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PHYSICAL CHEMISTRY  
OF SURFACE PHENOMENA

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## Sorption of Inorganic Salts on Carbon Nanomaterials and Magnetite

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Received January 18, 2016

**Abstract**—Magnetic composites based on graphene oxides and functionalized carbon nanotubes containing magnetite nanoparticles are synthesized. The dispersing ability of these composites in water at different pH values is studied. It is shown that the solubility of  $\text{Fe}_3\text{O}_4$  composites is constant in the pH range of 3.5–10, though these composites are unstable at both lower and higher pH values. Magnetic sorbents for extracting  $\text{Ce}(\text{NO}_3)_3$  and  $\text{La}(\text{NO}_3)_3$  from solutions are tested. Dependences of the volume on the sorbent's composition, pH value, and salt concentration in the solution are found. Maximum sorption capacity in relation to  $\text{Ce}^{3+}$  and  $\text{La}^{3+}$  at pH 7.5 and 8.5 are found to be 1040 and 920 mg/g respectively.

DOI: 10.1134/S0036024416110169

### INTRODUCTION

Technological prospects for the use of carbon nanotubes (CNTs) have grown due to the expanded production of CNTs and the start of graphene manufacturing. Ion exchange sorption is only one field of possible application for graphene oxides (GOs) and functionalized (oxidized) CNTs (f-CNTs). A number of works have been devoted to this process, e.g., [1–4]. It has been shown that high sorption capacity for cations can be achieved. However, the use of these materials is limited by the high solubility (dispersing ability) of GOs and f-CNTs in water [5] and hinders filtration in phase separation. (The term solubility used here in describing CNTs and GOs, and the products of their interaction, is conditional.)

To eliminate these disadvantages, CNTs with magnetic nanoparticles in their internal cavities that reside after removing most of the synthesis catalyst (Fe, Co or Ni) were tested in [6]. The concentration of nanoparticles is usually low, since some are dissolved during CNT functionalization. The use of these magnetic materials as ion exchange adsorbents is therefore limited. A multistage technique for filling open CNTs with a magnetic liquid was developed in [7, 8]. It is, however, quite complicated and has found no wide application.

OGs and f-CNTs with magnetic  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ , Fe,  $\text{CoFe}_2\text{O}_4$  nanoparticles grafted to their external surfaces have much better prospects for application. These particles have pronounced magnetic properties, so solid and liquid phases are easily separated by magnets after both adsorption and desorption. Of the

greatest interest to researchers are superparamagnetic  $\text{Fe}_3\text{O}_4$  nanoparticles [9–12].

The aim of this work was to obtain GO- and f-CNT-based magnetic composites and study their properties as ion exchange sorbents.

### EXPERIMENTAL

#### *Preparation and Characterization of the Oxidized Samples*

Graphenes and CNTs produced by Global CO (Khimki, Russia) were used in this work. The specific surface of graphene no. 171 is  $1380 \text{ m}^2/\text{g}$ , and bulk density  $\rho_{\text{bulk}}$  is  $0.018 \text{ g}/\text{cm}^3$ . For the CNTs and graphene samples no. 201 and no. 1981,  $\rho_{\text{bulk}}$  was 0.19, 0.12, and  $0.05 \text{ g}/\text{cm}^3$ , respectively. The samples were oxidized using a mixture of concentrated acids ( $\text{H}_2\text{SO}_4$  (98%) and  $\text{HNO}_3$  (68.4%)) with a volume ratio of 3 : 1 and a ratio of the total volume of the acids to the weight of the carbon material of 1 : 10 mL/mg. The process was conducted in a Samsung M 1712 NR microwave oven for 2 min at a power of 450 W. The products of oxidation were separated from the solution by centrifuging on a PC-6 centrifuge (1100 g; rotor diameter, 37.5 cm), and were washed with water to remove any acid residue and then with dilute HCl (3.5%). The precipitates were dried for 24 h at  $65^\circ\text{C}$ . The yield of functionalized materials was determined from the weight ratio of the obtained and initial materials. GOs denoted as GO-1, GO-2, and GO-3 were obtained from graphenes no. 171, no. 201, and no. 1981, respectively.

**Table 1.** Characteristics of the oxidized samples

Sample	Yield, %	Solubility, g/L
f-CNTs	78.60	4.2
GO-1	87.87	3.5
GO-2	83.50	2.6
GO-3	55.28	10.0

The GO-3 sample was obtained using graphene with  $\rho_{\text{bulk}} = 0.05 \text{ g/cm}^3$ , oxidized for 5 min.

**Table 2.** Dependence of  $m_{\text{CNT}} : m_{\text{Fe}_3\text{O}_4}$  on values  $x, y, z$ 

$x, \text{ mol/L}$	$y, \text{ mol/L}$	$z, \text{ mg}$	$m_{\text{CNT}} : m_{\text{Fe}_3\text{O}_4}$
0.12	0.067	50	1 : 9
0.12	0.067	250	3 : 7
0.12	0.067	350	2 : 3
0.12	0.067	500	1 : 1
0.03	0.0167	150	3 : 2
0.03	0.0167	250	7 : 3
0.012	0.013	450	9 : 1

To determine their solubility, 200 mg samples of GOs and f-CNTs were introduced into 35 mL of water and sonicated with an UZG 13-0.1/22 horn disperser for 2 min. The dispersion was separated from the precipitate on the centrifuge and dried, and the precipitate was then weighed. The solubilities and yields of the four samples are given in Table 1.

The following reagents were also used in this work:  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (pure grade, GOST 3757-75) and  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (chemically pure grade, TU 6-09-4676-83).

#### Preparation and Characterization of Magnetic OG and f-CNT Samples

Reagents  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (GOST 4147-74) and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (GOST 4148-78) were used for synthesizing the GO and f-CNT samples described above: 50 mL of an  $\text{FeCl}_3$  ( $x, \text{ mol/L}$ ) and  $\text{FeSO}_4$  ( $y, \text{ mol/L}$ ) solution with molar ratio  $n_{\text{Fe}^{3+}} : n_{\text{Fe}^{2+}} = 1.8 : 1.0$  were prepared at room temperature. The solution was sonicated for 5 min, and  $z \text{ mg}$  CNM (GO-1, GO-2, GO-3, or f-CNTs) was added and mixed with a magnetic stirrer for 1 h.  $\text{NH}_4\text{OH}$  solution was then added dropwise under stirring until pH 10–11. Then the solution was heated to 80°C and kept for 1 h. The resulting dispersion was then cooled, and the precipitate was cen-

trifuged, washed with water and ethanol, and dried at 60°C for 24 h. The  $x, y, z$  values were varied to obtain magnetic samples of CNMs with different CNM :  $\text{Fe}_3\text{O}_4$  ratios. To determine mass ratios  $m_{\text{CNM}} : m_{\text{Fe}_3\text{O}_4}$ , the samples were calcined in air at 750°C for 3 h and weighed in the form of  $\text{Fe}_2\text{O}_3$ . The results are presented in Table 2.

To determine the dependence of the resulting  $\text{Fe}_3\text{O}_4$ –CNMs' solubility on that of the initial materials, mass ratio  $m_{\text{CNM}} : m_{\text{Fe}_3\text{O}_4}$ , and the pH value of the solution, the weights of purified and dried  $\text{Fe}_3\text{O}_4$ –CNM compounds (100 mg) with different  $m_{\text{CNM}} : m_{\text{Fe}_3\text{O}_4}$  ratios were introduced into 100 mL of water. The dispersion was sonicated for 2.5 and 10 min, and then centrifuged for 15 min. The resulting dispersion was separated from the precipitate and dried. To determine the  $m_{\text{CNM}} : m_{\text{Fe}_3\text{O}_4}$  ratio in the precipitate after centrifuging, the dry precipitate was calcined in air at 750°C for 3 h and weighed in the form of  $\text{Fe}_2\text{O}_3$ . Its content in the dispersion was calculated according to the material balance equation.

#### $\text{La}^{3+}$ and $\text{Ce}^{3+}$ Sorption

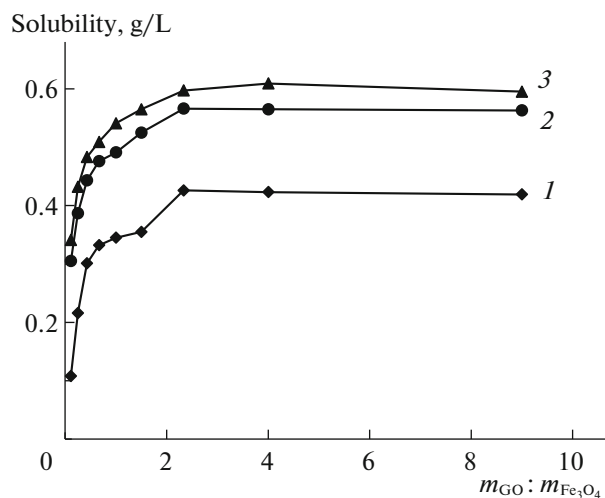
A weighed amount of  $\text{Fe}_3\text{O}_4$ –GO-1 and  $\text{Fe}_3\text{O}_4$ –f-CNTs with the ratio  $m_{\text{CNM}} : m_{\text{Fe}_3\text{O}_4} = 9 : 1$  (50 mg) was introduced into 300 mL of a  $\text{Ce}(\text{NO}_3)_3$  (pH 7.5) or  $\text{La}(\text{NO}_3)_3$  (pH 8.5) solution with a concentration of 200 mg/L. The solution was then sonicated for 2 min, kept for 24 h, and the precipitate was separated by centrifugation. The absorbed amount of  $\text{Ce}^{3+}$  or  $\text{La}^{3+}$  was determined in the following manner:  $\text{NH}_4\text{OH}$  was added to the clarified solution, and the precipitate was filtered through a blue-band paper filter and dried. The dry precipitate was calcined in air at 700°C for 3 h and weighed in the form of  $\text{CeO}_2$  or  $\text{La}_2\text{O}_3$ . To study the effect of pH, its value was adjusted by addition of calculated amounts of HCl or  $\text{NH}_4\text{OH}$  and simultaneously measured with a pH-56 meter (Martini).

Desorption was studied using a centrifuged precipitate, washed with 5–40 mL of 2 M  $\text{HNO}_3$  and separated by centrifuging. The amount of desorbed Ce or La was determined in the following manner:  $\text{NH}_4\text{OH}$  was added to the solution, and the precipitate was filtered through a blue-band paper filter and dried. The dry precipitate was calcined in air at 700°C for 3 h and weighed in the form of  $\text{CeO}_2$  or  $\text{La}_2\text{O}_3$ .

## RESULTS AND DISCUSSION

### Effect of the $m_{\text{CNM}} : m_{\text{Fe}_3\text{O}_4}$ Ratio on $\text{Fe}_3\text{O}_4$ –CNM Solubility

Figure 1 shows that the solubility of  $\text{Fe}_3\text{O}_4$ –CNM remained the same at the ratios higher than 2 under the conditions of our experiment. A rise in solubility was observed after raising the duration of sonication



**Fig. 1.** Solubility of Fe<sub>3</sub>O<sub>4</sub>-GO-1 as a function of the  $m_{\text{GO}} : m_{\text{Fe}_3\text{O}_4}$  ratio at pH 5.2 and durations of sonication of (1) 2, (2) 5, and (3) 10 min.

from 2 to 5 min, with the solubility changing only slightly between 5 to 10 min. Subsequent experiments were therefore performed with sonication time of 5 min.

#### Effect of the Initial CNMs' Solubility

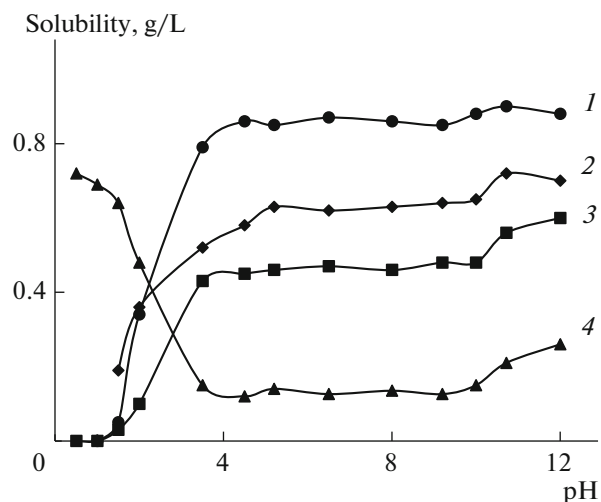
Upon the oxidation CNMs, the concentration of functional groups on their surfaces, their solubility, and presumably the morphology of the CNMs themselves, change. From the data presented in Table 3, it follows that the higher the degree of CNM oxidation, the greater the Fe<sub>3</sub>O<sub>4</sub>-CNM solubility.

#### Effect of the pH Value on Solubility

The solubility of magnetic CNMs with composites depends on the acidity of the medium and the composites' components. From Fig. 2, it follows that the solubility of Fe<sub>3</sub>O<sub>4</sub>-GO composites is higher than that of Fe<sub>3</sub>O<sub>4</sub>. The solubility of Fe<sub>3</sub>O<sub>4</sub>-GO rises along with the  $m_{\text{GO}} : m_{\text{Fe}_3\text{O}_4}$  ratio. The solubility of Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>-CNM remains constant at pH values of 3.5–5.0 to 10.

#### Effect of the Cerium Concentration on Capacity

An increase in cerium concentration results in a substantial rise in adsorbent capacity, the ratio of the weight of the sorbent to the volume of the solution (S : L) being constant. The capacities of the composites with GO-1 and f-CNTs are seen to be very close



**Fig. 2.** Dependence of the pH value of Fe<sub>3</sub>O<sub>4</sub>-GO-1 solubility at mass ratios  $m_{\text{GO}} : m_{\text{Fe}_3\text{O}_4} = (1) 9 : 1, (2) 1 : 1, (3) 3 : 7,$  and (4) 0 : 1.

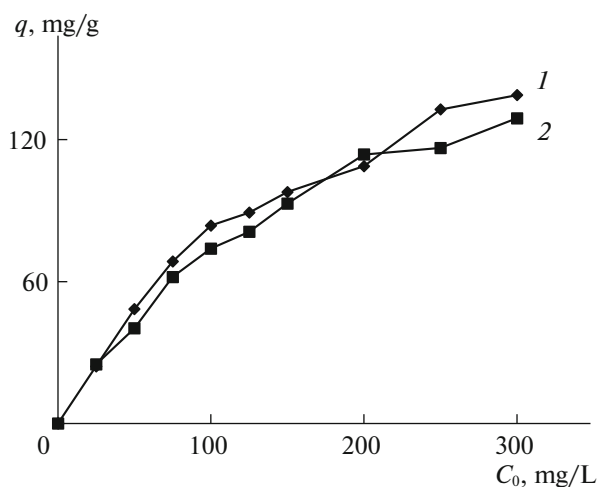
(Fig. 3). The increase in capacity could be partly due to the change in the ion composition of Ce salt in an aqueous solution.

#### Effect of pH

The equilibrium capacity of the tested magnetic carbon sorbents was strongly dependent on the acidity of the solution (Figs. 4 and 5), due to the change in the ion composition of the solution with an increase in the pH value:  $\text{Ln}^{3+} - \text{LnOH}^{2+} - \text{Ln}(\text{OH})_2^+ - \text{Ln}(\text{OH})_3$  [13, 14]. Different ions are therefore adsorbed. The change in the concentration of acid centers on the surfaces of f-CNTs and GOs depending on the pH is also of considerable importance [5]. The sharp drop in capacity for Ce<sup>3+</sup> at pH ~ 8 and the somewhat higher pH value for La<sup>3+</sup> are associated with the precipitation of metal hydroxides. The pH of Ln(OH)<sub>3</sub> precipitation onset is known to fall in the La-Lu series [16]. However, we

**Table 3.** Solubilities (g/L) of (A) the initial CNM and (B) Fe<sub>3</sub>O<sub>4</sub>-CNM,  $m_{\text{CNM}} : m_{\text{Fe}_3\text{O}_4}$  ratio in solution ( $\alpha_1$ ) and precipitate ( $\alpha_2$ ) at pH 5.2

Initial CNM	A	B	$\alpha_1$	$\alpha_2$
GO-1	2.60	0.54	0.78	1.34
GO-2	3.50	0.61	1.05	0.93
f-CNT	4.20	0.65	1.24	0.67
GO-3	10.00	0.67	1.40	0.50



**Fig. 3.** Equilibrium capacity of (1) Fe<sub>3</sub>O<sub>4</sub>-GO-1 and (2) Fe<sub>3</sub>O<sub>4</sub>-f-CNTs as a function of the initial Ce concentration at pH 2,  $t = 23.4^\circ\text{C}$ , and ratio S : L = 1 : 1 in a Ce(NO<sub>3</sub>)<sub>3</sub> solution.

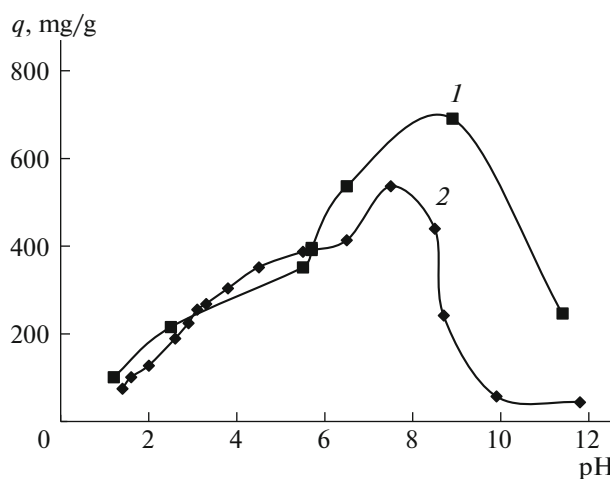
may state that the tested GOs and f-CNTs sorbents were found to have high capacities with respect to REE ions.

#### Desorption Tests

The adsorbed metal ions were stripped with 2M HNO<sub>3</sub> to examine experimentally the possibility of concentrating REEs. The degrees of lanthanum and cerium desorption were calculated using the formula  $R_{\text{des}} = (m_{\text{des}}/m_{\text{ads}}) \times 100\%$ , where  $m_{\text{ads}}$  is the mass of Ce or La adsorbed on Fe<sub>3</sub>O<sub>4</sub>-CNM, and  $m_{\text{des}}$  is the mass of Ce or La in the concentrate after desorption. The optimum volume of the 2M HNO<sub>3</sub> solution was determined by varying the volume of HNO<sub>3</sub> used for washing the centrifuged precipitate from 5 to 50 mL. From the data presented in Table 4, it follows that La and Ce are characterized by equal degrees of desorption, with that of the latter being 94–95% if 20–25 mL 2 M HNO<sub>3</sub> is used for washing. Under these conditions, the degree of volume compression was 12–15, and the concentrations of La and Ce in the resulting solutions were 2.47 and 2.30 g/L, respectively.

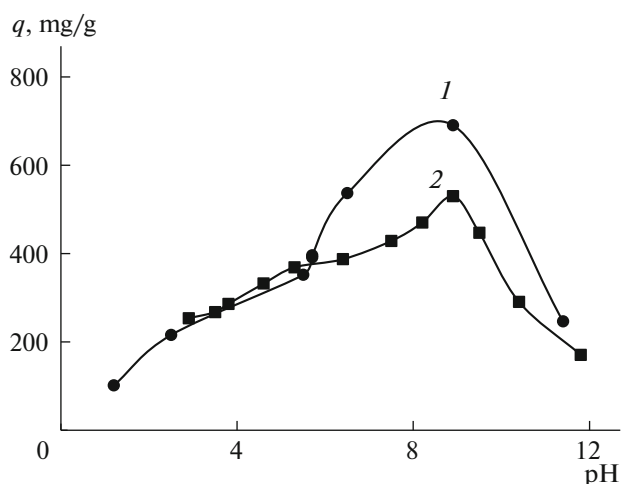
#### CONCLUSIONS

The capacity of a magnetic sorbent containing carbon nanomaterial (f-CNTs or GOs with oxygen-containing functional groups) and Fe<sub>3</sub>O<sub>4</sub> nanoparticles is determined by the  $m_{\text{GO(f-CNT)}} : m_{\text{Fe}_3\text{O}_4}$  ratio, the concentration of Ce<sup>3+</sup> and La<sup>3+</sup> in the initial aqueous solution, and the acidity of the solution. The maximum adsorption capacity with respect to Ce<sup>3+</sup> and La<sup>3+</sup> at pH 7.5 and 8.5 is 1040 and 920 mg/g, respectively.



**Fig. 4.** Dependence of (1) Fe<sub>3</sub>O<sub>4</sub>-GO-1 and (2) Fe<sub>3</sub>O<sub>4</sub>-f-CNTs equilibrium capacity on pH at  $t = 22^\circ\text{C}$  and S : L = 1 : 1 in a Ce(NO<sub>3</sub>)<sub>3</sub> solution with an initial Ce<sup>3+</sup> ion concentration of 200 mg/L.

The adsorption of La<sup>3+</sup> and Nd<sup>3+</sup> on carbon materials with high specific surfaces (up to 1800 m<sup>2</sup>/g) was described in [16, 17]. Judging from the microphotos presented in those works, the materials were obtained in a manner similar to the one described in [5], i.e., via the pyrolysis of CH<sub>4</sub> on MgO particles, with subsequent dissolution of the MgO. These sorbents might be expected to have high capacities, but they turned out to be lower than 1 mg/g. The discrepancy between these data and our results can be explained by there having been no oxidation [16, 17]. There



**Fig. 5.** Dependences of (1) Fe<sub>3</sub>O<sub>4</sub>-GO-1 and (2) Fe<sub>3</sub>O<sub>4</sub>-f-CNT equilibrium capacities on pH at  $t = 22^\circ\text{C}$  and S : L = 1 : 1 in a La(NO<sub>3</sub>)<sub>3</sub> solution with an initial La<sup>3+</sup> ion concentration of 200 mg/L.

**Table 4.** Dependence of the degree of desorption on the volume of 2 M HNO<sub>3</sub> solution

$V_{\text{HNO}_3}$ , mL	$R_{\text{des}}(\text{Ce})$ , %	$R_{\text{des}}(\text{La})$ , %
5	78	74
10	82	83
15	87	85
20	95	94
25	94	95
30	95	93
35	96	95
40	95	94

were thus no carboxyl, carbonyl, or other oxygen-containing ion-exchanging groups on the materials' surfaces. In addition, the hydrolysis and co-precipitation of La<sup>3+</sup> and Nd<sup>3+</sup> at high pH values were not considered in [16, 17].

Our results also show that in addition to filling CNTs with magnetic nanoparticles, coating magnetic particles with carbon (graphene) is also of practical interest. For example, carbon coated Fe and Ni particles were studied in detail in [18].

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*Translated by D. E. Yakusheva*