

Effect of Synthesis Conditions of Asphaltene Sulfocationites on their Composition and Sorption Properties

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Abstract

Background/Objectives: The possibility of using asphaltenes from heavy crude oil to obtain sulfocationites with high total exchange capacity and sorption capacity with respect to cations Mg^{2+} , Ca^{2+} , Mn^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , and Fe^{3+} has been shown. **Methods/Statistical Analysis:** The main method of asphaltene sulfocationite synthesis is the chemical interaction of asphaltene concentrates with sulfuric acid or oleum. However the main disadvantage of the obtained materials is that it is impossible to control grain size, using the method of sulfonation of deasphalting residues (asphaltites) only powdered sulfocationites can be obtained. So, in order to produce this material in the form of grains and to increase their mechanical strength, a mixture of tarry residue with rubber crumb was used as the raw material. **Findings:** It was shown that the main advantage of asphaltene sulfocationites involves increased kinetic sorption capacity. During 1 hour asphaltene sulfocationites under static conditions adsorb from water solution at least 60% of magnesium and calcium, and 90% of heavy metals. In terms of these characteristics, asphaltene sulfocationites are superior to sulfonated coal, and come close to synthetic cation-exchange resin. However, at sufficiently high concentrations in the mixed salt solutions, the sorption capacity of asphaltene sulfocationites significantly reduces. As a result of the research performed we have shown that, on the basis of heavy oil asphaltenes, the efficient sulfocationites can be synthesized, which are characterized by a sorption capacity value with respect to different metals that stands at the same level as for conventional ion exchange materials. The cheapness of the raw materials and simplicity of asphaltene sulfocationite production technology mean they are promising for application in a variety of industrial and waste water treatment systems. **Applications/Improvements:** The main advantage of asphaltene sulfocationites is their increased kinetic sorption capacity.

Keywords: Asphaltenes, Cations, Heavy Crude Oil, Sorption Capacity, Water Treatment

1. Introduction

Under current conditions industrial plants and factories have specific requirements for water according to peculiar characteristics of production processes. Industrial water treatment is performed using complex filtering systems and combines a variety of methods and technologies, depending on the objectives and quality of the available water medium. In most cases, one of water treatment

stages is ion-exchange sorption, and an urgent task herewith is to find new low-cost and effective ion-exchange materials for water cleaning from various contaminants¹⁻⁷. Currently, only chemically synthesized ion-exchangers are used, for which the products of petrochemical synthesis (styrole, divinylbenzene, butadiene, phenols, aldehydes, organic acids, etc.) are utilized as the raw material. The increased cost of such ion-exchangers significantly limits their utilization in many water purification processes.

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At the same time concentrated tarry asphaltenes from petrochemical processes can be considered as a raw material for production of ion-exchange materials that allows not only the obtaining of chip ion-exchangers, but also to increase oil refining efficiency. The development of methods of ion-exchanger production from crude oil asphaltenes and tar to the fullest extent becomes a challenging task for processing heavy oil and natural bitumen, in which the proportion of tarry asphaltene components is maximized.

2. Materials and Methods

The main method of asphaltene sulfocationite synthesis is the chemical interaction of asphaltene concentrates with sulfuric acid or oleum⁸⁻¹³. However the main disadvantage of the obtained materials is that it is impossible to control grain size, using the method of sulfonation of deasphalting residues (asphaltites) only powdered sulfocationites can be obtained. So, in order to produce this material in the form of grains and to increase their mechanical strength, a mixture of tarry residue with rubber crumb was used as the raw material.

3. Results and Discussion

Asphaltenes can be obtained from heavy crude oil or petroleum residues through the deasphalting process. However the composition and properties of the asphaltenes obtained are affected by differences in the composition of initial oil and deasphalting conditions¹⁴.

In order to obtain Asphaltene Sulfocationites (AS) we used heavy crude oil asphaltenes from the Ashalchinskoye field. Asphaltenes were prepared by the conventional method of oil diluting with a 20-fold excess of n-hexane followed by filtration and drying under vacuum for 6 hours at 90 °C. The resulting asphaltene powder was passed through metal sieves to obtain particles (grains) measuring 0.50-0.63 mm. Thus obtained granular asphaltenes were treated with sulfuric acid of concentrations 80 and 94% at 100 °C. This process was performed with stirring of the reaction mixture and varying of reaction time (10 minutes and 2 hours), as well as the amount of (3- and 20-fold excess) of sulfuric acid.

We have carried out analysis of obtained asphaltene sulfocationites in H⁺ form measuring of Total Exchange Capacity (TEC) (Table 1) accordingly ASTM D2187-

94(2009) Standard Test Methods for Physical and Chemical Properties of Particulate Ion-Exchange Resins. Method F^{15,16}. Additionally we have investigated traditional sulfocationites such as technical sulfonated coal (TSC) and cation-exchange resin *Amberlite IR120* and have determined that their total exchange capacities are 2,20 и 3,38 meq/g respectively.

In order to carry out comparative analysis of the main features of asphaltene sulfocationites structural composition the spectral absorption coefficients in the infra-red spectrum were estimated: aliphaticity (Al), aromaticity (Ar), degree of condensation (Cn), oxidation (Ox) and sulfonation (Sc) degrees (Table 2).

The results of spectral coefficient calculation (Table 2) evidence a significant conversion of the structural composition of asphaltenes during exposure to concentrated sulfuric acid. With an increase in the amount and

Table 1. Synthesis conditions and total exchange capacity (TEC) of asphaltene sulfocationites (AS)

Sample	Synthesis conditions	TEC, meq/g
AS-1	3-fold mass excess of 80 % H ₂ SO ₄ , 10 minutes	0,12
AS-2	20-fold mass excess of 80 % H ₂ SO ₄ , 2 hours	0,24
AS-3	3-fold mass excess of 94 % H ₂ SO ₄ , 10 minutes	1,13
AS-4	20-fold mass excess of 94 % H ₂ SO ₄ , 2 hours	2,36

Al = $D_{720+1380}/D_{1600}$ – shows the proportion of methylene and methyl groups with respect to aromatic C=C bonds;

Ar = $D_{1600}/D_{720+1380}$ – shows the proportion of C=C bonds in aromatic groups with respect to C-H bonds in aliphatic structures;

Cn = $D_{1600}/D_{740+860}$ – shows the proportion of C=C bonds in aromatic groups with respect to C-H bonds in aromatic structures;

Ox = D_{1700}/D_{1600} – shows the proportion of carbonyl groups R-C=O (in the presence of an OH-group) with respect to C=C bonds in aromatic structures;

Sc1 = D_{1030}/D_{1600} – shows the proportion of S=O-bonds in sulfoxide groups (either in sulphonates or sulfonic acids provided that absorption bands in the range of 1260-1150 cm⁻¹ and 700-600 cm⁻¹) with respect to C=C bonds in aromatic groups;

Sc2 = D_{1160}/D_{1600} – shows the proportion of S=O-bonds in sulfonatic groups with respect to C=C bonds in aromatic groups.

Table 2. Spectral absorption coefficients of original asphaltenes and asphaltene sulfocationites

Sample	Al	Ar	Cn	Ox	Sc1	Sc2
Asphaltenes	1,76	0,58	1,62	0,24	0,48	0,57
AS-1	2,17	0,47	0,53	0,59	1,10	1,27
AS-2	1,77	0,56	1,29	0,23	0,77	1,14
AS-3	0,93	1,07	1,73	0,64	1,31	1,51
AS-4	0,83	1,20	2,03	0,85	1,32	1,38

concentration of sulfuric acid, as well as with increased time of asphaltene treatment with sulfuric acid, the degree of conversion rises. For samples AS-1 and AS-2 the values of the majority of spectral coefficients are close to those of the original asphaltenes. Samples AS-3 and AS-4 differ slightly one from the other in terms of the value of spectral coefficients, and these samples demonstrate substantially reduced aliphaticity and significantly increased aromaticity, degree of oxidation, and sulfur content.

It should be noted that in the IR-spectrum bands of cation exchangers AS-1 and AS-2 a negligible increase of absorption band intensity of S=O bonds can be observed (1025-1035 and 1160-1230 cm^{-1}) compared to the IR-spectrum bands of original asphaltene. In the IR-spectrum of the sample AS-3 further growing of absorption band intensity of S=O bonds occurred along with the appearance of absorption bands peculiar to C=O bonds in carboxyl groups (1690-1710 cm^{-1}). In IR-spectrum bands of cation exchanger AS-4 there are intensive characteristic absorption bands of S=O bonds in the range of 1035 cm^{-1} (sulfoxide groups and sulfonic acids) and in the range of 1220-1170 cm^{-1} (sulfonic acids), as well as intensive characteristic absorption bands of C=O bonds of stretching vibrations in carboxylic groups in the range of 1699 cm^{-1} . Maximum absorption in the range of 3200-3550 cm^{-1} (broad band) occurs due to absorption by hydrogen bonds formed by associates of functional groups and associated water. At the same time there is a reduction in the intensity of absorption bands peculiar to deformation vibrations of methyl and methylene groups in naphthene-aliphatic structures (1360-1380 and 1450-1460 cm^{-1}) as well as to stretching vibrations of aromatic groups (1600 cm^{-1}).

Thus, comparison data on TEC values and IR-spectrum analysis of the obtained asphaltene sulfocationites proves that AS-4 shows maximum difference from the original asphaltene and maximum total exchange capacity.

Therefore, for further analysis we determined sorption capacity with respect to metal cations only for the sample AS-4. For comparison purposes we also analyzed sulfonated carbon and cation-exchange resin Amberlite IR120. The separate water solutions of salts of the following metals were prepared: magnesium, calcium, manganese, iron, nickel, copper, zinc and cadmium. To the preliminary dried sulfocationite in H^+ -form the salt solution was added (ratio 1:50) and the resulting mixture was incubated at room temperature for 1 hour and 3 days.

Metal ion concentration in the solution before and after contact with the adsorbent was determined by a method of atomic absorption spectroscopy using equipment of the model AAS-1N (Carl Zeiss Jena). The degree of extraction of metal cations, a , %, (Table 3, 4) was calculated using the following equation:

$$a = \frac{C_o^a - C_{eq}^a}{C_o^a} 100$$

where C_o^a and C_{eq}^a – initial and equilibrium concentration of metal cation, g-atom/l.

Sorption capacity of cation exchanger, A , mg/g, (Tables 3, 4) was determined using the following equation:

$$A = \frac{C_o^A - C_{eq}^A}{m} V,$$

where C_o^A and C_{eq}^A – initial and equilibrium concentration of metal cation, mg/l, m – mass of adsorbent, g; V – volume of metal salt solution in water, l.

Analysis of the data on sulfocationite sorption capacity shows that the degree of extraction of the investigated metal cations from water solutions of salts (Table 3) after 1 hour of contacting with AS-4 and Amberlite IR120 stands at 65-75% for heavy metal cations and 40-60% for magnesium and calcium cations. After reaching sorption equilibrium (after 3 days) cation-exchange resin Amberlite IR120 almost completely adsorbs all the investigated cations, and AS-4, obtained by us, extracts cations by 85-90%. In relation to sorption capacity AS-4 demonstrates almost the same values as Amberlite IR120: 10-15 mg/g for cations Mg^{2+} and Ca^{2+} , about 30 mg/g for cations of heavy metals Mn^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , and Fe^{3+} . Sorption capacity for Cd^{2+} is 51.0 mg/g (for AS-4) and 68.8 mg/g (for Amberlite IR120). In all cases sulfonated carbon shows worse results in relation to both the degree

Table 3. Sorption properties of sulfocationites with respect to heavy metal cations and metals of hardness salts in solutions of individual salts

	Degree of extraction of metal cations, a, %						Sorption capacity of cation exchanger, A, mg/g		
Cation	TSC		AS-4		Amberlite IR120		TSC	AS-4	Amberlite IR120
	1 hour	3 days	1 hour	3 days	1 hour	3 days	3 days		
Initial concentration [Mg ²⁺] = [Ca ²⁺] = [Mn ²⁺] = [Ni ²⁺] = [Cu ²⁺] = [Zn ²⁺] = [Fe ³⁺] = 0.01 mol/l									
Mg ²⁺	10,1	22,8	40,4	64,9	43,0	95,6	3,2	9,0	13,3
Ca ²⁺	40,5	50,0	59,5	85,7	65,5	98,2	8,4	14,6	16,6
Mn ²⁺	9,7	22,0	64,5	88,0	69,8	99,8	6,0	24,1	29,1
Ni ²⁺	3,5	19,8	64,7	87,9	74,2	99,9	5,3	23,5	28,5
Cu ²⁺	21,0	37,8	75,3	90,8	75,3	99,8	11,8	28,3	28,1
Zn ²⁺	19,7	25,6	63,9	75,9	70,3	99,8	11,3	33,0	29,7
Cd ²⁺	21,6	30,3	75,5	83,5	72,4	99,7	18,5	51,0	68,8
Fe ³⁺	2,2	9,3	75,6	87,6	78,4	99,9	2,5	23,7	28,4

of metal cation extraction and the sorption capacity compared to AS-4.

We also investigated the sorption properties of AS-4 with respect to metal cations Mg^{2+} , Ca^{2+} , Mn^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , and Fe^{3+} under different concentrations in water solutions of a mixture of salts (Table 4).

At low concentrations of salts in the mixed solution (concentration of single metal cations 0.002 mol/l) AS-4 and Amberlite IR120 extract from salt water solutions (contacting time 1 hour) the cations of the investigated metals to 50-70 and 65-85%, while sulfonated coal (TSC) — only to 6-12% (magnesium and calcium) and 18-35% (heavy metals) (Table 4). After reaching sorption equilibrium (after 3 days) the degree of extraction of metal cations Mg^{2+} , Ca^{2+} becomes equal to 24.0 and 29.4 % for sulfonated coal (TSC), 96.0 and 88.2 % – for AS-4, 98.4 and 96.2 % – for Amberlite IR120. Under these conditions the degree of extraction of heavy metal cations increases up to 26-42 % for sulfonated coal (TSC), up to 60-70 % – for AS-4, and up to 99% – for Amberlite IR120. In terms of the value of sorption capacity, AS-4 is comparable to Amberlite IR120: ~ 3.0 mg/g for cations Mg^{2+} , Ca^{2+} and 3.6-8.4 mg/g for cations of heavy metals. The sorption capacity of sulfonated coal (TSC) is significantly lower and stands at 0.4-1.0 mg/g for magnesium and calcium cations and 1.4-2.1 mg/g for heavy metal cations.

In the case of more concentrated solutions (0.01 mol/l), after 1 hour of contact, AS-4 and Amberlite IR120 adsorb cations Mg^{2+} , Ca^{2+} to 34-37 and 53-56 %, while

sulfonated carbon — only to 5-11 % (Table 4). The degree of extraction of heavy metal cations after 1 hour for AS-4 and Amberlite IR120 is equal to 10-23 and 42-53 %, and for sulfonated coal (TSC) — 7-13 %, respectively. After 3 days the degree of extraction of Ca^{2+} cations by AS-4 rises to 44.3 %, and remains unchanged with respect to Mg^{2+} . In the case of sulfonated coal (TSC) the degree of extraction of Mg^{2+} and Ca^{2+} cations rises to 14.9 and 21.5 %, and for Amberlite IR120 — up to 97.2 and 84.7 %, respectively. The degree of extraction of heavy metal cations increases insignificantly. In terms of the value of sorption capacity with respect to Mg^{2+} and Ca^{2+} cations, AS-4 holds an intermediate position between Amberlite IR120 and sulfonated coal (TSC).

4. Conclusion

Thus, it was shown that the main advantage of asphaltene sulfocationites involves increased kinetic sorption capacity. During 1 hour asphaltene sulfocationites under static conditions adsorb from water solution at least 60% of magnesium and calcium, and 90% of heavy metals. In terms of these characteristics, asphaltene sulfocationites are superior to sulfonated coal, and come close to synthetic cation-exchange resin. However, at sufficiently high concentrations in the mixed salt solutions, the sorption capacity of asphaltene sulfocationites significantly reduces.

As a result of the research performed we have shown that, on the basis of heavy oil asphaltene, the

Table 4. Sorption properties of sulfocationites with respect to heavy metal cations and metals of hardness salts in solutions of a mixture of salts

	Degree of extraction of metal cations, a, %						Sorption capacity of cation exchanger, A, mg/g		
Cation	TSC		AS-4		Amberlite IR120		TSC	AS-4	Amberlite IR120
	1 hour	3 days	1 hour	3 days	1 hour	3 days	3 days		
Initial concentration [Mg ²⁺] = [Ca ²⁺] = 0.002 mol/l The total initial concentration Σ [Me ²⁺] = 0.004 mol/l									
Mg ²⁺	12,0	24,0	68,0	96,0	60,3	98,4	0,9	2,9	3,1
Ca ²⁺	5,9	29,4	58,8	88,2	67,1	96,2	1,0	3,0	3,3
Initial concentration [Mn ²⁺] = [Ni ²⁺] = [Cu ²⁺] = [Zn ²⁺] = [Fe ³⁺] = 0.002 mol/l The total initial concentration Σ [Me ²⁺] = 0.01 mol/l									
Mn ²⁺	26,3	26,3	61,9	66,7	79,0	99,5	1,5	3,7	5,3
Ni ²⁺	35,0	35,0	60,0	70,0	85,0	99,5	2,1	4,1	5,9
Cu ²⁺	21,1	42,1	61,1	61,1	68,4	99,5	2,6	3,8	6,1
Zn ²⁺	19,2	30,8	53,3	63,3	65,4	99,6	2,4	6,4	8,4
Fe ³⁺	17,7	29,4	50,0	72,2	64,7	94,1	1,4	3,6	4,6
Initial concentration [Mg ²⁺] = [Ca ²⁺] = 0.01 mol/l The total initial concentration Σ [Me ²⁺] = 0.02 mol/l									
Mg ²⁺	11,6	14,9	33,9	35,5	56,0	97,2	2,1	5,2	14,3
Ca ²⁺	5,1	21,5	36,7	44,3	52,9	84,7	3,4	7,1	13,5
Initial concentration [Mn ²⁺] = [Ni ²⁺] = [Cu ²⁺] = [Zn ²⁺] = [Fe ³⁺] = 0.01 mol/l The total initial concentration Σ [Me ²⁺] = 0.05 mol/l									
Mn ²⁺	9,3	10,2	14,7	14,7	44,4	51,9	3,1	4,1	15,4
Ni ²⁺	6,6	7,6	12,8	13,7	47,2	51,9	2,5	4,3	16,2
Cu ²⁺	13,2	15,1	13,4	13,4	42,5	50,9	5,0	3,5	17,2
Zn ²⁺	7,0	7,0	10,3	12,2	46,8	54,4	4,0	6,1	30,4
Fe ³⁺	12,8	12,8	22,5	23,6	53,2	80,9	3,4	5,8	21,4

efficient sulfocationites can be synthesized, which are characterized by a sorption capacity value with respect to different metals that stands at the same level as for conventional ion exchange materials. The cheapness of the raw materials and simplicity of asphaltene sulfocationite production technology mean they are promising for application in a variety of industrial and waste water treatment systems.

5. References

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