ISSN 1070-4272, Russian Journal of Applied Chemistry, 2018, Vol. 91, No. 11, pp. 1849−1855. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © S.S. Grazhulene, N.I. Zolotareva, A.N. Red'kin, N.N. Shilkina, A.A. Mitina, A.M. Kolesnikova, 2018, published in Zhurnal Prikladnoi Khimii, 2018, Vol. 91, No. 11, pp. 1642−1648.

SORPTION
AND ION EXCHANGE PROCESSES

Magnetic Sorbent Based on Magnetite and Modified Carbon Nanotubes for Extraction of Some Toxic Elements

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Received June 1, 2018

Abstract—Magnetic sorbent MNP@CNT was synthesized on the basis of magnetic nanoparticles of magnetite (MNPs) and carbon nanotubes (CNTs). The sorbent was studied in extraction of toxic elements from aqueous media and its synthesis conditions were optimized. Isotherms of sorption of the metal ions under study from aqueous solutions were plotted in relation to their concentrations and solution pH values. The optimal conditions for extraction of Pb(II), Cr(III), and Bi(III) at pH 6 and Cd(II) at pH 4.5–5.0 were found. It was shown that the sorption capacity of the MNP@CNT sorbent for the elements under study is comparable with the capacity of carbon nanotubes, being 4.0, 3.8, 3.5, and 3.5 mg g^{-1} for Bi(III), Pb(II), Ct(III), and Cd(II), respectively. An important advantage of the magnetic composite sorbent over carbon nanotubes is the simple separation of the liquid and solid phases, compared with the conventional column variation of the solid-phase extraction. The resulting composite magnetic sorbent can be used both for analytical purposes, to preliminarily concentrate impurities, and for purification of various technological media and water basins in the environment to remove toxic elements.

Keywords: sorption, magnetic composite, magnetic solid-phase extraction, carbon nanotubes, magnetic nanoparticles, toxic metal ions

DOI: 10.1134/S1070427218110162

One of ways to improve the efficiency of sorption materials is to use a highly dispersed sorbent having a large surface area. However, their use involves problems associated with the difficult separation of the solid and liquid phases after the sorption by labor-consuming processes of filtration and centrifugation. In dynamic separation methods, difficulties are also encountered, associated with the increase in the hydrodynamic resistance to a flow of a fluid on packing columns with the sorbent. A promising method for overcoming these difficulties is the method of magnetic solid-phase extraction (MSPE), which consists in that elements are sorbed on a magnetic sorbent with the subsequent phase separation with a permanent magnet [1–3]. Nanocomposites based on carbon nanotubes (CNTs) and magnetic nanoparticles (NPs) of, in particular, Fe_3O_4, have been successfully considered recently as sorbents of this kind. The constituents in the composite have a successful combination of properties: high sorption capacity, fast mass-exchange kinetics, completeness of sorption and desorption, possibility of multiple regeneration, and supermagnetism. Owing to this circumstance, sorbents of this kind can be successfully used in analytics for concentration and fabrication of sensors, in medicine for targeted delivery of medicinal preparations, and also for purification of various environmental objects. The attractiveness of the magnetic composite MNP@CNT is also due to the relative simplicity of its synthesis, cost effectiveness, and accessibility of its constituents, magnetite [4] and CNTs, including those modified with various organic and inorganic compounds. However, publications devoted to this issue are scarce, being mostly concerned with the sorption of organic compounds and containing contradictory data on the synthesis conditions of the composite [5–10].

Of interest and topical, in addition to applied aspects, is revealing the contribution to the total amount of sorption by the composite of metal ions from the sorption properties of its constituents, about which there are also contradictory data in the literature. In our opinion, these discrepancies are due to the synthesis conditions of both the composite and its constituents, MNPs and CNTs. The synthesis conditions are correlated with the composition, morphology, and kinetics of extraction of elements from aqueous solutions.

The goal of our study was to synthesize the MNP@CNT magnetic component and examine the dependence of its sorption properties on some specific features of CNT synthesis [for the example of extraction of toxic metal ions Bi(III), Cd(II), Cr(III), and Pb(II) from aqueous media] and also examine the contribution of each component of the composite to its sorption properties. The sorption of the above metal ions can be monitored by various spectroscopic methods, including modern plasma techniques. However, we used in the study the simplest and most economical multiple-element arc method of atomic-emission analysis (AEA), with preliminary development of a procedure for analysis and optimization of its conditions as applied to the objects under study.

EXPERIMENTAL

Magnetic nanoparticles were synthesized by the procedure suggested in [11]. We used freshly prepared solutions of iron(III) and (II) chlorides at their 2 : 1 ratio, which contained 11.7 g of $FeCl_3·6H_2O$ and 4.3 g of $FeCl_2·4H_2O$, placed in a 200-mL three-necked round-bottomed flask. The synthesis was performed at 80°C in the atmosphere of an inert gas (argon) under vigorous agitation for 1 h. Then, 20 mL of a 25–30% solution of NH_4OH was rapidly added until pH 10 was reached. After the mixture was cooled, the precipitate was retained in the flask with a magnet, washed with deionized water and ethanol to pH 7, dried to dry residue in a drying box at 60°C, and placed in a desiccator in a closed weighing bottle for further use to synthesize the composite.

The thus synthesized powder was subjected to an X-ray diffraction (XRD) analysis on a DRON-UM-2 diffractometer (CrK_α radiation, V-filter) as a suspension in Vaseline oil. The X-ray diffraction patterns were interpreted using the Power Diffraction (PDF-2) database. The average size of crystallites (coherent scattering regions, CSRs) was calculated by the method of second moments by the Size&Strain software contained in the PDWin software package for mono- and polycrystalline samples from Research-and-Production Enterprise Burevestnik.

Carbon nanotubes were synthesized by the previously developed method of catalytic pyrolysis of the ethanol vapor (CVD) [12]. The CNTs were deposited onto the surface of a nickel catalyst, which was washed after the synthesis with 30% HNO_3. Then the samples were washed to remove the acid with deionized water to neutral reaction and dried. To perform an acid modification, the CNTs were boiled in conc. HNO_3 (special purity) for 1.5 h, washed to remove the acid with deionized water to pH 7, dried, and used to synthesize the composite.

Synthesis of MNP@CNT magnetic sorbent. A 100-mL conical flask was charged with 200 mg of MNPs and 100 mg of CNTs. These were poured-over with 30 mL of deionized water and the mixture was agitated at room temperature on a reciprocating rocker for 30 min. The magnetic sorbent being formed was retained within the flask with a magnet, and carbon nanotubes not bound with MNPs were poured-off into a quartz cup. The sorbent remaining in the flask was twice washed with deionized water, and the washing water was poured-off into the same cup, dried under an IR lamp, and weighed. The difference between the masses of the starting and unbound CNTs was used to determine the amount of CNTs in the magnetic sorbent. The magnetic sorbent was left in the flask in the humid state and used to examine the sorption of metal ions from aqueous solutions.

Study of the sorption of metal ions in aqueous solutions. Starting solutions of the elements under study (standard solutions of the enterprise) with element concentrations of 1000 ppm were prepared by dissolution of weighed (to 4th significant digit) portions of the metals in the corresponding acids. For example, a 200-mg portion of a special-purity metal was placed in a 200-mL measuring flask, dissolved in 10 mL of an acid, and the solution was brought to the mark with deionized water. Bismuth, cadmium, and lead were dissolved in 10 mL of 1 : 1 HNO_3, and chromium, under heating in 10 mL of H_2SO_4. The working solutions of the elements under study with necessary concentrations were prepared via dissolution of the standard solutions with deionized water. To plot sorption isotherms and determine the sorption capacity of the sorbent, a set of samples was prepared with the concentrations of the elements under study in the range from 5 to 50 μg mL^{-1}. A 25-mL aliquot was taken from each solution, the sorption was performed until the sorption equilibrium was attained, and then the elements to be determined were eluted under the chosen conditions. The pH value the optimal for the sorption of the ions under study was created dropwise a 10% solution of NH_4OH or a 5% solution of HNO_3. After the sorption process was complete, the sorbent with elements extracted from solution was retained in the flask with a magnet. The solution was poured-off into a quartz cup with 500 mg of a graphite powder and evaporated to dryness under an IR lamp to be subjected to analysis and determine the amount of sorption. The sorbed metal ions were eluted with 5 mL of 0.5 N HNO_3 under permanent agitation. Then, the sorbent was again retained in the flask with a magnet, and the eluate was poured-off into another quartz cup with 500 mg of graphite powder, evaporated to dryness under an IR lamp and analyzed to determine the elution completeness. A graphite powder of special purity (special-purity 8-4 brand) was used.

The metrological characteristics of the chemical-spectral analysis were determined with 50-mL portions of solutions into which elements to be determined were introduced. The ions were concentrated under the sorption and elution conditions similarly to those for which the sorption isotherms were plotted. The content of the elements after the elution and evaporation on a graphite powder was determined by AEA in a dc (10 A) arc on a PGS-2 diffraction spectrograph with a grating with 651 grooves per millimeter, which provides an inverse linear dispersion of 0.74 nm/mm. A sample was packed into the crater of the lower electrode (anode) having a depth and diameter of 4 mm and wall thickness of 1 mm. The end of the upper electrode (cathode) was tooled for a cone. The distance between the electrodes was 4 mm. A three-lens system of slit illumination was used. The emission spectra were recorded with a photoelectric system based on linear arrays of charge-coupled devices, developed at the laboratory [13]. The analysis was made with standard State samples based on a graphite powder (SOG-21 set, UGTU-UPI). To calculate the content of the elements in solution, their concentration in the graphite powder was divided by the concentration factor equal to 100, defined as the ratio between the mass of a solution being analyzed and that of the graphite powder.

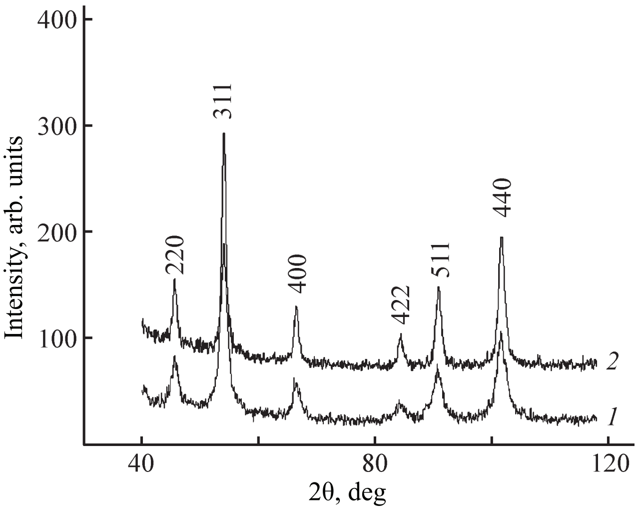

Fig. 1. Diffraction patterns of MNP samples obtained at (*1*) room temperature and (*2*) 80°C.

RESULTS AND DISCUSSION

It is known that the MNP@CNT magnetic sorbent can be synthesized in one or two stages. In the first case CNTs and a mixture of iron(II) and (III) chlorides are mixed together. Then the MNP@CNT composite is precipitated from solution by addition of ammonia. In the second variant, used in the present study, the processes in which CNTs and MNPs are obtained are separated. First, a MNP powder is produced from a mixture of iron(II) and (III) chlorides by precipitation with ammonia. The powder is isolated, dried, and then coprecipitated in an aqueous medium with carbon nanotubes. We examined the precipitation of MNPs with ammonia from a mixture of iron(II) and (III) chlorides at various temperatures: 80 and 25°C. Figure 1 shows diffraction patterns of MNP samples. It can be seen that the curves are identical and correspond to a single-phase magnetite (PDF file 11-614). However, a more finely dispersed MNP powder is obtained at 80°C, compared with room temperature. The average size of MNP particles precipitated at 80°C was 15.0 nm, and that for MNPs precipitated at room temperature was 21.7 nm. In further study, we used MNPs precipitated at 80°C.

The results of characterization of CNTs synthesized by the method of catalytic pyrolysis of ethanol vapor on a nickel catalyst coincide with those reported previously [14, 15]. The average diameter of CNTs (20–40 nm), the tube length of several micrometers, and the specific surface area of 160–180 m^2 g^{-1} were determined by scanning and transmission electron microscopies and

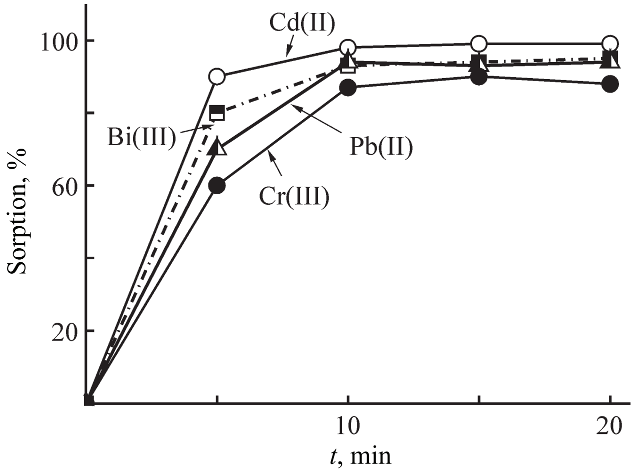

Fig. 2. Sorption of Bi(III), Pb(II), Cr(III), and Cd(II) on MNP@ CNT vs. time of contact with the sorbent (pH 6).

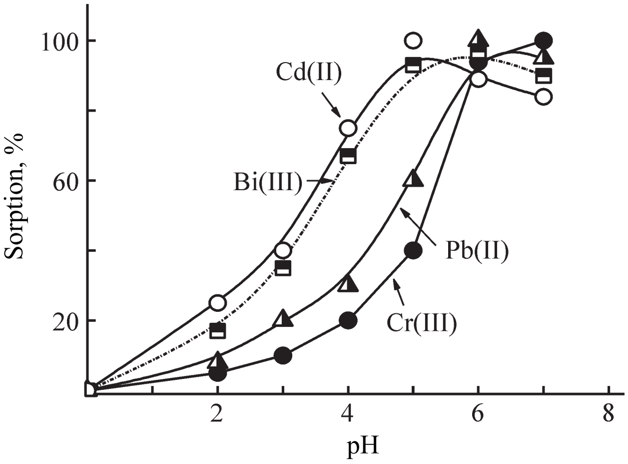

Fig. 3. Sorption of Bi(III), Pb(II), Cr(III), and Cd(II) on MNP@ CNT vs. pH (concentration of elements 10 μg mL^{-1}).

by the BET method based on finding the amount of the adsorbed inert gas.

It is known that, to raise the solubilization and the cation-exchange of CNTs, it is necessary to perform their oxidative modification, e.g., by treatment with concentrated HNO_3 in order to introduce oxygen-containing (carboxy, carbonyl) groups. Therefore, CNTs were washed with 30% HNO_3 to remove the catalyst, and the oxidative modification with conc. HNO_3 under boiling for 1.5 h and used to obtain the composite. It has been shown previously [15, 16], the ability of CNTs to undergo modification and the related sorption capacity strongly depends on the synthesis conditions: temperature and catalyst, which determine the morphology of the resulting material. A nickel catalyst and a synthesis temperature of 450°C were suggested as the optimal conditions. Further studies demonstrated that the sorption properties of CNTs are also strongly affected by the rate at which ethanol is delivered in the course of synthesis. Therefore, we additionally examined in the present study the influence exerted by this factor. CNTs were synthesized on a nickel catalyst at temperatures of 450, 500, and 550°C at various ethanol delivery rates of 10, 20, and 30 mL h^{-1}. The installation in which the synthesis was performed was described in [12]. The resulting CNT samples were washed to remove the catalyst and subjected to an oxidative modification in accordance with the above-described procedure to obtain the MNP@ CNT sorbent. Our study demonstrated that the maximum coprecipitation of CNTs with MNPs is reached for CNT samples obtained at a temperature of 500°C and ethanol passing rate of 20 mL h^{-1}. In this case, 50–60 mg of CNTs is bound with 200 mg of MNPs. These conditions were chosen optimal for obtaining CNTs to be used in a synthesis of the magnetic sorbent. To determine the optimal time required for obtaining the magnetic sorbent, we examined how the amount of CNTs precipitated on MNPs depends on the duration of their contact. It was found that the maximum co-precipitation of CNTs occurs during 30 min, and this time of agitation of the constituent components was taken to be the optimal.

The sorption capacity of the resulting MNP@CNT was examined for the example of toxic metal ions Bi(III), Cd(II), Ct(III), and Pb(II) because determining these ions in potable water and water of natural water basins is a rather topical issue. To find the time required for the sorption equilibrium to be attained, we examined in the static mode the distribution of the elements under study among the sorbent and the aqueous solution in relation to phase contact duration. It was found that, for all the elements under study, the sorption equilibrium is attained in no less than 10 min (Fig. 2), which was used in all further experiments. We examined how the amount of sorption of the metals under study on the MNP@CNT depends on the solution pH (Fig. 3). It follows from the figure that Pb(II),Ct(III), and Bi(III) are completely sorbed at pH 6, and Cd(II), at pH 4.5–5.0.

Figure 4 shows sorption isotherms (25°C) of the metal ions under study. It can be seen that the sorption capacity of MNP@CNT is 4.0, 3.8, 3.5, and 3.5 mg g^{-1} for Bi(III), Pb(II), Ct(III) and Cd(II), respectively. The results obtained in determining the completeness of

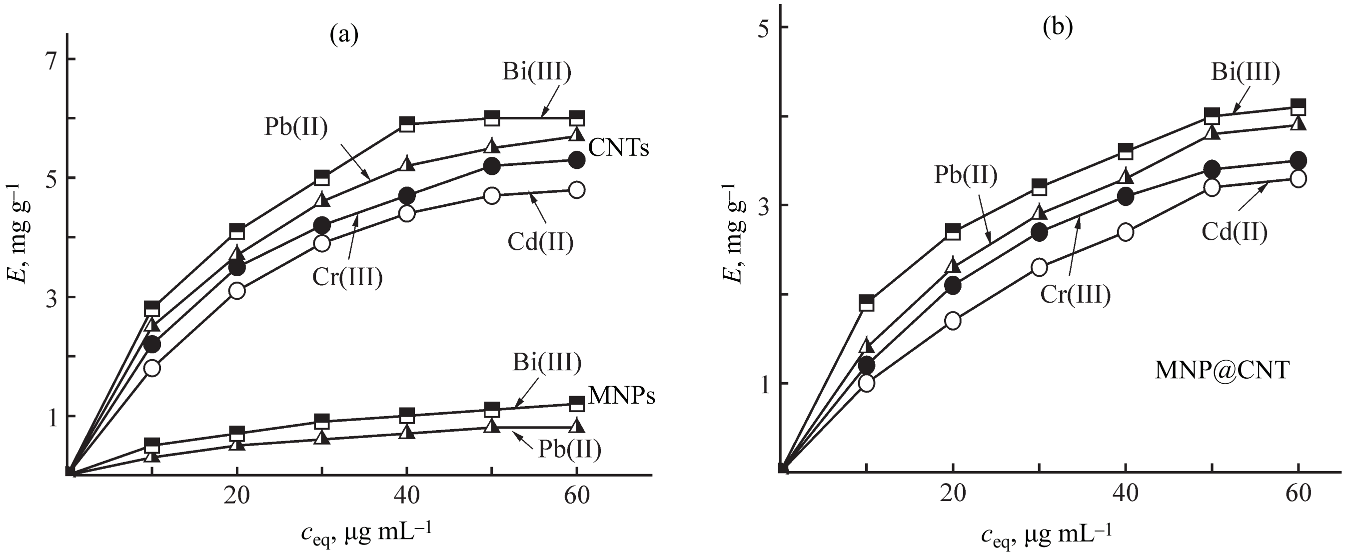

Fig. 4. Comparative isotherms (25°C) of the sorption of Bi(III), Pb(II), Cr(III), and Cd(II) on (a) CNTs and MNPs and (b) MNP@CNT [at pH 5 for Cd(II) and pH 6 for the rest of the elements].

sorption are presented in Table 1, from which it can be seen that it exceeds 95%.

The impurities were eluted from the sorbent with 5 mL of 0.5 N HNO_3. It was found that just this HNO_3 concentration is the optimal. At a lower concentration, elements are not fully desorbed from the sorbent, and raising the HNO_3 concentration results in that the content of iron in the eluate increases, which, in turn, hinders the processing of atomic-emission spectra of the concentrated impurities. The elements were eluted from the sorbent under permanent agitation on a rocker for 15 min. It was found that a 100% desorption of all the elements from the sorbent occurs during this time (Table 1).

Aqueous solutions of the elements under study were analyzed by the arc chemical-technological method under the optimal conditions we found. The correctness of the determinations was verified by the introduced-found method (Table 2). The data in Table 2 indicate that there is no systematic error in determining the metal ions under study in aqueous solutions in the case of their preliminary concentration on the MNP@CNT magnetic sorbent.

To find the contribution to the total amount of sorption from constituent components of the composite, we performed a comparative evaluation of the sorption properties of MNPs and CNTs for the metal ions under study. The sorption of MNPs was examined at various values of the solution pH. The dependence obtained is shown in Fig. 5. It can be seen that the sorption on MNPs occurs only at pH 6 and more, which coincides with the results reported in [17]. It has been found previously for CNTs [18] that the quantitative sorption of Pb(II) and Cr(III) occurs on CNTs at pH 5.5, and that of Bi(III) and Cd(II) at pH 4.0–4.5.

In accordance with these results, the sorption capacity of MNPs and CNTs was determined at the optimal pH for extraction of the metal ions. The isotherms of sorption on MNPs and CNTs are also presented in Fig. 4. For MNPs, curves are only presented for Bi(III) and Pb(II), because for the rest of the elements these dependences are similar. It can be seen in Fig. 4 that the amount of

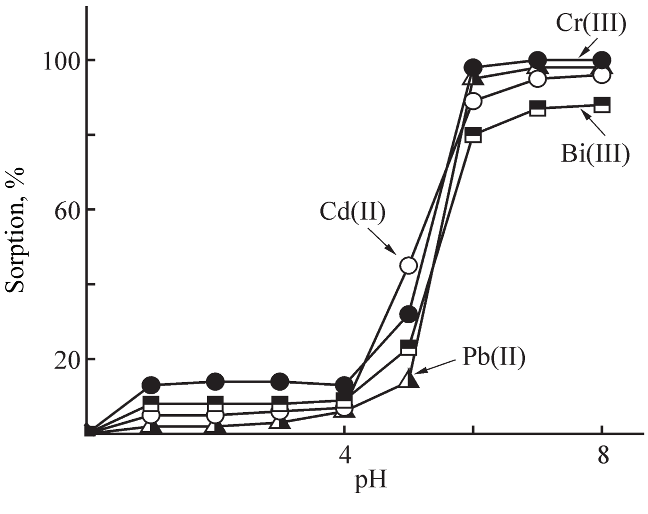

Fig. 5. Sorption of Bi(III), Pb(II), Cr(III), and Cd(II) on MNPs vs. pH (concentration of elements 10 μg mL^{-1}).

Table 1. Completeness f sorption and desorption of metal ions Bi(III), Pb(II), Cr(III), and Cd(II) from the MNP@CNT magnetic sorbent (5 mL of 0.5 M HNO_3, elution time 15 min)

Element	Introduced, μg	Sorption, μg	Desorption, μg	Degree of desorption, %
Bi(III)	50.0	49.5	48.7	98.0
Cd(II)	50.0	49.0	47.0	96.0
Cr(III)	50.0	49.4	47.9	97.0
Pb(II)	50.0	49.5	47.2	95.0

Table 2. Verification of the correctness of determinations of metal ions Bi(III), Pb(II), Cr(III), and Cd(II) in aqueous solutions by the arc atomic-emission method after their preliminary concentration on MNP@CNT ($n = 4$, $P = 0.95$, solution volume 50 mL, $K_{conc} = 100$)[a]

Element	Introduced, μg	Found, μg	Sr
Bi(III)	5.0	4.5 ± 0.9	0.12
Cd(II)	5.0	4.4 ± 0.9	0.13
Cr(III)	5.0	5.1 ± 0.9	0.11
Pb(II)	5.0	4.9 ± 0.9	0.12

[a] n is the number of parallel measurements, P is the confidence probability, and Kconc is the concentration factor.

sorption of the metal ions on the MNPs is approximately 1 mg g^{-1}, which is substantially lower than that of the composite and CNTs. The sorption capacity of MNP@CNT is comparable with that of CNTs.

CONCLUSIONS

Preliminarily synthesized magnetic nanoparticles and carbon nanotubes we used to obtain the MNP@CNT magnetic sorbent. The conditions of its synthesis were examined and optimized keeping in mind the completeness of interaction between the magnetic nanoparticles and carbon nanotubes, depending on the conditions in which these are obtained. The sorption properties of the resulting magnetic sorbent were examined for the example of extraction of toxic metal ions from aqueous media in comparison with the sorption on magnetic nanoparticles and carbon nanotubes. The optimal conditions of sorption and desorption were found in relation to the solution concentration and pH value. The sorption capacity of the MNP@CNT sorbent is 4.0, 3.8, 3.5, and 3.5 mg g^{-1} for Bi(III), Pb(II), Cr(III), and Cd(II), respectively. These values substantially exceed the sorption capacity of magnetic nanoparticles and are comparable with the capacity of carbon nanotubes. However, an important advantage of the magnetic sorbent over carbon nanotubes is the simple and effective separation of the liquid and solid phases, compared with the conventional column variant of the solid-phase extraction. The magnetic sorbent synthesized in the study can be used without preliminary concentration of metal ions in various analytical techniques and for purification to remove toxic elements from various technological media and water basins in the environment.

ACKNOWLEDGMENTS

The authors are grateful to Z.K. Mil’nikova for assistance in the presentation of results.

The study was supported by the Russian Foundation for Basic Research (grant no. 18-02099473).

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