



## Study of adsorption properties of functionalized nanodiamonds in aqueous solutions of metal salts using optical spectroscopy



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### ABSTRACT

This paper presents results of a study of adsorption properties of the original (I6) and carboxyl-modified (I6COOH) detonation nanodiamonds (DNDs) dispersed in aqueous solutions, with respect to dissolved ions:  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{NO}_3^-$ . Application of complementary spectroscopic methods allows comparative analysis of the adsorption activity of DNDs in aqueous solutions of metal salts. It was shown that both types of functionalized NDs readily adsorb nitrate ions and metal cations, and the adsorption efficiency of I6COOH is approx. three times higher than that of I6. Hypothetic mechanism of nitrate and copper ions adsorption on NDs surface is proposed.

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### 1. Introduction

New efficient sorbents of inorganic ions are very important for production of high-purity materials and drugs, for impurities removal from liquids and gases, and for biomedicine. It was shown that due to large specific surface, multi-functionality of surface groups, possibility of targeted modification of the surface, adsorption properties of nanodiamond (ND) particles exceed adsorption capacity of many carbon sorbents [1–4]. For goal-oriented synthesis of required nanomaterials it is very important to study adsorption properties of materials and intermolecular interactions on the adsorbate–adsorbent interface.

Adsorption properties of powdered detonation nanodiamonds (DNDs) are described in many papers [1–10]. One of the most important problems for wide application of DND is lack of standard procedure of conditioning and unification of surface properties of nanomaterials from different manufacturers [5]. Even after identical treatment, NDs from different manufacturers may reveal drastically different adsorption properties. Nevertheless, principal trends of adsorption activity of NDs in respect to inorganic compounds can be established. In [6,7], the mechanism of selective adsorption of toxins on NDs powders was described: ions of heavy metals are adsorbed mainly on hydrophobic surfaces (according to

degree of adsorption activity:  $\text{Fe} > \text{Ni} > \text{Pb} > \text{Cd}$ ), whereas toxins of organic origin on the hydrophilic surface. Adsorption of nickel (II) and of propidium iodide was studied in [8,9], correspondingly. In [10], introduction of large amounts of sodium ions into the cell interior by NDs in serum-free medium was demonstrated.

It is obvious that in many applied problems (especially in biomedicine) it is advisable to use NDs dispersed in water. Practical use of ND as adsorbent is complicated because of their tendency to form aggregates. Recently efficient methods of aggregates destruction down to single-digit nanoparticles in water [11,12] or of their synthesis in water [13,14] were elaborated. These works triggered studies of the DND adsorption properties in stable aqueous suspensions. Sorption of dissolved inorganic compounds by dispersed DND is studied in [2,3,15–17]. Authors of [15] showed that  $\zeta$ -potential of ND is affected by the adsorption of ions such as  $\text{SO}_4^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{PO}_4^{3-}$ , and  $\text{OH}^-$ , while cations with valence +1 (except  $\text{H}^+$ ) and  $\text{Cl}^-$  anions have little influence on it. Based on titration it was shown [16] that in aqueous solution of 0.9 M NaCl DND suspensions (ratio DND/water is 0.01). 20–30% of metal cations Fe(III), Rh(III) and Au(III) were adsorbed. In [17], authors achieved virtually quantitative adsorption of tungstate-ions ( $\text{WO}_4^{2-}$ ) on DNDs. For dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ) and molybdate ( $\text{MoO}_4^{2-}$ ) anions, adsorption on the surface of ND in water suspensions is 30% and 65%, respectively. At the same time, no adsorption of copper ions was found. Therefore, despite numerous studies, the results are often contradictory, and no generally accepted mechanism of ions adsorption on ND surface exists.

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**Table 1**  
Characterization of aqueous solutions of salts and aqueous mixtures–suspensions of salts and NDs.

Sample, ND processing	Hydrodynamic radius (DLS), $\zeta$ -potential	pH value	NO <sub>3</sub> concentration in supernatant. Absorp./RS (M)	Cu and Pb concentration in supernatant. Absorp. (M)
I6 initial Wet synthesis; CrO <sub>3</sub> in H <sub>2</sub> SO <sub>4</sub> ; NaOH + H <sub>2</sub> O <sub>2</sub> ; fractionated	64.5 nm, 19.6 ± 3.4 mV	5.57		
I6COOH initial Sample I6 treated in air at 420 °C	190 nm, –27.6 ± 17 mV	3.5		
Cu(NO <sub>3</sub> ) <sub>2</sub> initial, 0.5 M		2.57		
I6 + Cu(NO <sub>3</sub> ) <sub>2</sub> (0.5 M)	443 nm	3.09	0.24/0.23	0.19
I6COOH + Cu(NO <sub>3</sub> ) <sub>2</sub> (0.5 M)	1110 nm	2.8	0.24/0.25	0.18
Cu(NO <sub>3</sub> ) <sub>2</sub> initial, 0.75 M		2.36		
I6 + Cu(NO <sub>3</sub> ) <sub>2</sub> (0.75 M)	450 nm	2.63	0.33/0.37	0.27
I6COOH + Cu(NO <sub>3</sub> ) <sub>2</sub> (0.75 M)	1520 nm	2.59	0.32/0.26	0.25
Pb(NO <sub>3</sub> ) <sub>2</sub> initial, 0.5 M		3.76		
I6 + Pb(NO <sub>3</sub> ) <sub>2</sub> (0.5 M)	615 nm	4.34	0.21/0.26	0.16
I6COOH + Pb(NO <sub>3</sub> ) <sub>2</sub> (0.5 M)	1250 nm	3.35	0.17/0.21	0.10
Pb(NO <sub>3</sub> ) <sub>2</sub> initial, 0.75 M		3.58		
I6 + Pb(NO <sub>3</sub> ) <sub>2</sub> (0.75 M)	575 nm	3.98	0.27/0.26	0.24
I6COOH + Pb(NO <sub>3</sub> ) <sub>2</sub> (0.75 M)	1050 nm	3.1	0.25/0.22	0.24

This paper presents the results of a study of adsorption properties of the original and modified NDs dispersed in aqueous solutions, with respect to dissolved salts of various metals: Cu<sup>2+</sup>, Pb<sup>2+</sup>, NO<sub>3</sub><sup>–</sup>, using several complementary spectroscopic methods – photon correlation, adsorption, Raman and IR.

## 2. Experimental

Adsorption properties of initial (I6, produced by “New Technologies”, Chelyabinsk, Russia) and modified (I6COOH) nanodiamond in aqueous solutions of nitrates Cu(NO<sub>3</sub>)<sub>2</sub> and Pb(NO<sub>3</sub>)<sub>2</sub> were investigated. The modification was performed at the International Technology Centre, Raleigh, North Carolina (USA). Characterization of the ND samples is presented in [18,19].

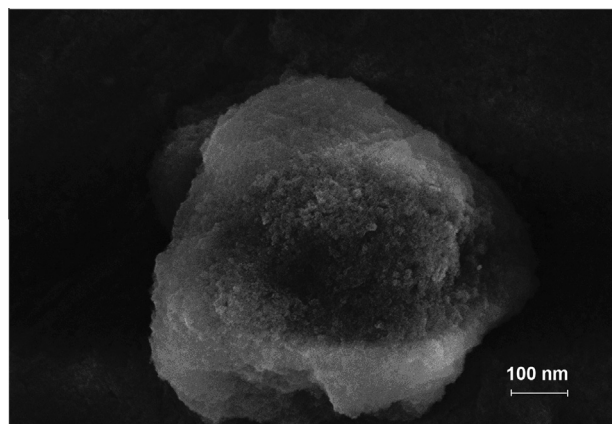
### 2.1. Aqueous solutions and ND suspensions, characterization

Initial solutions of copper and lead nitrates with concentrations 0.5 and 0.75 M and initial suspensions of NDs I6 and I6COOH with concentration 0.5 mg/ml were prepared in deionized bidistilled water. Suspensions of I6 and I6COOH in water were treated during 4 h in ultrasonic bath (Bandelin Sonorex rk 31).

The obtained solutions and suspensions were characterized by titration, dynamic light scattering (DLS), electron microscopy (Table 1, Fig. 1). Measured parameters have shown stability of obtained aqua suspensions of NDs. The hydrodynamic radius of modified I6COOH (190 nm) is almost three times bigger than that of I6 (65 nm), indicating stronger tendency to aggregation of I6COOH at a given concentration in water.

### 2.2. Determination of ionic concentrations in solutions

To study the adsorption of Cu<sup>2+</sup>, Pb<sup>2+</sup>, NO<sub>3</sub><sup>–</sup> ions, the solutions of salts with known concentrations (Table 1) were added to initial ND aqua suspensions. The values of pH and size distribution of nanoparticles were measured in mixtures–suspensions of



**Fig. 1.** SEM image of aggregate (adsorbate + adsorbent) extracted from aqua suspension I6COOH + Cu(NO<sub>3</sub>)<sub>2</sub> (0.5M).

salts and NDs. After several hours, supernatants and aggregates (adsorbate + adsorbent) were extracted from the mixtures. Then pH, size distribution of nanoparticles, and concentrations of ions in the supernatants were measured (Table 1).

Concentrations of nitrate, copper and lead ions before and after adsorption by NDs were estimated by absorption spectroscopy. The second approach is based on concentration dependence of the NO<sub>3</sub><sup>–</sup> (1045 cm<sup>–1</sup>) Raman line intensity [20–22]. For each sample, at least 3–4 spectra were obtained. Results of absorption spectroscopy and Raman spectroscopy are in good accordance (Table 1). In all samples in Table 1, concentration of ND was 0.5 mg/ml. Absorp. – absorption spectroscopy. RS – Raman Spectroscopy.

## 3. Results and discussion

### 3.1. Adsorption efficiency of NDs

Adsorption efficiency of ND is determined by the amount of ions adsorbed on the surface unit area of ND. In this paper it is assumed that ions concentration in solution changes due to sorption by NDs only, and the efficiency was calculated from the ratio of ions concentration in initial solution and in supernatant. Calculations (see Supplementary Data) demonstrated that ratio of areas of the total adsorbing surface of the aggregates was  $S_{I6}/S_{I6COOH} \sim 3$ , thus explaining higher adsorption efficiency of I6COOH relative to I6 (Table 1). Lead cations are adsorbed by the modified ND slightly better than copper cations yielding four times higher sorption efficiency of I6COOH for Pb ions.

### 3.2. Raman spectroscopy

The analysis of Raman spectra of all solutions, suspensions and supernatants showed that the addition of I6 and I6COOH to solutions of both salts shifts water valence band (2800–4000 cm<sup>–1</sup>) to higher frequencies. Moreover, this shift is larger in suspensions of I6COOH than that in suspensions of I6. It means that the carboxyl surface groups actively form hydrogen bonds with water molecules and with each other, and that these bonds are weaker than hydrogen bonds in pure water [18,22]. However, this network of hydrogen bonds causes stronger aggregation of I6COOH in the suspensions, as confirmed by DLS data. In Raman spectra of the supernatant (after adsorption), the maximum of water Raman valence band in all solutions of salts and NDs has lower frequency than in suspensions and in initial salts solutions. However, this frequency is higher than that in distilled water (Fig. 2). It means that salts concentration in supernatant is lower than in initial solutions, but is higher than in distilled water, indicating only partial salt adsorption.

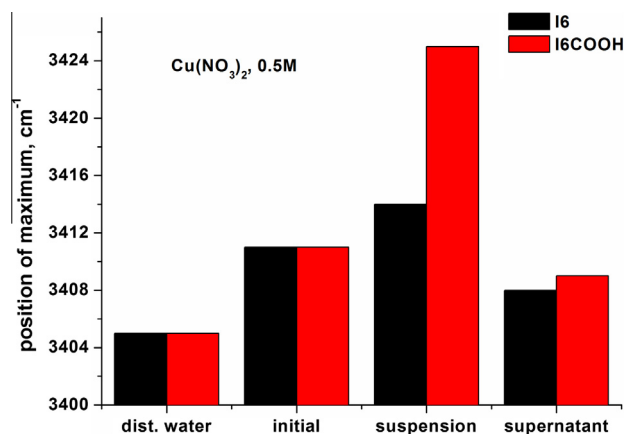


Fig. 2. Change of position of water Raman valence band maximum in solutions of  $\text{Cu}(\text{NO}_3)_2$ .

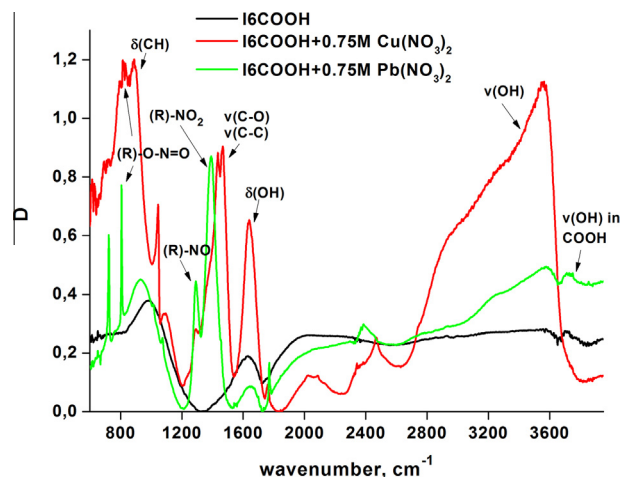


Fig. 3b. IR absorption spectra of nanodiamonds I6COOH and I6COOH with adsorbed ions.

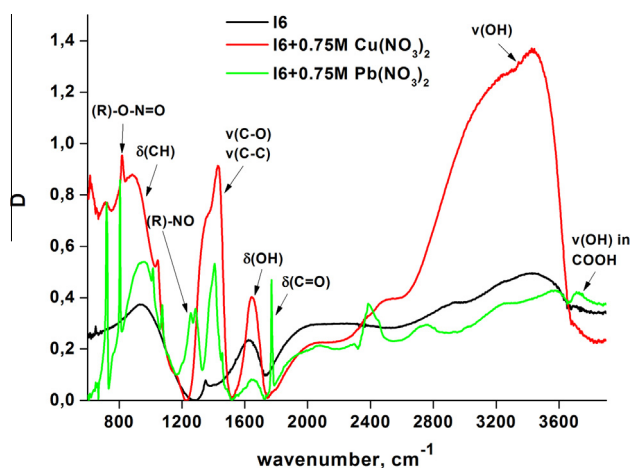


Fig. 3a. IR absorption spectra of nanodiamonds I6 and I6 with adsorbed ions.

cation forms a stable hydration shell in water. We suppose that on adsorption of copper cations on ND surface, the hydration shell remains largely intact. In this scenario, hydrogen bonds are formed between surface functional groups of NDs and water molecules from the hydration shell. As both NDs possess many oxygenated surface groups, both NDs actively adsorb copper by hydrogen bonding. Absence of the band of valence vibrations  $\text{Cu}-\text{O}$  near  $640\text{ cm}^{-1}$  (Figs. 3a and 3b) confirms that the main role in adsorption of copper on the surface of NDs is played by physical adsorption. I6COOH (its surface was modified by oxygen-containing groups) adsorbs copper more actively in comparison with I6.

It is known that in water solutions nitrate anions are not bound or clustered, and all bonds  $\text{N}=\text{O}$  are double. In IR spectra of adsorbent with adsorbate, bands corresponding to groups both with double and single bonds are observed (Figs. 3a and 3b). This indicates that new chemical bonds of nitrates with functional groups are formed on the surface of both NDs.

#### 4. Conclusions

The adsorption properties of ND I6 and I6COOH in aqueous solutions of nitrates of copper and lead were studied experimentally with the methods of correlation spectroscopy, absorption spectroscopy, Raman spectroscopy and infrared absorption. It was found that both NDs actively adsorb nitrate ions and metal cations, and the adsorption efficiency of I6COOH is about three times higher than that of I6 in respect to the ions.

On the basis of the IR and Raman results, we propose a hypothesis about mechanisms of adsorption of nitrate ions and copper cations on the surface of the NDs, according to which the dominant role in the adsorption of Cu is played by physical adsorption and the dominant role in the adsorption of nitrate anions is played by chemical adsorption.

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#### 3.3. IR spectroscopy and mechanisms of ion adsorption

In order to clarify mechanisms of ion adsorption on ND surfaces, IR spectra of powders I6, I6COOH and powders (adsorbent + adsorbate) extracted from the aqueous mixtures–suspensions (Figs. 3a and 3b) were obtained. From the spectra analysis it follows that:

1. On the surface of both NDs suspended in solutions of copper nitrate, many hydroxyl groups were adsorbed.
2. In the IR spectra of both NDs suspended in solutions of copper nitrate, there is no line of stretching vibrations of  $\text{Cu}-\text{O}$  ( $640\text{ cm}^{-1}$ ). This means that adsorbed Cu forms no chemical bonds with surface groups of ND.

Unfortunately, it was impossible to measure IR spectra in the range from  $200\text{ cm}^{-1}$  where one can see bands of lead compounds.

3. In the IR spectra of aggregate (adsorbent + adsorbate), intense vibrational lines of chemically bound nitrogen oxides and of compounds, are observed.

Presence of large amount of hydroxyl groups in powders of adsorbent with adsorbate extracted from the solutions of copper nitrate can be explained by strong hydration of copper cations. A

## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jallcom.2013.01.055>.

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