuric acid is 1:1.5, however, the resulting product contains derivatives of di-naphthylsulfones. Therefore, when studying the plasticizing effect of mono-, di-, and other derivatives, the derivatives of polyhydric alcohols are of particular importance. From the obtained results, it can be seen that at a mol ratio of pyrolysis oil, sulfuric acid, and formaldehyde of 1:1.5 and a process duration of 3 hours, the yield of sulfokation exchanger was the highest. The study was conducted using a MIRA 2 LMU scanning electron microscope equipped with an INCA Energy 350 energy-dispersive microanalytical system.

Figure 3. *Electron-microscopic analyses of sulfokationite*



The microscope's resolution is 1 nm, and the sensitivity of the INCA Energy detector is 133 eV/10 mm^2, allowing for the analysis of elements from beryllium to plutonium. Analyses using the scanning electron microscope are carried out under high vacuum conditions. Using the same device, a microanalysis of chemical elements was performed, and areas were studied with an accelerating voltage of 20 keV and a beam current of 1 nA. In this work, images from the electron scanner were obtained at an accelerating voltage of 30 keV with a magnification of 50 times. The results of the elemental analysis and the scanning electron microscope data are presented in Figure 3.

Table 2. *Table of results from SEM analysis of sulfonated cation exchange resin*

Elements	Atomic number	The mass is normal %	Abs program [%]
C	6	64.13	1.88
O	8	15.64	0.56
N	7	9.66	0.58
Na	11	6.45	0.32
S	16	3.94	0.14
Mg	12	0.18	0.03
		100	

An electron microscopic image of the superplasticizer SP-Na revealed that the mass fraction of the functional group in the elemental composition consists of: 15.64% oxygen, 64.13% carbon, 9.66% nitrogen, 20.6% sodium metal, and 3.94% sulfur.

Conclusion

Pyrolysis oil reacts with concentrated sulfuric acid to form naphthalenesulfonic acid at high temperatures. Polysulfonation products and sulfonates may also form, which affects the purity of the target product. When condensing with formaldehyde after sulfonation, the acidity of the system significantly influences the degree of condensation. At low sulfuric acid concentrations, the sulfonation reaction does not yield good results. High acidity can easily trigger explosive polymerization, leading to high viscosity and reduced water solubility. It is theorized that the sulfonation process proceeds more effectively if the amount of sulfuric acid during sulfonation exceeds the amount of pyrolysis oil.

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Contact: hasanbeknazarov130@gmail.com