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Magnetite-based highly dispersed materials for the sorption of asphaltenes

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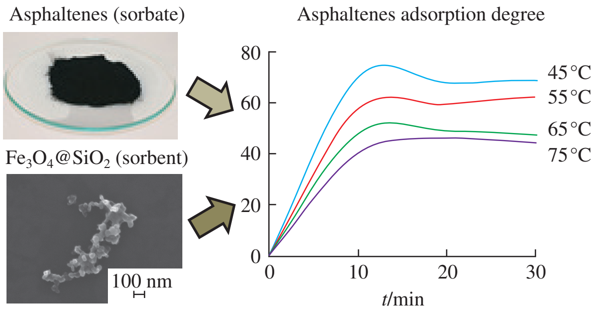
Highly dispersed materials Fe_3O_4@TEOS and Fe_3O_4@PVP for asphaltenes extraction from organic media have been synthesized *via* modifications of nanosized magnetite with tetraethoxysilane and *N*-polyvinylpyrrolidone. Using model compounds simulating the main functional groups of asphaltenes and some natural asphaltenes isolated from crude oil, the sorption capacity was estimated for Fe_3O_4@TEOS. It was found that the extraction degree of asphaltenes from a toluene solution at 45 °C reached 65–70%, and the sorption capacity was 28 mg g^{-1}.

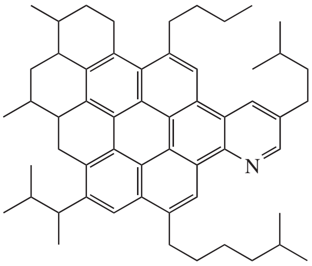


A depletion of reserves of the light oil and the resulting increase in the share of heavy, highly viscous oils and natural bitumens in the overall production balance are crucial problems leading to a need for the development of new technological processes to utilize heavy oils containing asphaltenes and other compounds in order to make the oil suitable for the refining.

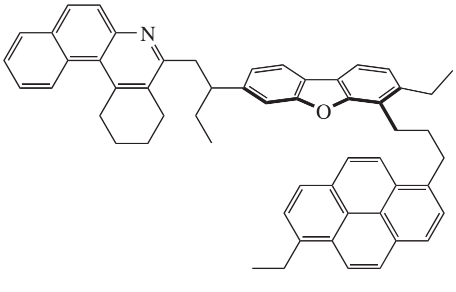
A supercritical fluid extraction is among the promising tools for the design of techniques for the removal of asphaltenes from the oil stock. However, this approach is limited by its non-selectivity towards the substances being extracted. To increase the extraction efficiency, various mineral additives possessing good sorption properties towards the extracted substances may be employed in the processing.[1,2] The possibility to selectively remove the asphaltenes depends on the surface properties of used sorption materials and on the asphaltene structures, which determine various types of intermolecular interactions (such as electrostatic, π–π, van der Waals, coordination, *etc.*) in non-polar organic media.

The most interesting for practical purposes are iron oxides, primarily the magnetite and maghemite.[3–6] These sorbents are readily available, cheap, and environmentally friendly. We have previously demonstrated that chemical modification of the surface of nanosized magnetite upon microwave heating allowed one to obtain products possessing the desired properties for a wide range of technological, biomedical and analytical applications.[7,8] Magnetic properties of these oxides make it possible to remove the sorbent by magnetic separation, which simplifies the entire procedure. The materials proposed earlier were intended for aqueous media. This work was aimed at the obtaining of surface-modified sorbents exhibiting an affinity for asphaltenes in organic media and at the investigation of their physicochemical properties and sorption capacity in order to develop new promising materials for the oil industry.

The molecular structure of asphaltenes was fairly studied.[1,9] They are characterized by an average molecular weight of ~750, may be charged (+1), and incorporate polar N-, O- and S-containing groups, polycyclic (including polyaromatic) structures, and/or aliphatic chains (*e.g.* 'island' or 'archipelago' molecules). Obviously, such molecules will interact with the polar surfaces of sorption materials primarily through electrostatic and π–π interactions.



'island' molecule



'archipelago' molecule

In the present work, modified materials for the asphaltene extraction were prepared *via* an immobilization of organosilicon and polymeric substances containing donor heteroatoms on the highly dispersed carrier, magnetite.[†] Tetraethoxysilane (TEOS)

[†] Magnetite Fe_3O_4 was synthesized *via* its precipitation from aqueous solutions of iron salts $Fe(NH_4)_2SO_4 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ upon treatment with ammonia (25–28 wt%) under microwave heating.[10] Its structure and composition were confirmed by IR spectroscopy and X-ray diffraction

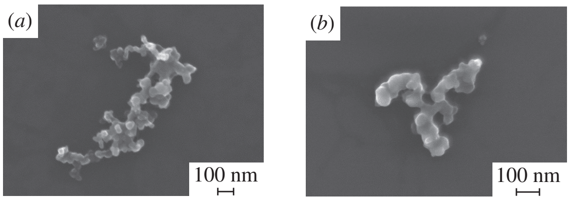


Figure 1 SEM images of obtained (*a*) Fe_3O_4@TEOS and (*b*) Fe_3O_4@PVP sorbents.

and *N*-polyvinylpyrrolidone (PVP) were selected as the surface modifiers due to the possibility of obtaining hydrophilic surfaces bearing sorption centers of various nature. The physicochemical properties of Fe_3O_4@TEOS and Fe_3O_4@PVP (dimension, sedimentation stability, specific surface area, pore size, elemental composition, *etc.*) were also investigated.

The scanning electron microscopy (SEM) has revealed that the synthesized materials are single nanoscale particles and their associates sized from 50–80 to 400–700 nm (Figure 1). The surface of Fe_3O_4@TEOS is a developed one [113.4 $m^2\ g^{-1}$ according to the Brunauer–Emmett–Teller (BET) method], the average pore size is 10.4 nm, and the mass content of major components, SiO_2 and Fe_3O_4, is 36.0 and 61.4%, respectively. The sedimentation stability of sorbent has been estimated by the change in the optical density of suspension in an optically transparent medium (86% glycerol), whose kinematic viscosity is close to that of heavy oils (105 and ~80–220 cSt, respectively)[12,13] (Figure 2). It was found that the sorbent remained in the suspension for a long time (at least 1 h), while the complete (*i.e.*, 100%) sedimentation was not achieved during the entire time of experiment (more than one day). In this case, the viscosity of medium did not interfere with the magnetic separation of sorbent [see Figure 2(*a*)].

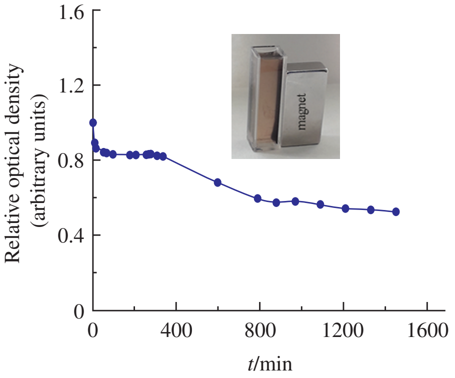


Figure 2 Kinetics of Fe_3O_4@TEOS sedimentation in 86% glycerol. The inset shows their magnetic separation from the glycerol suspension after 5 min.

Table 1 The degree of model substances extraction by the Fe_3O_4@TEOS and Fe_3O_4@PVP (%).

Analyte	C_0/ mg dm^{-3}	Phase contact time/min	Amount of substances sorbed (%)	
			Fe_3O_4@TEOS	Fe_3O_4@PVP
Oleic acid	21	5	13.4	2.0
		20	10.7	49.2
4-Nonyl-phenol	12	10	74.1	66.7
		20	76.7	75.8
Naphthalene	2.5	5	77.3	32.0
		20	88.9	75.3
Anthracene	2.5	5	55.6	48.0
		20	77.8	72.0
		35	81.5	70.5

The sorption capacity of Fe_3O_4@TEOS and Fe_3O_4@PVP has been evaluated for a number of model organic compounds (naphthalene, anthracene, 4-nonylphenol, and oleic acid), whose molecules simulate the main polyaromatic and aliphatic structural moieties of asphaltenes (Table 1). Thus, different types of covalent sorbate–sorbent interactions were simulated, so the acquired data allowed us to assess the properties of reported sorbents. Taking into account the known data,[1] *n*-heptane and toluene were selected as the solvents for experiments on the model sorption. As one can see from Table 1, Fe_3O_4@TEOS possesses a higher sorption capacity towards the model substances (except for oleic acid) and, therefore, it was selected for experiments on the sorption of natural asphaltenes. It should be noted that in the presence of model compounds, the initially hydrophilic Fe_3O_4@TEOS is well dispersed in organic solvents, which is important for practical applications of the sorbent.

For natural asphaltenes,[‡] the kinetic characteristics for the extraction by Fe_3O_4@TEOS from toluene solutions were investigated at room temperature under static conditions. The concentration of asphaltenes was 20 mg dm^{-3}, which corresponded approximately to their average content in oils. The $V\!:\!m$ was 5, 20, or 45 : 10 mg ml^{-1}. The obtained dependence (Table 2) indicates an increase in the degree of extraction ($R_{\mathrm{Asp.}}$) upon raising the mass of sorbent. Under these conditions, the R_{Asp} value reached ~60% in 30–40 min, and the calculated sorption capacity of Fe_3O_4@TEOS was 2.7 mg g^{-1} (0.024 mg m^{-2}).

The analysis of temperature dependence of R_{Asp} has revealed (Table 3) that the efficiency of asphaltenes removal with Fe_3O_4@TEOS at 45 °C reaches 65–70% already at $V\!:\!m = 5 : 10$ mg ml^{-1}, and the extraction time is reduced to 10–15 min. This may be caused by both temperature effects and exposure to an electromagnetic field. The sorption capacity of Fe_3O_4@TEOS increased by an order of magnitude and was 28 mg g^{-1} (0.25 mg m^{-2}). However, a further increase in temperature only diminished the *R* value (see Table 3).

Table 2 The relationship between the recovery R_{Asp} and $V\!:\!m$ ratios.

Amount of Fe_3O_4@ TEOS/mg	Phase contact time/min	R_{Asp} (%)	Amount of Fe_3O_4@ TEOS/mg	Phase contact time/min	R_{Asp} (%)
5	10	62.4	20	30	62.1
5	20	59.1	20	45	56.8
5	30	47.3	45	10	72.4
5	40	44.1	45	20	66.3
5	50	30.1	45	35	57.1
20	10	67.4	45	65	63.2
20	20	64.2			

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analysis. Stabilization and modification of nanosized magnetite were carried out using PVP (Fisher Scientific) and TEOS (Reakhim, Russia) in a Discover SP-D microwave system (CEM, USA) equipped with a temperature IR sensor for the operation under atmospheric and elevated pressures at 2.45 GHz and 300 W. Fe_3O_4@TEOS was prepared according to the known procedure.[11] Fe_3O_4@PVP was synthesized *via* the magnetite modification by its treatment with a water–ethanol (1 : 1) solution of PVP and the heating of obtained mixture at 90 °C for 10 min.

Optical density in the study of the sedimentation of modified magnetite particles was measured on a UV-1800 spectrophotometer (Shimadzu, Japan). Spectrophotometric determination of silicon content was carried out after acid decomposition of the sample. The iron content was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Particle images were recorded using a JEOL JSM-6700F (Japan) scanning electron microscope. The quantitative determination of the content of model organic substances in solutions before and after sorption was carried out on an LC-20 Prominence liquid chromatograph (Shimadzu). Asphaltene determination was performed spectrophotometrically at 350 nm.

[‡] Isolated from a Lukoil-UNP commercial tar.

Table 3 Temperature dependence of asphaltenes extraction (R_{Asp}) from a toluene solution by Fe_3O_4@TEOS (m_{sorbent} = 5 mg).[a]

T/°C	t/min	R_{Asp}(%)	T/°C	t/min	R_{Asp}(%)
45	10	69.8	55	40	59.5
45	20	67.7	65	10	48.0
45	30	68.8	65	20	49.0
45	40	64.6	65	30	47.0
45	50	66.7	75	10	40.3
55	10	57.6	75	20	46.1
55	20	59.5	75	30	44.2
55	30	62.4			

[a] The experiment was performed under microwave heating (Discover SP-D).

Figure 3 depicts the sorption isotherm for Fe_3O_4@TEOS recorded for toluene solutions at room temperature. Previously, it has been shown for nanosized Fe_3O_4 and Fe_3O_4@TEOS that the S-shaped dependence is typical of the adsorption of ionic surfactants on the surface of inorganic oxides[14–16] and reflects the self-assembling of sorbate molecules into layers due to inter- and intramolecular interactions.[17] According to the data on the formation of supramolecular nanosized asphaltene aggregates, these interactions may play a significant role in the behavior of asphaltenes.[1] According to our data on the sorption capacity of Fe_3O_4@TEOS, it can be assumed that the degree of surface covering at 45 °C will approximate to the saturated monolayer.

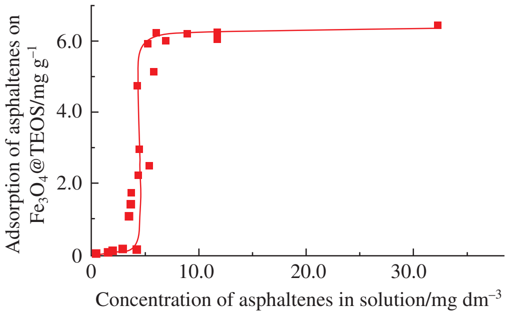

Figure 3 Adsorption isotherm for the asphaltenes in toluene solutions at Fe_3O_4@TEOS surface at room temperature.

The further sorption of asphaltenes will occur *via* the mechanism of multilayer shell formation on the sorbent surface.

In summary, the reported results can be valuable for the development of a modified technology for the supercritical deasphalting of oils due to the maintained selectivity of separation and removal of asphaltenes, which may result in the improved quality of petroleum products.

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