ISSN 1061-9348, Journal of Analytical Chemistry, 2015, Vol. 70, No. 11, pp. 1313–1321. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © V.V. Tolmacheva, V.V. Apyari, B.N. Ibragimova, E.V. Kochuk, S.G. Dmitrienko, Yu.A. Zolotov, 2015, published in Zhurnal Analiticheskoi Khimii, 2015, Vol. 70, No. 11, pp. 1149–1157.

ARTICLES

A Polymeric Magnetic Adsorbent Based on Fe_3O_4 Nanoparticles and Hypercrosslinked Polystyrene for the Preconcentration of Tetracycline Antibiotics

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Received March 19, 2015; in final form, April 16, 2015

Abstract—A magnetic adsorbent based on hypercrosslinked polystyrene (HCPS) and Fe_3O_4 nanoparticles (HCPS–Fe_3O_4) is synthesized and investigated. The conditions for its preparation are optimized by varying the weight of adsorbent and the concentration of Fe_3O_4. A comparative evaluation of the adsorption properties of HCPS–Fe_3O_4, HCPS, and Fe_3O_4 to tetracyclines is performed. It is shown that the magnetic adsorbent based on HCPS retains adsorptive properties towards tetracyclines and is easily separated from a solution by applying a magnetic field. The quantitative desorption of tetracyclines is achieved using 4 mL of an acetonitrile–methanol (1 : 1) mixture.

Keywords: magnetic adsorbent, Fe_3O_4 nanoparticles, hypercrosslinked polystyrene, tetracyclines
DOI: 10.1134/S1061934815110155

Currently, magnetic solid-phase extraction (MSPE) is increasingly used in analytical practice for the isolation and purification of substances [1–3]. The essence of this method lies in the adsorption of target analytes by a magnetic adsorbent and the separation of the adsorbent under the action of a magnetic field. After removing the external magnetic field, the adsorbent immediately loses its magnetic properties and becomes again a suspension. A solution for washing is added first to this suspension, followed by an eluent for the desorption of the preconcentrated compounds. Compared with the conventional version of solid-phase extraction, MSPE has several advantages, such as simplicity, rapidity, and lesser losses at the sample preparation stage [4, 5]. Furthermore, increasing area of phase contact due to a uniform distribution of the magnetic adsorbent in a sample solution ensures rapid mass transfer. In some cases, it is possible to isolate analytes from complex objects like, milk, honey, or eggs without separating the matrix components.

Nanosize Fe_3O_4 particles are a convenient material for the preparation of adsorbents with magnetic properties, because they can be easily synthesized and have better magnetic characteristics in comparison with other iron oxides [6]. Magnetic adsorbents based on Fe_3O_4 are prepared by the targeted modification of their surfaces [7, 8], among others, under the conditions of microwave heating [9, 10]. To increase the aggregate stability of magnetite and to impart hydrophobic properties to the particles, the surface of Fe_3O_4 is modified by surfactants or organic acids. A common method is to coat the magnetic core by a layer of silica gel, metal oxides, or polymers, including polymers with molecular imprints, thereby forming particles of the core–shell type (core–shell nanoparticles) [11–13]. Nanocomposites are among the most effective magnetic adsorbents, in which iron oxide nanoparticles are embedded in a matrix of carbon [14] or polymer [15] adsorbents.

Among polymeric adsorbents that found the application in the preparation of magnetic adsorbents, hypercrosslinked polystyrene is of great interest. Existing methods for synthesizing magnetic hypercrosslinked polystyrene can be divided into two groups. One group includes the methods based on polymerization performed in the presence of Fe_3O_4 nanoparticles, which are introduced into the reaction mixture comprising all the components necessary for the synthesis of the polymer [16–20]. Such a process is laborious and requires a large number of operations. Methods of another group are based on the impregnation of commercial HCPS samples by solutions of iron(II, III) salts, followed by the precipitation of Fe_3O_4 particles in the polymer matrix by the action of aqueous ammonia [21–23].

In this paper, we propose a simple method for producing a magnetic polymeric adsorbent, based on the adsorption of presynthesized Fe_3O_4 nanoparticles at HCPS. This approach was used for the preparation of magnetic carbon adsorbents [24, 25]. The goal of this work was to synthesize a magnetic adsorbent based on a commercially available sample of hypercrosslinked polystyrene, to study its structural and magnetic properties, and to compare the adsorption behavior of tetracyclines with respect to HCPS–Fe_3O_4, HCPS, and Fe_3O_4 nanoparticles.

EXPERIMENTAL

Reagents and materials. To synthesize Fe_3O_4 nanoparticles, we used $FeCl_3 \cdot 6H_2O$ and $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ (analytical grade) and NH_3 (high-purity grade). A Diapak P-3 HCPS sample (BioKhim-Mak ST) was selected as a starting material for the preparation of magnetic adsorbent. A stock solution of tetracyclines with the concentration 1 mg/mL was prepared by dissolving their accurately weighed portions in methanol. Working solutions of these compounds were obtained by diluting the initial solutions immediately before use. We used tetracycline and chlortetracycline hydrochlorides, oxytetracycline dihydrate (99.0%, Acros Organics), and doxycycline hydrate (>98.0%, Sigma).

Apparatus. Electron microscopic study was performed using transmission (TEM images) and scanning (SEM images) electron microscopes with a field emission source (LEO912 AB OMEGA, LEO SUPRA 50VP, Carl Zeiss, Germany). The magnetization curves of samples were measured using an apparatus for studying the topochemical reactions of ferromagnetic nanoparticles, developed on the basis of a vibrating magnetometer, at a frequency of 73 Hz in the field range of up to 6.5 kOe at room temperature. This setup is described in [26]. The specific surface of samples was measured by low-temperature nitrogen adsorption using an ASAP 2010 N facility (Micromeritics, United States). Diffuse reflection in the visible region were recorded by an Eye-One Pro minispectrophotometer (X-Rite), proposed in our group as an alternative to a diffuse reflectance spectrometer [27, 28]. The concentration of Fe_3O_4 nanoparticles in an HCPS matrix was estimated by the Kubelka–Munk function (F) at a wavelength corresponding to the maximum absorption (λ_{max}), that is,

$$F(R) = (1 - R)^2/2R,$$

where R is diffuse reflectance.

The absorption spectra and absorbance values of solutions were recorded using an SF-103 spectrophotometer (Akvilon, Russia); pH was monitored by an Ekspert 001 potentiometer (Russia). Magnetic solid-phase extraction was performed in an electromechanical vibromixer. The magnetic adsorbent was separated from solution using a Nd–Fe–B magnet (20 × 20 × 20 mm). Distilled water was further purified by using a Millipore water purification system.

Synthesis of Fe_3O_4. Nanosize Fe_3O_4 particles were obtained by gradual introduction of a mixture of $FeCl_3 \cdot 6H_2O$ (1 mL of a 1 M solution in 2 M HCl) and $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ (1 mL of 0.5 M solution) in deionized water to aqueous ammonia (40 mL, 0.5 M), followed by stirring for 30 min at room temperature. Magnetite obtained by chemical deposition, was a black suspension transforming into a magnetic powder of black-brown color after drying.

Preparation of magnetic hypercrosslinked polystyrene HCPS–Fe_3O_4. To obtain the adsorbent, 2, 5, 10, and 15 mL of the Fe_3O_4 nanoparticle suspension synthesized by the above procedure were used. The Fe_3O_4 precipitate was removed by magnetic separation, washed several times with deionized water to pH 6–7, diluted with methanol to 10 mL, and added to 100 mg of HCPS dispersed in 1 mL of methanol. The mixture was then stirred in the electromechanical vibromixer for 40 min; the adsorbent was separated by magnetic separation, washed with water, dried, and used for the adsorption of tetracyclines.

Procedure for studying the adsorption of tetracyclines. The adsorption of tetracyclines (TC) at HCPS–Fe_3O_4, HCPS, and Fe_3O_4 particles was studied under static conditions at room temperature. For this purpose, weighed portions of the adsorbents (0.020 ± 0.001 g) were placed in test tubes with ground stoppers; a solution of the test substance was added; and the mixtures were shaken in the electromechanical vibromixer until the equilibrium adsorption was achieved. Thereafter, the adsorbent was removed from the solution by magnetic separation or, in the case of HCPS, centrifugation, and the concentration of tetracyclines in the equilibrium aqueous phase was determined spectrophotometrically by their intrinsic light absorption. When selecting the conditions, we varied the equilibration time, the adsorbent weight, volume and pH of the solution, and the composition of eluent. Before desorption, the adsorbent is washed with 5 mL of water.

RESULTS AND DISCUSSION

Preparation and study of HCPS–Fe_3O_4 magnetic adsorbent. The adsorbent was prepared in two steps: first, nanosize Fe_3O_4 particles were synthesized, and then, they were adsorbed at HCPS.

According to the data of transmission electron microscopy (Fig. 1a), the synthesized Fe_3O_4 particles are a system of aggregated round-shape particles of approximately the same size. The diameter of these particles is 10–20 nm. The electron diffraction pattern (Fig. 1b) confirmed the presence of Fe_3O_4 nanoparticles in the sample. The surface area of a dry sample of synthesized nanoparticles is 70 m^2/g, which is close to the value expected for ideally spherical Fe_3O_4 nanoparticles with a diameter of 17 nm. Magnetic measurements showed that the Fe_3O_4 nanoparticles are superparamagnetic. There is no magnetic hysteresis loop in the magnetization curve of the sample (Fig. 2a), which is typical of magnetic particles in the nanoscale state

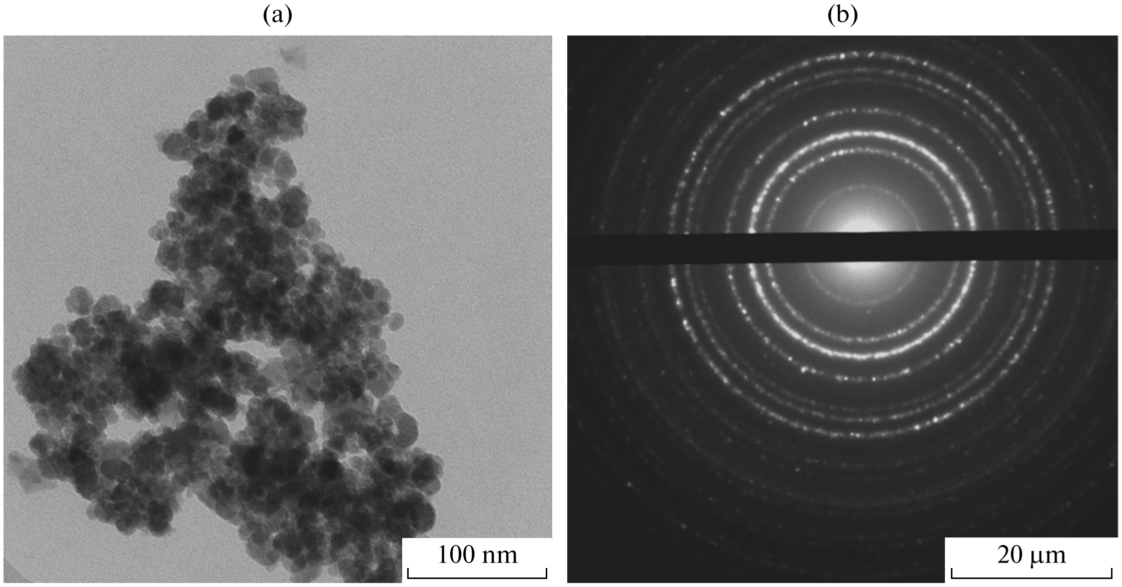


Fig. 1. (a) TEM image and (b) electron diffraction pattern of magnetic Fe_3O_4 nanoparticles.

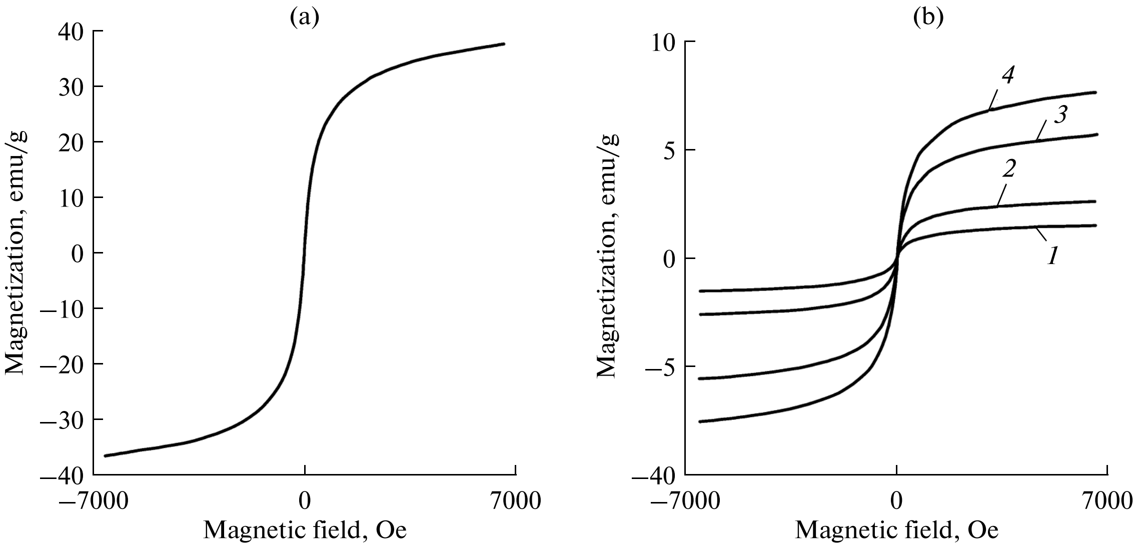


Fig. 2. Magnetization curves of (a) Fe_3O_4 and (b) magnetic HCPS–Fe_3O_4 adsorbents with the Fe_3O_4 concentration of (*1*) 4.3, (*2*) 10.0, (*3*) 18.3, and (*4*) 25.0 wt %.

(<25 nm). The sample is characterized by a saturation magnetization of 41.68 emu/g.

The adsorption of Fe_3O_4 at HCPS was performed from its aqueous, methanol, and acetonitrile solutions. The resulting magnetic composites were dried, and their adsorption and magnetic properties were studied. The main quality parameters in selecting the conditions for obtaining a magnetic adsorbent was structural uniformity (integrity) of the magnetic composite, the ability to magnetization, no traces in the solution after magnetic separation of the adsorbent, and efficiency of extraction of tetracyclines. It is found that Fe_3O_4 particles are best adsorbed and retained by HCPS from methanol solutions. Using the procedure described in Experimental section, four samples of magnetic HCPS–Fe_3O_4 adsorbents with different concentration of Fe_3O_4 were synthesized. The adsorbents are powders of black-brown color. The obtained

Table 1. Structural, magnetic, and adsorption characteristics of HCPS and HCPS–Fe_3O_4

Characteristic	HCPS	HCPS/Fe_3O_4 (5%)	HCPS/Fe_3O_4 (12%)	HCPS/Fe_3O_4 (20%)	HCPS/Fe_3O_4 (30%)
Specific surface, m^2/g	1132	1080	1046	1018	944
Micropore surface area, m^2/g	707	685	645	636	585
Mesopore surface area, m^2/g	219	202	212	200	191
Pore volume, cm^3/g	0.60	0.58	0.56	0.55	0.51
Micropore volume, cm^3/g	0.32	0.30	0.29	0.29	0.27
Mesopore volume, cm^3/g	0.25	0.25	0.24	0.25	0.24
Average pore diameter, nm	2.11	2.14	2.15	2.16	2.18
Saturation magnetization, emu/g	–	1.69	2.94	6.37	8.47
Residual magnetization, emu/g	–	0.05	0.02	0.02	0.005
Recovery of oxytetracycline*, %	97 ± 3	96 ± 2	95 ± 3	97 ± 2	95 ± 3
Degree of desorption of oxytetracycline**, %	98	95	70	65	50

* Conditions of adsorption of oxytetracycline: $c_{TC} = 5 \times 10^{-5}$ M, $V = 25$ mL, $m_{ads} = 0.02$ g, and $t = 20$ min.
** Conditions of desorption of oxytetracycline: 4 mL of an acetonitrile–methanol (1 : 1) mixture.

samples are listed in Table 1; their structural, magnetic, and adsorption characteristics are given.

It is found by diffuse reflectance spectroscopy that the spectral characteristics of Fe_3O_4 and magnetic HCPS–Fe_3O_4 adsorbents are identical. In the diffuse reflectance spectra of magnetic adsorbents (Fig. 3), there is a band with a maximum at 400 nm, the amplitude of which increases with the concentration of Fe_3O_4 in HCPS. It is seen from the comparison of the electron micrographs (Fig. 4) that the Fe_3O_4 nanoparticles are disposed on the surface of the spherical HCPS particles in the form of clusters. The presence of iron on the surface of HCPS was confirmed by energy-dispersive X-ray emission spectroscopy (Fig. 5). The results presented in Table 1 show that with increasing concentration of Fe_3O_4 nanoparticles in HCPS, a slight decrease of the specific surface and pore volume of adsorbents is observed, but these characteristics are sufficiently high for using the composites obtained as adsorbents.

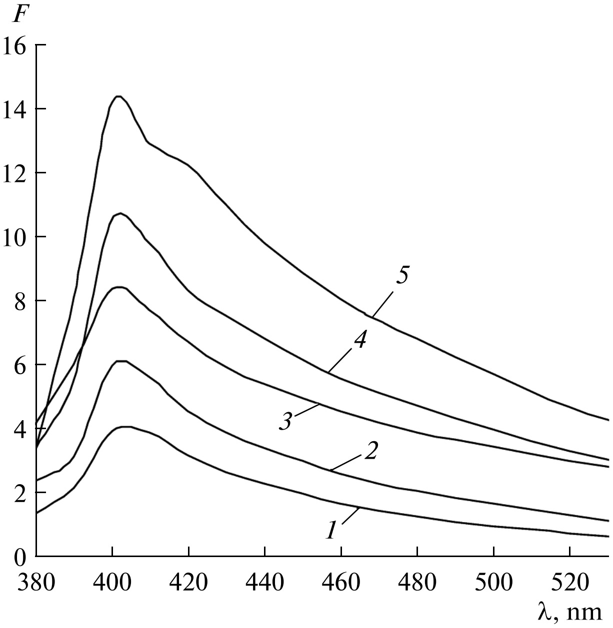


Fig. 3. Diffuse reflectance spectra of (*1*) HCPS and (*2*)–(*5*) magnetic HCP–Fe_3O_4 adsorbents with the Fe_3O_4 concentration of (*1*) 0, (*2*) 5, (*3*) 12, (*4*) 20, and (*5*) 30 wt %.

Magnetic adsorbents based on HCPS exhibit magnetic properties only when an external magnetic field is applied, which explains the absence of the phenomenon of magnetic hysteresis in the magnetization

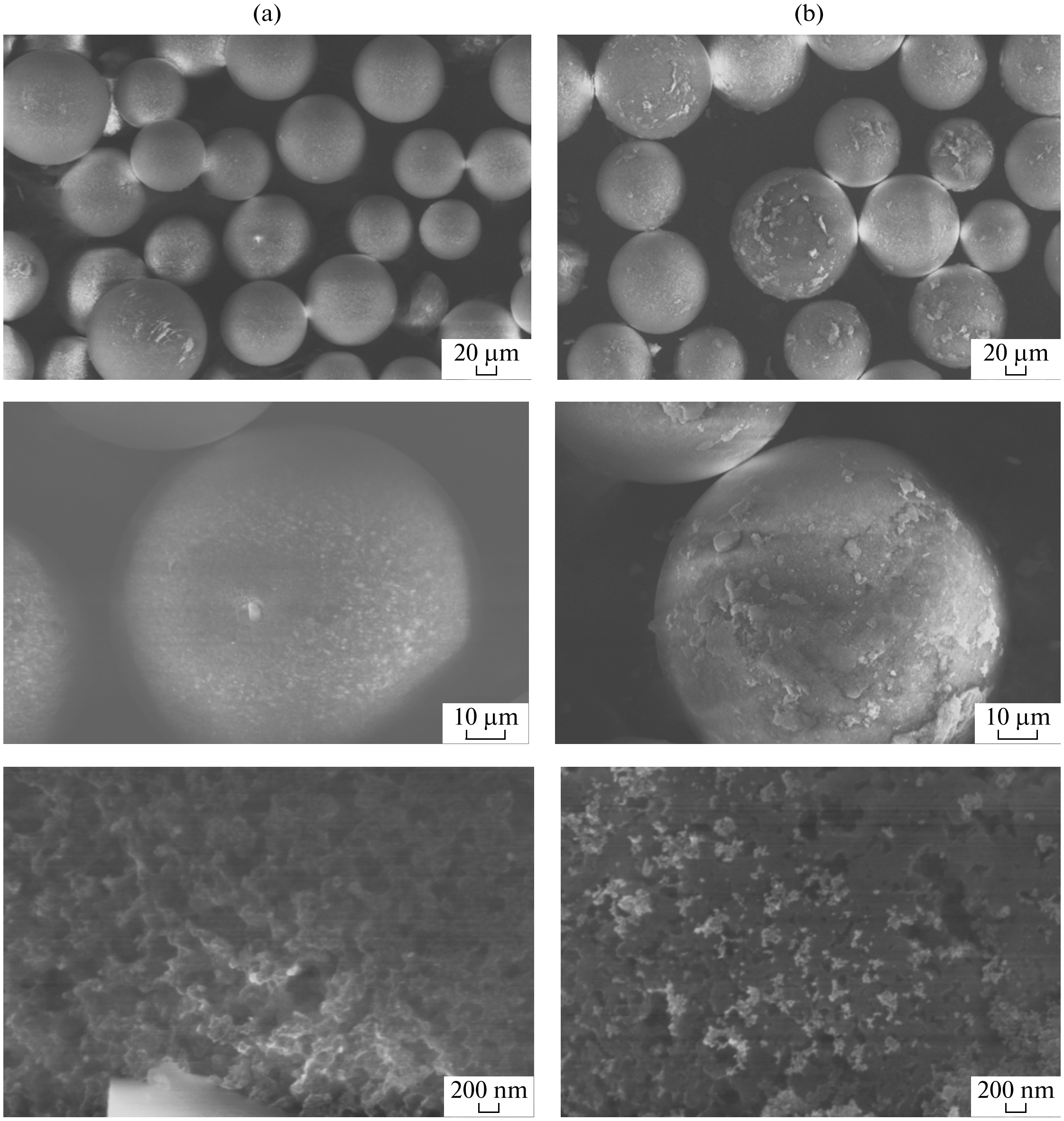
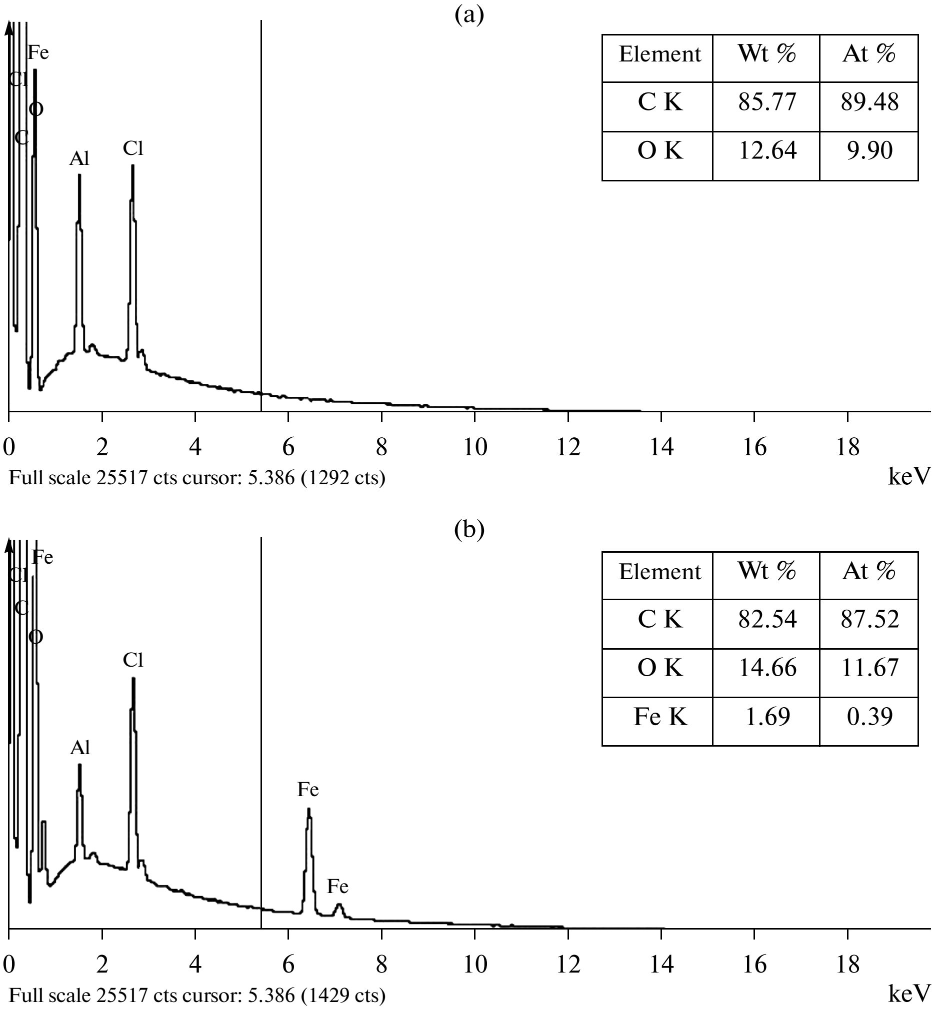


Fig. 4. SEM images of (a)L HCPS and (b) magnetic HCPS–Fe_3O_4 adsorbent.

curves (Fig. 2b). Depending on the concentration of Fe_3O_4, the saturation magnetization (at 300 K) increases from 1.7 to 8.5 emu/g (Table 1); this is enough to remove the adsorbent from the solution by a magnetic field of the permanent magnet. A decrease in the specific magnetization of HCPS–Fe_3O_4 composites compared to Fe_3O_4 is a consequence of the presence of diamagnetic HCPS in the composite. The composites are characterized by low residual magnetization (Table 1), which is important to preserve the stability of an aqueous suspension.

Otherwise, after exposure to a magnetic field, the particles would form large stable aggregates that are virtually impossible to suspend. The comparison of the recoveries of oxytetracycline at HCPS and HCPS–Fe_3O_4 indicates that the introduction of Fe_3O_4 nanoparticles into a matrix of hypercrosslinked polystyrene does not affect its adsorption capacity. The recoveries are 95–97%. However, the degrees of desorption of oxytetracycline by an acetonitrile–methanol (1 : 1) mixture decrease with increasing concentration of Fe_3O_4 in the HCPS matrix (Table 1), which is apparently because of the interaction of oxytetracycline with iron oxides [29]. For the further investigations of the adsorption capacity of magnetic HCPS relative to tet-



(a)

Element	Wt %	At %
C K	85.77	89.48
O K	12.64	9.90

(b)

Element	Wt %	At %
C K	82.54	87.52
O K	14.66	11.67
Fe K	1.69	0.39

Fig. 5. Energy-dispersive X-ray emission spectra of (a) HCPS and (b) HCPS–Fe_3O_4.

racyclines, we selected the adsorbent containing 5% of Fe_3O_4.

Adsorption of tetracyclines on magnetic HCPS–Fe_3O_4 adsorbent, HCPS, and Fe_3O_4 nanoparticles. We compared the adsorption behavior of tetracyclines with respect to an HCPS–Fe_3O_4 (5%) magnetic adsorbent, HCPS, and Fe_3O_4 nanoparticles as a function of phase contact time, pH, and concentration of the extracted compounds. As an example, an experimental dependence for oxytetracycline (OTC) is shown in Fig. 6. For the other tetracyclines, the curves are similar. It is seen from the figure that the change of HCPS to the magnetic adsorbent HCPS–Fe_3O_4 lowers the time of achievement of the adsorption equilibrium from 20 to 10 min compared to HCPS. Tetracyclines are also adsorbed on Fe_3O_4 particles, but to a lesser degree (Fig. 6a, curve *3*). The pH-dependence of the degree of recovery (Fig. 6b) indicates that unlike HCPS, at which tetracyclines are adsorbed in the zwitter-ionic and cationic forms, the magnetic HCPS–Fe_3O_4 adsorbent and Fe_3O_4 particles absorb the analytes only in the zwitter-ionic form (Fig. 6, curves *2* and *3*). Adsorption is the highest at pH 3–8, in the region of dominance of this form of tetracyclines. A decrease in adsorption in an acidic medium, compared with adsorption on HCPS, can be explained by the electrostatic repulsion of protonated forms of tetracycline and positively charged magnetic Fe_3O_4 nanoparticles. According to [30], the isoelectric point of magnetite is at pH 7.9 ± 0.1. The adsorption isotherms of oxytetracycline demonstrate high affinity of these adsorbents to tetracyclines (Fig. 6c). In the range of equilibrium concentrations, 0.002–0.45 mM, the adsorption isotherms are described by the Langmuir equation. The maximum adsorption increases from 0.05 for Fe_3O_4 to 0.42 and 0.44 mmol/g for HCPS and HCPS–Fe_3O_4, respectively.

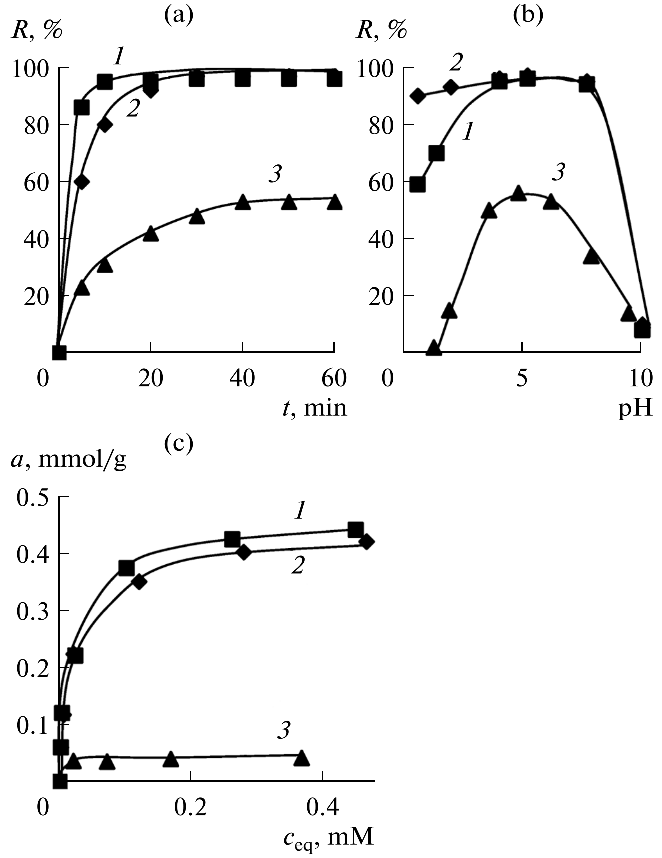


Fig. 6. Dependence of the recoveries of oxytetracycline by (*1*) magnetic HCPS–Fe_3O_4 adsorbent, (*2*) HCPS, and (*3*) Fe_3O_4 nanoparticles on (a) the phase contact time and (b) solution pH, and (c) adsorption isotherms of oxytetracycline; $V = 25$ mL, $m_{ads} = 0.020 \pm 0.001$ g, $c_{OTC} = 5 \times 10^{-5}$ M, pH ~ 6 (a and c).

Table 2. Recoveries (*R*, %) of tetracyclines at HCPS–Fe_3O_4, HCPS, and Fe_3O_4 nanoparticles: $c_{TC} = 5 \times 10^{-5}$ M, $V = 25$ mL, pH ~ 6, $m_{ads} = 0.02$ g, and $t = 15$ min

Compound	HCPS/Fe_3O_4	HCPS	Fe_3O_4
Tetracycline	96 ± 2	97 ± 2	52
Oxytetracycline	96 ± 2	97 ± 3	54
Chlortetracycline	97 ± 3	97 ± 2	57
Doxycycline	95 ± 3	96 ± 2	53

The adsorption properties of HCPS–Fe_3O_4, Fe_3O_4 particles, and HCPS towards tetracycline, oxytetracycline, and chlortetracycline, and doxycycline are compared under similar conditions (Table 2). It is seen that HCPS and magnetic HCPS adsorb quantitatively all tetracyclines (up to 95–97%), whereas for Fe_3O_4 particles, the recoveries ranged from 52 to 57%.

When selecting the conditions for desorption, acetonitrile, methanol, and a mixture of acetonitrile and methanol (1 : 1) were used as eluents. Desorption was carried out using 2 and 4 mL of solvents. It is seen from Table 3 that the quantitative desorption of tetracyclines is achieved in the case of 4 mL of the acetonitrile–methanol (1 : 1) mixture.

The degrees of recovery of tetracyclines from 100 mL of their aqueous solution into 4 mL of the methanol–acetonitrile eluate are listed in Table 4; they indicate that the magnetic HCPS–Fe_3O_4 adsorbent can be used for the group adsorption preconcentration of these compounds. The accuracy and reproducibility of the results was confirmed by the standard addition method using a model mixture prepared based on river water (the Moscow River). The compounds were determined by reverse-phase HPLC with

Table 3. Degrees of desorption (R_{des}, %) of tetracyclines from a magnetic HCPS–Fe_3O_4 adsorbent by different eluents

Compound	Acetonitrile		Methanol		Acetonitrile–methanol (1 : 1)	
	2 mL	4 mL	2 mL	4 mL	2 mL	4 mL
Tetracycline	63	69	61	72	82	94
Oxytetracycline	63	68	65	73	84	95
Chlortetracycline	60	65	63	69	80	93
Doxycycline	61	68	62	70	88	96

Table 4. Accuracy of the determination of tetracyclines in a model mixture based on river water after the adsorption preconcentration from 100 mL by the standard addition method; $m_{HCPS-Fe_3O_4} = 0.02$ g, $c_{EDTA} = 0.02$ M, pH ~ 6, $t = 15$ min, $n = 3$, $P = 0.95$

Compound	Added, μg/mL	Found, μg/mL	Recovery, %	RSD, %
Tetracycline	0	0		
	0.25	0.23 ± 0.03	90	5
Oxytetracycline	0	0		
	0.25	0.24 ± 0.02	96	3
Chlortetracycline	0	0		
	0.25	0.23 ± 0.04	90	7
Doxycycline	0	0		
	0.25	0.24 ± 0.05	95	8

amperometric detection according to the procedure developed previously [31].

The presented data on the synthetic procedure, structure, and magnetic and adsorption properties of the polymeric adsorbent based on magnetic Fe_3O_4 nanoparticles and hypercrosslinked polystyrene form a basis for further study of its analytical capabilities and application to the preconcentration of organic compounds.

ACKNOWLEDGMENTS

The authors are grateful to G.V. Pankina and P.A. Chernavskii (Department of Chemistry, Moscow State University) for the recording and interpretation of magnetic curves. This work was supported by the Russian Scientific Foundation, project no. 14-23-00012.

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Translated by O. Zhukova