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RECOVERY OF PHENOLS FROM WASTE WATERS BY AN ENCAPSULATED MAGNETIC SORBENT

**P. T. Sukhanov,[1] A. S. Gubin,[1] A. A. Kushnir,[1]
A. A. Bogdaev,[2] S. V. Safonov,[3] and A. V. Kretinin[3]**

Magnetic nanoparticles of an iron oxide (Fe_3O_4) encapsulated in hyper-cross-linked polystyrene (PS) were used as a sorbent for recovery of phenols from waste waters. The encapsulated magnetic sorbent Fe_3O_4-PS was prepared by suspension polymerization. Sorption of phenol and 4-nitrophenol onto Fe_3O_4-PS was studied under dynamic and static conditions. The recovery of 4-nitrophenol was 96%; of phenol, 64%.

Keywords: hyper-cross-linked polystyrene, encapsulated magnetic sorbent, suspension polymerization, sorption, phenol, 4-nitrophenol, nanoparticles, waste waters.

Contemporary approaches to waste-water purification call for the use of nontoxic and highly effective extractants and sorbents that have the minimum water-purification losses and simple and fast regeneration, in particular, a new type of sorbent based on magnetic nanoparticles of iron oxide Fe_3O_4. Modified Fe_3O_4 nanoparticles are effective sorbents for many organic compounds, including phenols [1–4]. However, encapsulation of particles of various compounds is also used to increase the selectivity and achieve the greatest extraction.

The goals of the present work were to study the sorption of phenol and 4-nitrophenol on a magnetic sorbent under static and dynamic conditions and to evaluate the possibility of using an encapsulated magnetic sorbent based on Fe_3O_4 nanoparticles to purify waste waters.

Experimental. *Instruments, reagents, and equipment.* Phenol, 4-nitrophenol, Fe(III) chloride, and dichloroethane (all chemically pure); 5% NH_4OH solution; grade SDEB styrene (GOST 10003, 99.8%); polyvinyl alcohol (pure); benzoyl peroxide (76.5% pure); divinylbenzene (80% pure); and 4-chlorostyrene were used in the experiments.

The reaction mixture was stirred by an ES-8300D overhead stirrer during syntheses of magnetic particles and coating of them with polymers. An MM-5 magnetic stirrer was used for sorption under static conditions.

A KFK-3-01 photoelectrocolorimeter was used for photometric determination of the substances. Sorbent particle size and structure were assessed using a JSM-6510LV scanning electron microscope at Voronezh State University Technopark Center for Collective Use.

Synthesis of Fe_3O_4 nanoparticles. The published method was used as a basis for synthesizing the Fe_3O_4 nanoparticles [5]. The following well-known reaction was used:

$$2FeCl_3 + FeSO_4 + 8NH_3 + 4H_2O \rightarrow Fe_3O_4 + 6NH_4Cl + (NH_4)_2SO_4.$$
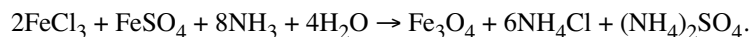
[1] Voronezh State University of Engineering Technologies, Voronezh, Russia; e-mail: pavel.suhanov@mail.ru.

[2] RVK-Voronezh, Voronezh, Russia.

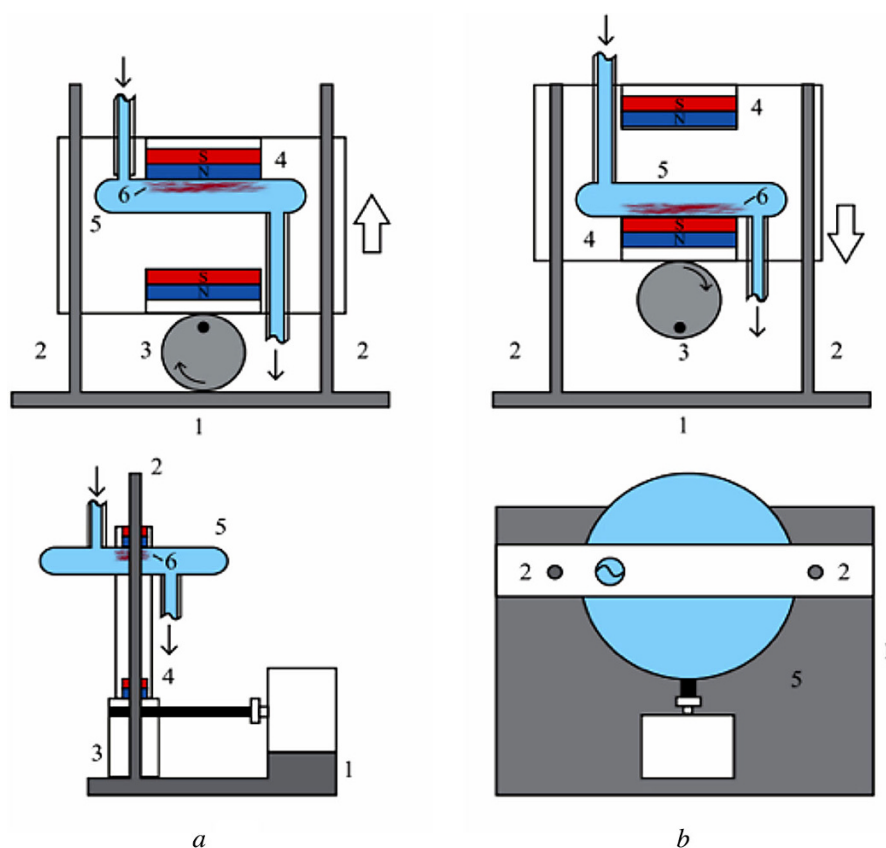[3] Voronezh State Technical University, Voronezh, Russia.

Fig. 1. Apparatus for periodic action by permanent magnets on a concentrating column: *a*) in the lowest position; *b*) in the highest position; *1*) base; *2*) guides for the magnet block; *3*) eccentric; *4*) permanent magnet on base; *5*) cartridge; *6*) absorbent.

When the reaction was finished, the Fe_3O_4 particles were extracted from the solution using a magnet and rinsed with doubly distilled H_2O, EtOH, and toluene. The particles were stored in toluene (10 cm^3).

Preparation of encapsulated sorbent based on Fe_3O_4 nanoparticles. The encapsulated magnetic sorbent Fe_3O_4-PS was synthesized in two steps using suspension polymerization. The published method was used as a prototype [6]. First, poly-vinyl alcohol (0.5 g) was dissolved in H_2O (100 cm^3) and treated with benzoyl peroxide (0.05 g) and a mixture (12 cm^3) of 4-chlorostyrene, styrene, and divinylbenzene (1:1:1). Then, the pore-former (toluene, 10 cm^3) with the previously stored Fe_3O_4 particles was added. The mixture was heated to 80°C and stirred first for 1 h at 200 rpm and then for 12 h at 100 rpm.

The resulting Fe_3O_4 particles coated with chloropolystyrene were extracted using a magnet, rinsed with doubly distilled H_2O and an EtOH–Me_2CO mixture (1:1), stirred in dichloroethane (50 cm^3) for 20 min at 500 rpm, treated with dichloroethane (50 cm^3) in which iron chloride was dissolved, and stirred at 75°C first for 20 min at 500 rpm and then for 10 h at 200 rpm.

The resulting Fe_3O_4-PS particles were extracted with a magnet; rinsed with a mixture of HCl, EtOH, and doubly distilled H_2O (1:10:10); and dried.

Determination of sorbent particle size. Ground sorbent samples of arbitrary masses were placed onto a graphite foil. The particle size was determined under a moderate vacuum at accelerating potential 30 kV.

Sorption under static conditions. Sorption of substances under static conditions was studied by placing a weighed portion of Fe_3O_4-PS sorbent (0.05 ± 0.001 g) into a chemical beaker, adding the studied substance (10 cm^3) with initial con-centration c_0, and stirred using an external permanent magnet for 30 min at 20 ± 2°C. Then, the sorbent was separated from the solution using a magnet. The concentration c of the studied substance in the equilibrium aqueous phase was determined
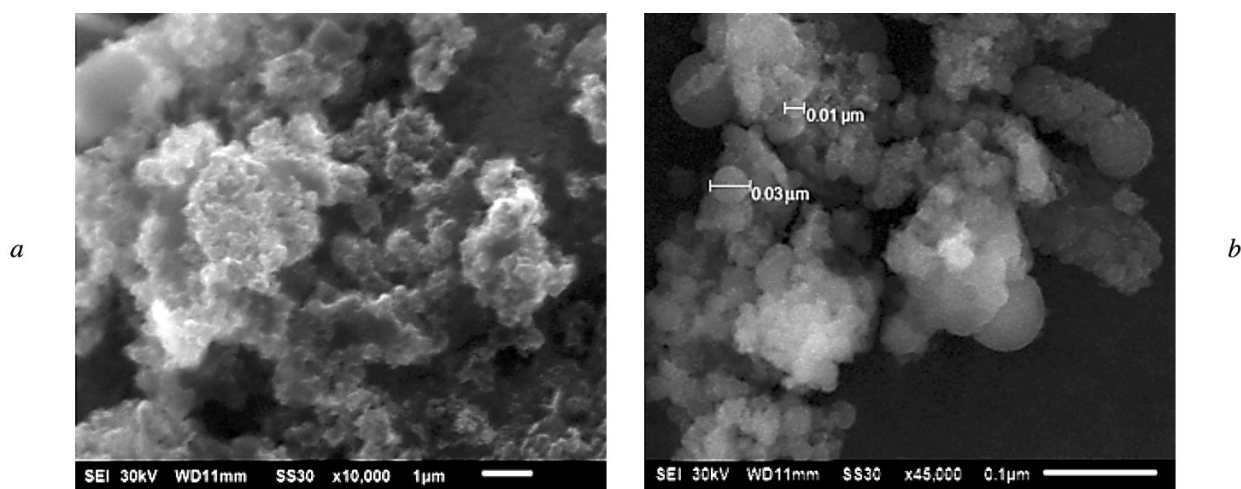
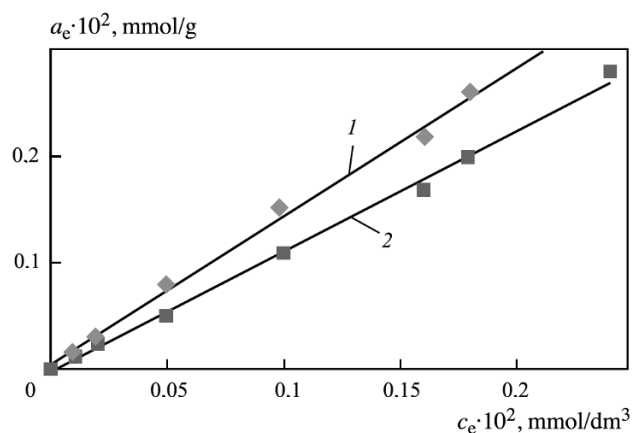Fig. 2. SEM images of the structures of Fe_3O_4-PS; magnification ×10000 (*a*) and ×45000 (*b*).

Fig. 3. Sorption isotherms for 4-nitrophenol (*1*) and phenol (*2*) on Fe_3O_4-PS.

photometrically. Sorption isotherms were constructed using the experimental results. In an analogous manner, sorption on uncoated Fe_3O_4 nanoparticles was studied.

The equilibrium concentration a_e (mmol/g) of substance in the sorbent under static conditions, degree of extraction R (%), and distribution coefficient D (cm^3/g) were calculated using known equations [7].

Sorption under dynamic conditions. A weighed portion of Fe_3O_4-PS sorbent (0.02 ± 0.001 g) was placed into a concentrating column using a balanced density method. For this, a suspension of the sorbent in H_2O was prepared and passed through the cartridge column. The sorbent particles were held and suspended inside the column by the continuous effect of a permanent magnet, the sections of which shifted up and down and left and right on the outside of the column during the sorption. Figure 1 shows a diagram of the apparatus for sorption under dynamic conditions with shifting of the magnet up and down.

Portions (5 cm^3) of the solution were collected at the column outlet. The concentration of substances in them was determined by photoelectrometry. Then, elution curves were constructed for substance sorption in coordinates of c/c_0 vs. V_{pa}, where c and c_0 are phenol concentrations (mg/cm^3) at the column outlet and inlet, respectively; V_{pa}, volume of sample (cm^3) passed through the column [8].

The desorption of the substance began as soon as its concentration in the filtrate reached the initial one. The desorption used NH_4OH solution (5%, 2 cm^3) at flow rate $w = 0.5$ cm^3/min. The substance concentration in the eluent was determined by photoelectrometry.

TABLE 1. Parameters for Phenol Absorption in Static Mode

Compound	R, %		Fe₃O₄-PS absorption		
	Fe_3O_4-PS	Fe_3O_4	D, cm³/g	K_F	n
4-nitrophenol	96 ± 3	49 ± 2	3002 ± 31	4.72	0.82
Phenol	64 ± 2	51 ± 2	851 ± 15	2.02	0.96

TABLE 2. Effect of 4-Nitrophenol Solution Flow Rate on Volume $V_{10\%}$ and DEC

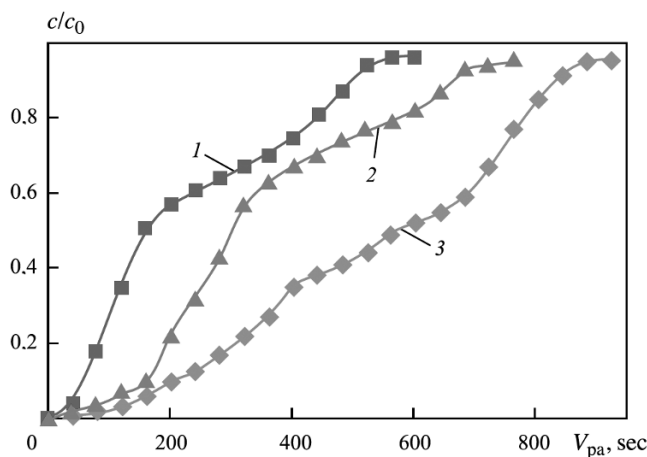| w, cm³/min	$V_{10\%}$, cm³	DEC, mg/g
0.25	250	0.25
0.5	150	0.15
1	50	0.05

Fig. 4. Elution curves for absorption of 4-nitrophenol from aqueous solution ($c_0 = 1$ mg/dm³) at solution flow rates $w = 1, 0.5$, and 0.25 cm³/min (curves 1, 2, and 3, respectively).

The breakthrough volume $V_{10\%}$ (cm³) and dynamic exchange capacity (DEC, mg/g) were determined during the studies of sorption under dynamic conditions [8].

Results. The structure of the Fe_3O_4-PS sorbent was studied using scanning electron microscopy (SEM) that enabled the particle size to be evaluated, information on their ordering (or lack of it) to be obtained, and impurities and particle aggregation to be observed. An analysis of the obtained images (Fig. 2) found that, in general, the sorbent particles were spherical and of size 10–90 nm.

The dependence of the equilibrium concentration a_e of a substance in a sorbent on its solution concentration c_e at constant temperature is plotted as sorption isotherms that allow physicochemical sorption parameters (constants of Freundlich and Langmuir equations) to be determined and the extraction mechanism to be established. Figure 3 shows sorption isotherms for Fe_3O_4-PS prepared at 20 ± 2°C, pH 7, and 30 min.

The greatest correlation coefficients ($r^2 = 0.97$–0.998) were obtained for sorption isotherms plotted in coordinates of the Freundlich equation. They were used to describe sections of the sorption isotherms of the analyzed substances on Fe_3O_4-PS. The correlation coefficients were <0.8 if the Langmuir model was used. Such values are considered unsatisfactory.

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Table 1 presents distribution coefficients D, degrees of extraction R for sorption of phenols under static conditions (confidence internals were calculated for three parallel measurements and confidence probability $P = 0.95$), and constants K_F and n of the Freundlich equation. It can be seen that 4-nitrophenol had the greatest values of D and R.

The potential of the sorbent for sorption under dynamic conditions was estimated from the elution curves. Figure 4 shows these curves for 4-nitrophenol. The shapes of the curves suggest that penetration of sorbate molecules into the polymer bulk was the limiting step. It was established that increasing flow rate w decreased the DEC and; correspondingly, decreased the breakthrough volume (Table 2).

The DEC was an indicator of the sorption effectiveness under dynamic conditions and could act as a criterion for comparing sorption conditions.

Conclusions

1. The degrees of extraction of phenol and 4-nitrophenol were 64 and 96%, respectively, if a magnetic sorbent encapsulated in hyper-cross-linked PS was used to purify waste waters. The sorbent had a significant specific surface area because of the small particle size.

2. The results indicated that use of the encapsulated magnetic sorbent Fe_3O_4-PS was effective for fine purification of waste waters.

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