

Preparation of Asphaltene-Based Anion-Exchange Resins and Their Adsorption Capacity in the Treatment of Phenol-Containing Wastewater

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Abstract—Novel anion-exchange resins were prepared from asphaltenes by nitration with nitric acid followed by reduction of the nitrated asphaltenes with sodium sulfide. The aminated asphaltenes were investigated as anion exchange resins for the treatment of phenol-containing wastewater. Their maximum adsorption capacity was found to be 2.3-fold superior to that of an industrial AV-17-8 (OH⁻ form) AER sample.

Keywords: asphaltenes, nitration, reduction, sorbents, phenol, wastewater

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Asphaltenes are unique native petroleum components with good potential applicability, which have attracted much interest among researchers. Recently, the application range of asphaltenes has been significantly extended due to the creation of various electrically conductive and polymeric materials, as well as graphene-like and fullerene-like structures [1–10]. Ion-exchange materials, such as sulfonic cation-exchange resins, have also been synthesized from asphaltenes and investigated. These exhibited high efficiency as acid catalysts and sorbents of metals (e.g., magnesium, calcium, iron, copper, etc.) [11–13]. However, the utilization of modified asphaltenes has not yet been sufficiently elaborated for the removal of rare-earth metals, phenols, and phenolics from wastewater. Industrial applications in this area generally use porous modified or unmodified carbon, aluminosilicates, silica gel, zeolites, various organic materials, etc. [14, 15]. At the same time, the structure of asphaltenes makes them a promising raw material for the preparation of anion-exchange resins (AER).

There have been virtually no descriptions of AER synthesis from amino group-containing asphaltenes in the available reports. Saudi researchers have attempted to produce aminated asphaltenes [16]. The IR spectroscopy showed a very insignificant formation of aminated

asphaltenes by the Sandmeyer reaction. Aminated asphaltenes have also been prepared by alkylation of chloromethylated asphaltenes with various amines [17–19]. However, no significant introduction of chloromethyl groups into the aromatic structure of asphaltenes by the Blanc reaction was achieved. This was not only because of steric hindrance, but also as a result of the periphery's loading with alkyl radicals [20]. There are a number of methods to produce anion-exchange resins from asphaltenes: the alkylation of halogenated compounds with primary or secondary amines; the reduction of a nitrile group's acid amides; conducting a Schmidt reaction; conducting an alcohol–ammonia reaction, etc. [21]. Nonetheless, the simplest and most convenient method is the nitration of asphaltenes with concentrated nitric acid followed by the reduction of the nitro group.

This paper describes the synthesis of anion-exchange resins with amino groups from asphaltenes and the investigation of their adsorption capacity in dephenolization of wastewater.

EXPERIMENTAL

We investigated asphaltenes (designated as Asp) from the vacuum residue of TANECO Company, specifically

a 0.2–0.3 mm fraction isolated according to ASTM D4124-09. Nitric acid ($d = 1.4 \text{ g/cm}^3$) was used as a nitrating agent, while 99.9% sulfur and sodium sulfide 9-hydrate were utilized to reduce the resulting nitro groups. All the reagents were purchased from Sigma Aldrich and were used without pretreatment.

The nitration procedure was as follows: 50 mL of nitric acid was placed in a three-neck flask equipped with a magnetic stirrer and a reflux condenser, and 1 g of asphaltenes was added. The reaction mixture was heated to 60°C and held for 4 h. The nitrated asphaltenes (designated as NA) were washed with distilled water to neutral and dried at room temperature for 72 h; 1.17 g was isolated.

The following NA reduction procedure was used. In a three-neck flask equipped with a magnetic stirrer and a reflux condenser, 1.3 g of elemental sulfur was added under stirring to a solution of 9.75 g $\text{Na}_2\text{S} \cdot \text{H}_2\text{O}$ in 10 mL of distilled water. The mixture was then heated in a water bath to 70–75°C, and 1 g NA was added. The reaction mixture was held for different periods of time (0.5; 1; 2; 4; 6; and 8 h), then cooled to room temperature. The solid products, namely aminated asphaltenes (designated as AA-0.5, AA-2, AA-4, AA-6, and AA-8, respectively), were isolated by filtering through a Büchner funnel, washed with distilled water until neutral to litmus, and dried at room temperature for 72 h. Depending on the aminated asphaltene reduction time, 0.86 to 0.92 g was isolated.

The total static exchange capacity (SEC) of AERs was determined in compliance with ASTM D 2187-94.

The elemental composition (CHNS/O) of the samples was determined on a EuroEA 3028-HT-OM high-temperature analyzer (Eurovector S.p.A., Italy). We calculated the carbonization (C/H) ratio of the asphaltene structure, as well as the sulfur-to-carbon, oxygen-to-carbon, and nitrogen-to-carbon (S/C, O/C, and N/C) ratios. The oxygen ratio was calculated disregarding the metal content.

The AER's IR spectra were recorded on a Vector-22 spectrometer (Bruker, Germany) in the range of 400–4000 cm^{-1} at a resolution of 4 cm^{-1} .

The molecular weights of asphaltenes (Asp) and resultant products were measured by the matrix-assisted laser desorption/ionization (MALDI) method using Bruker equipment from Germany. The spectra were obtained at an accelerating voltage of 25 kV and an ion

extraction delay time of 30 ns. The data were processed using the Flex Analysis 3.0 software (Bruker Daltonik GmbH, Germany). 1,8,9-Trihydroxyanthracene was used as a matrix. The number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (PDI) for the Asp, NA, and aminated asphaltenes were calculated using the formulas [22]:

$$M_n = \frac{\sum I_i M_i}{\sum I_i},$$

$$M_w = \frac{\sum I_i M_i^2}{\sum I_i M_i},$$

$$PDI = \frac{M_w}{M_n},$$

where I_i is the relative integral area, and M_i is the calculated molecular weight of the i th peak in the MALDI spectrum.

The adsorption properties were examined in a 12 mg/dm^3 phenol solution at 24°C under static conditions, with a maximum adsorption time of 96 h. The phenol concentrations in the aqueous solutions were determined by the standard fluorimetric method [23] on a Fluorat 02-3M fluorimeter (Lumex, Russia).

RESULTS AND DISCUSSION

Nitration of asphaltenes. Concentrated nitric acid was used to introduce nitro groups into the polyaromatic structure of asphaltenes, as described in relevant reports [24–26]. Asphaltene nitration may occur by two mechanisms, namely free-radical substitution (in alkane chains) and electrophilic aromatic substitution. The IR spectra (Fig. 1) display intensive absorption bands at 1342 and 1535 cm^{-1} , attributable to the symmetric and asymmetric stretching modes of the C–NO₂ group attached to the aliphatic and aromatic fragments of asphaltene molecules. It should be noted that a nitric acid reaction simultaneously involves oxidation and nitration [27]. Therefore, a number of functional groups other than nitro groups may be formed in asphaltenes, as evidenced by the absorption bands at 1277 (corresponding to the vibrations of a nitroso group), 1654 (nitrate group), and 1712 cm^{-1} (carbonyl group) [28].

Reduction of nitrated asphaltenes. Organic chemistry applications have generally used tin, zinc, iron (in the presence of HCl), and their chlorides [29], as well as sodium dithionite, sodium hydrocarbonate, and sodium

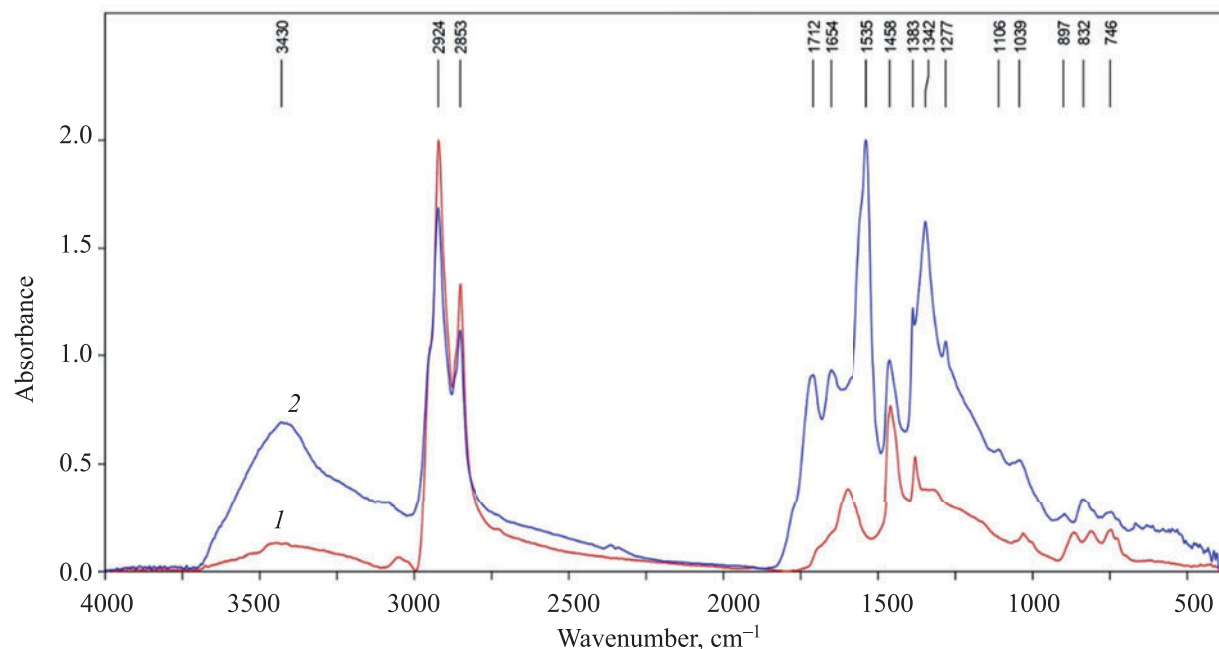


Fig. 1. IR spectra of initial (1) and nitrated (2) asphaltenes.

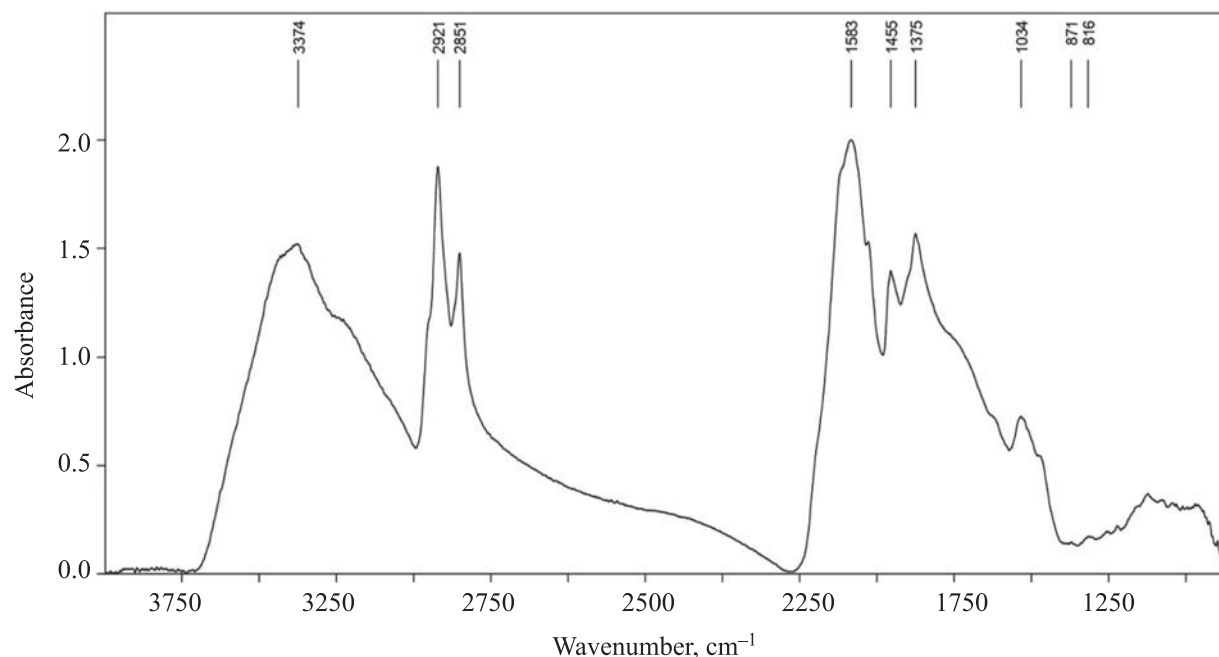


Fig. 2. IR spectrum of aminated asphaltenes (AA-2).

sulfide [30–32], as reducing agents for nitro derivatives. The nitroalkane chains are readily reduced, nearly always forming amines [33]. While nitro derivatives in the aromatic series are also capable of reduction, this, depending on the reaction conditions, may yield by-products. For example, a highly-alkaline environment favors the formation of azoxy and azo compounds. To

avoid this, sodium sulfide together with elemental sulfur has been used as a reducing agent [32]. It is this reaction that was employed for the reduction of nitro groups in the asphaltenes examined in our study. There have been no public reports on the reduction of nitro groups in asphaltenes.

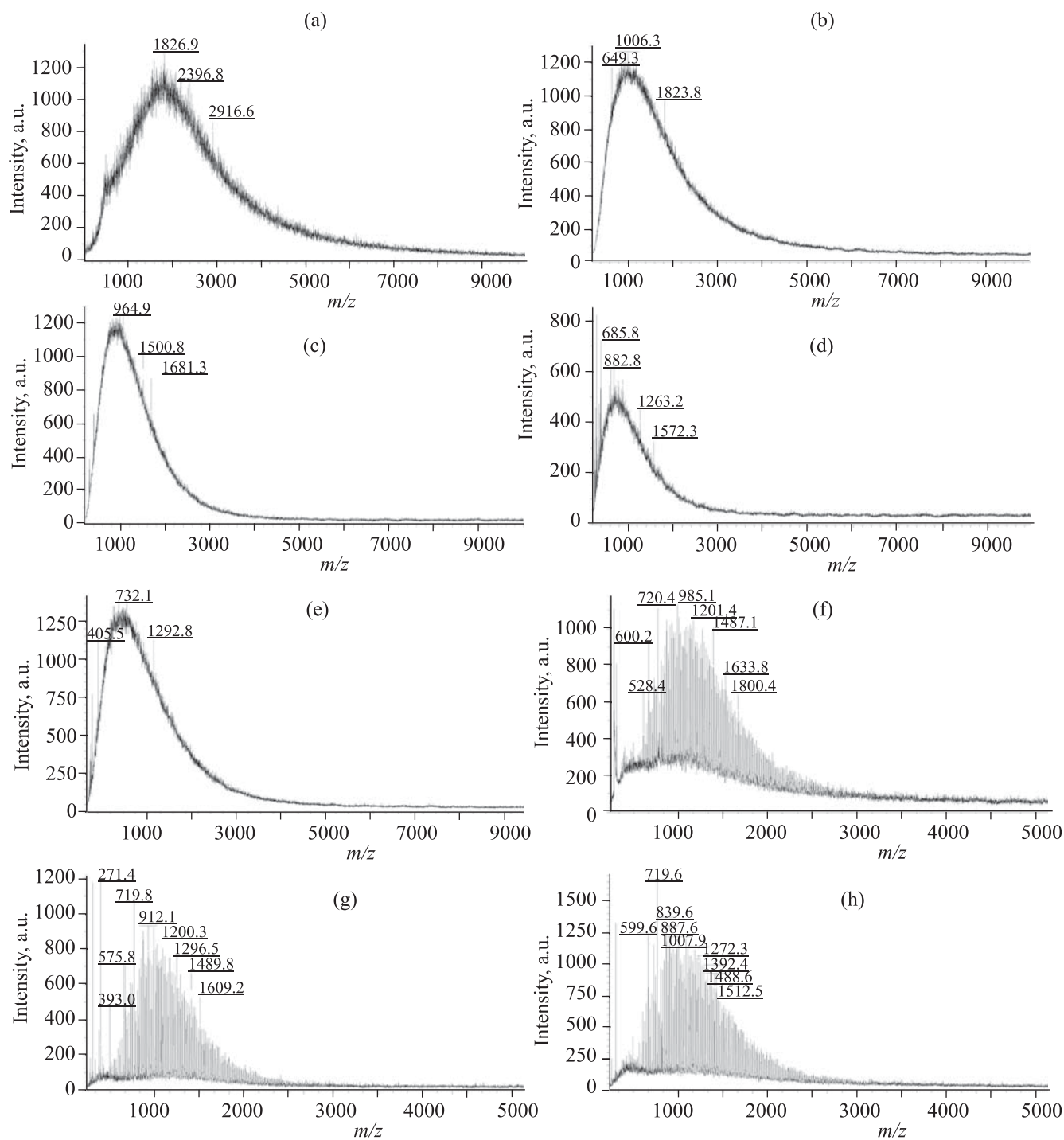


Fig. 3. Molecular weight distribution of asphaltenes according to MALDI mass spectrometry: (a) Asp; (b) NA; (c) AA-0.5; (d) AA-1; (e) AA-2; (f) AA-4; (g) AA-6; (h) AA-8.

The reduction of nitrated asphaltenes was conducted for different retention times (0.5; 1; 2; 4; 6; and 8 h). The absorption bands of the amino groups of the reduced nitrated asphaltenes are in the same frequency ranges and differ slightly in intensity. The occurrence of nitro group reduction is evidenced by the most intense band

near 1583 cm^{-1} (attributed to the N–H bending modes in amines) and a less intense band near 1034 cm^{-1} (the C–N stretching modes in aliphatic amines) (Fig. 2). The spectrum also contains absorption bands corresponding to the bending modes of the $-\text{CH}_2-$ (1455 cm^{-1}) and $-\text{CH}_3$ (1375 cm^{-1}) groups.

Table 1. Characteristic data for starting asphaltenes and reaction products

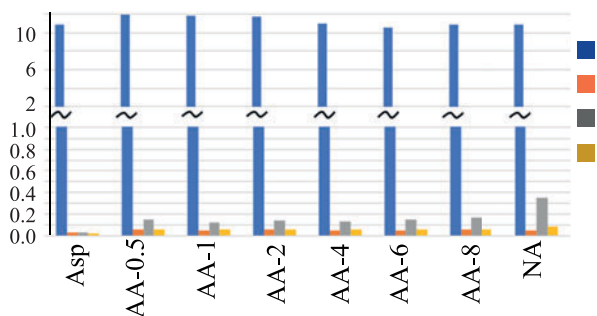
Asphaltenes	Molecular weight, Da		PDI
	M_n	M_w	
Asp	1800	2570	1.43
NA	1288	1813	1.40
AA-0.5	1135	1698	1.32
AA-1	1128	1587	1.41
AA-2	988	1320	1.34
AA-4	923	1264	1.37
AA-6	846	1138	1.35
AA-8	812	1118	1.38

To provide a relative assessment of the processes underlying the nitration and the reduction of the resultant nitro groups in asphaltenes, we determined, using the MALDI method, the number-average molecular weight (M_n), the weight-average molecular weight (M_w), and the polydispersity index (PDI) (see Table 1 and Fig. 3).

Table 1 clearly demonstrates that the starting asphaltenes have the highest number-average and weight-average molecular weights (1800 Da and 2570 Da, respectively), and that these weights decline in all the reaction products. Such a trend indicates the occurrence of various ion-radical processes both during the nitration and during the subsequent reduction of nitro groups in asphaltenes. This results in a decreasing polydispersity index (PDI) for both the nitrated and reduced asphaltenes (Table 1).

The C/H, S/C, O/C, and N/C ratios were derived from the elemental analysis data (Fig. 4).

Figure 4 shows an 11.7-fold increase in the oxygen-to-carbon weight ratio during the asphaltene nitration,

**Fig. 4.** Carbonization, sulfur-to-carbon, oxygen-to-carbon, and nitrogen-to-carbon ratios based on the elemental composition for Asp and reaction products.

indicative of the nitration and oxidation of asphaltene molecules. At the same time, the N/C ratio also increases, while the C/H and S/C ratios do not change significantly. During the reduction of nitro groups in nitrated asphaltenes, the O/C ratio declines by a factor of 2.1 to 2.9, indicative of the partial reduction of oxo derivatives. At the same time, there are no significant changes in the carbonization, sulfur-to-carbon, and nitrogen-to-carbon ratios.

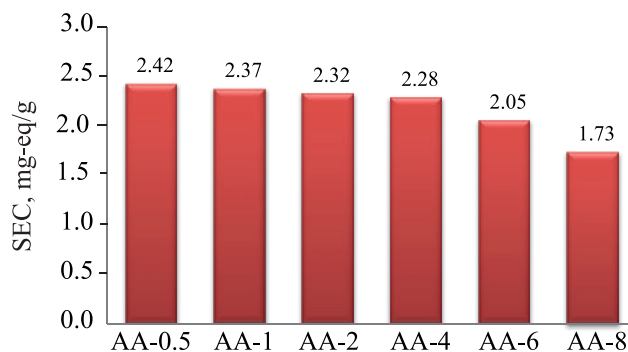
The most important property of ion-exchange resins is their absorption capacity, which is characterized by total static exchange capacity (SEC). The kinetic control of chemical reactions revealed that the highest SEC value (2.42 mg-eq/g) is reached when the synthesis lasts for 0.5 h. A further extension of the reaction time leads to a decrease in the SEC (Fig. 5).

Samples AA-0.5, AA-1, and AA-2 were examined as sorbents of phenol from an aqueous solution. Their adsorption properties were compared using an industrial AV-17-8 (OH⁻ form) AER sample and Asp. Based on the experimental data obtained, the adsorption capacities (A) of the AERs under examination and of the starting asphaltenes were calculated [34]:

$$A = (C_0 - C_{\text{cont}}) V/m,$$

where A is the phenol adsorption capacity (mmol/g); C_0 is the initial phenol concentration (mmol/dm³); C_{cont} is the phenol concentration after the adsorption (mmol/dm³); V is the solution volume (dm³); and m is the sorbent weight (g).

The adsorption capacities of AERs vs. starting asphaltenes show that AA-0.5, AA-1, and AA-2 are appreciably more effective in phenol extraction than the industrial AV-17-8 (OH⁻) AER (Fig. 6).

**Fig. 5.** Static exchange capacity of aminated asphaltenes.

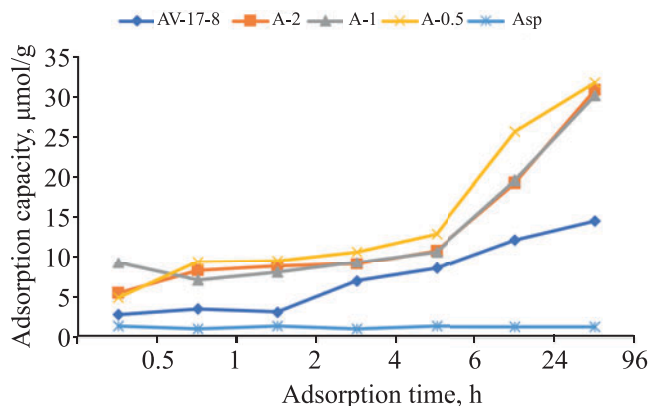


Fig. 6. Adsorption capacity of AERs and starting asphaltenes with respect to phenol solution as a function of adsorption time.

The mechanism of the interaction of aminated asphaltenes with phenol probably involves physical adsorption of phenol molecules due to dispersion of π -electrons between the phenol ring and the base AER plane, the latter having a superior electron density [35]. The adsorption capacity after 1 h adsorption ranges within 7–9.5 mmol/g for AA-0.5, AA-1, and AA-2. This parameter equals 1 mmol/g for the starting asphaltenes, and 3 mmol/g for the AV-17-8 OH^- form. Under the experimental conditions (after 96 h), AA-0.5 exhibits the highest sorption capacity, exceeding that of AV-17-8 by a factor of 2.3. The starting asphaltenes retain their initial adsorption capacity, proving a lack of adsorption capacity in this sample.

CONCLUSIONS

In the course of the study, we developed and tested a method for the preparation of anion-exchange resins by the nitration of asphaltenes with concentrated nitric acid followed by the reduction of nitrated asphaltenes with sodium sulfide. IR spectroscopy identified the appearance of nitro, nitroso, carbonyl, and hydroxyl groups in the nitrated asphaltenes, and the formation of amino groups in the reduced nitrated asphaltenes. This serves as evidence of various ion-radical reactions. The highest SEC value (2.42 mg-eq/g) is reached for AA-0.5. According to a comparative analysis, aminated asphaltenes exhibit a high phenol adsorption capacity, comparable to industrial AV-17-8 (OH^- form) AER, and can be considered as novel asphaltene-based anion-exchange resins to be utilized in industrial wastewater dephenolization applications.

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CONFLICT OF INTEREST

The authors declare no conflict of interest requiring disclosure in this article.

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