

Short Communication

Mechanisms of Ions Adsorption by Nanodiamonds in Aqueous Suspensions

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This work is devoted to the study of adsorption properties and adsorption mechanisms of the original (I6), modified (I6COOH) nanodiamonds and charcoal dispersed in water, with respect to dissolved ions (Cu^{2+} , Pb^{2+} , NO_3^- , CH_3COO^-) using optical spectroscopy methods: Raman and IR spectroscopies, absorption, dynamic light scattering. Mechanisms of anions and cations adsorption were studied.

Keywords: Nanodiamonds, Adsorption mechanisms, Dynamic light scattering, Raman spectroscopy, IR spectroscopy.

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1. INTRODUCTION

New efficient sorbents of inorganic and organic ions are very important for impurities removal from liquids and gases, for production of high-purity materials and drugs, 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. Adsorption properties of powdered detonation nanodiamonds are described in many papers [1, 2, 3]. It is obvious that in many applied problems (especially in biomedicine) it is advisable to use NDs dispersed in water. It is very important to understand mechanisms of adsorption in order to make targeted modifications of ND surface for increasing its adsorption efficiency.

This work presents the results of a study of adsorption properties and adsorption mechanisms of the original and modified NDs dispersed in aqueous solutions, with respect to dissolved ions Cu^{2+} , Pb^{2+} , NO_3^- , CH_3COO^- using several complementary spectroscopic methods – photon correlation, absorption, Raman and IR spectroscopies. Parallel experiments were carried out with charcoal in order to compare efficiency of adsorbents.

2. OBJECTS AND METHODS

Adsorption properties of initial (I6) and modified (I6COOH) nanodiamonds in aqueous solutions of $\text{Cu}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, $\text{Cu}(\text{CH}_3\text{COO})_2$ and $\text{Pb}(\text{CH}_3\text{COO})_2$ were investigated. Characterization of the ND samples is presented in [4, 5, 6] and in the Table 1.

Initial solutions of copper and lead salts with concentrations 0.5 and 0.75 M (for nitrates), 0.2 and 0.4 M (for acetates) and initial suspensions of NDs with concentration 0.5 mg/ml were prepared in deionized bidistilled water. The aqua NDs suspensions were

treated in ultrasonic bath during 3 hours. The obtained solutions and suspensions were characterized by different methods (titration, dynamic light scattering (DLS), electron microscopy (Table 1, Fig. 1). Measured parameters have shown stability of aqua suspensions of NDs. Then NDs suspensions and salts solutions were mixed and were characterized by the same methods.

Concentrations of ions before and after adsorption by NDs were estimated by absorption spectroscopy. The second approach is based on concentration dependence of the own Raman lines intensity of NO_3^- (1045 cm^{-1}) and CH_3COO^- (898 cm^{-1} , 2950 cm^{-1}) [7]. Results of absorption spectroscopy and Raman spectroscopy are in good accordance.

Adsorption efficiency of ND is determined by the amount of ions adsorbed on the surface unit area of ND. In this work 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 demonstrated that ratio of areas of the total adsorbing surface of the aggregates was $S_{\text{I6}}/S_{\text{I6COOH}} \sim 3$, thus explaining 3 times higher adsorption efficiency of

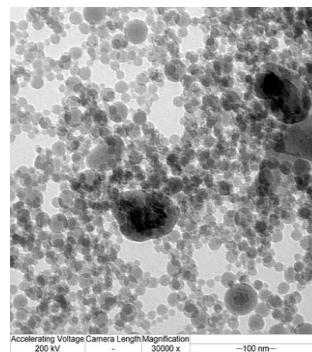


Fig. 1 – HRTEM image of I6 (International Technological Center, USA)

I6COOH relative to I6 (under approximately the equal change of Cu^{2+} and of the both anions concentrations).

Ions Pb^{2+} are adsorbed by the modified ND slightly better than Cu^{2+} yielding 4 times higher sorption efficiency of I6COOH for Pb^{2+} . In compare with charcoal, NDs adsorption efficiency didn't show essential advantage (Fig. 2). Despite of this fact, the study of NDs adsorption properties is very important to solve the problem of elaboration of a multifunctional biosensor on the base of NDs. Such biosensors can be used as sorbent, drug delivery and fluorescent marker simultaneously.

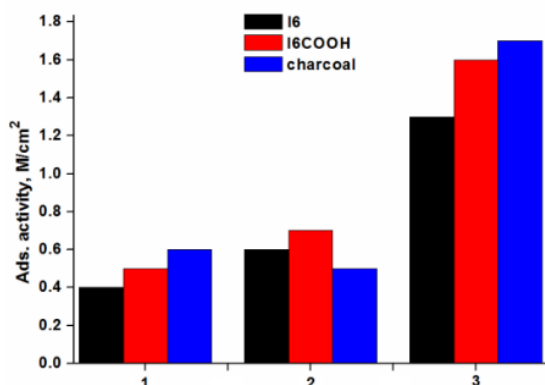


Fig. 2 – Adsorption activity of I6, I6COOH and charcoal: 1 – Cu^{2+} in $\text{Cu}(\text{CH}_3\text{COO})_2$, 2 – CH_3COO^- in $\text{Cu}(\text{CH}_3\text{COO})_2$, 3 – CH_3COO^- in $\text{Pb}(\text{CH}_3\text{COO})_2$

In order to clarify mechanisms of ion adsorption on ND surfaces, IR spectra of powders I6, I6COOH and powders, extracted from the aqueous mixtures-suspensions (adsorbent + adsorbate) were obtained (Fig. 3, 4) using confocal FTIR spectrometer (Perkin Elmer Spectrum One).

Presence of great amount of OH groups in IR absorption spectrum of powders (adsorbent + adsorbate) extracted from the aqueous mixtures-suspensions and absence of the valence band of Cu-O (640 cm^{-1}) show that a physical adsorption of Cu^{2+} ions plays a dominant role.

A cation forms a solid hydration shell in water, and it moves in the solution together with this shell. We suppose that adsorption of copper cations on the sur-

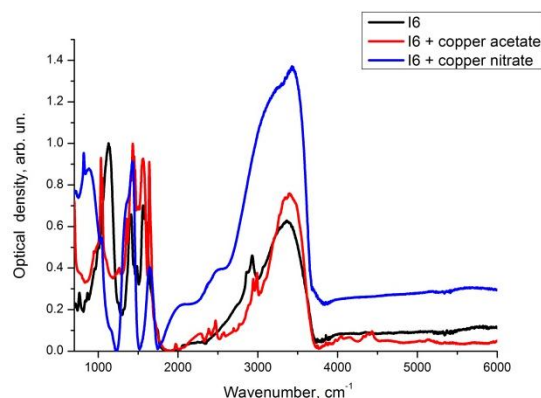


Fig. 3 – IR absorption spectra of nanodiamonds I6 and I6 with adsorbed ions

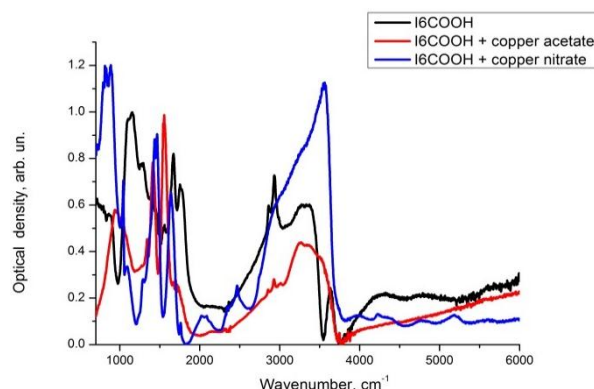


Fig. 4 – IR absorption spectra of nanodiamonds I6COOH with adsorbed ions

face of NDs occurs without destruction of their hydration shells (Fig. 5). As both NDs have many oxygen-containing surface functional groups, both NDs actively adsorb copper on their surface by hydrogen bonding. I6COOH (its surface was modified by oxygen-containing groups) adsorbs copper more actively in comparison with I6.

Appearance of vibrational lines of N-O and N=O bounds in compare with IR spectra of initial NDs shows formation of the new bonds between nitrates anions and NDs surface.

Table 1 – Characterization of aqueous suspensions of NDs

Sample	Methods of synthesis and treatment of studied samples	Size of crystallites*, [nm]	ζ -potential [mV] @pH 5.7, sizes of ND dispersions#, [nm]	pH value	Production
I6	Wet synthesis; CrO_3 in H_2SO_4 ; $\text{NaOH} + \text{H}_2\text{O}_2$; fractionated	6-10 nm	19.6 ± 3.4 mV 64.5 nm	5.57	Chelyabinsk (Russia)
I6COOH	Sample I6 treated in air at $420\text{ }^\circ\text{C}$	-	-27.6 ± 17 mV 190 nm	3.5	The modification was performed in the International Technology Centre, Raleigh (USA)
Chacoal			75nm, 385 nm		Russia

* Size was determined by Small Angle X-ray Scattering (SAXS), # Size was determined by DLS measurements.

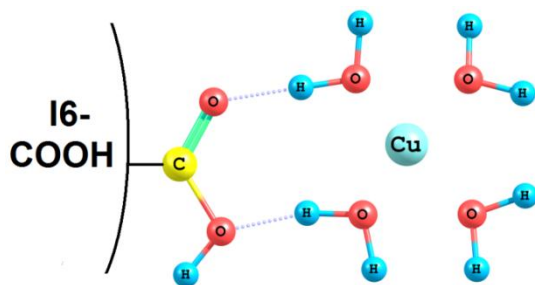


Fig. 5 – Scheme of adsorption of copper ions on ND surface

That means that chemical adsorption of nitrates anions plays a dominant role. Observed changes of IR spectrum of all powders (adsorbent + adsorbate) extracted from the aqueous mixtures-suspensions of $\text{Cu}(\text{CH}_3\text{COO})_2$ allow to say that chemical adsorption is the main mechanism of acetate ions adsorption by NDs.

3. CONCLUSIONS

In this research it was found that in nitrates salts solutions both NDs and charcoal actively adsorb nitrate

ions and metal cations, and the adsorption efficiency of modified ND is about 3 times higher than that of I6 in respect to the ions. In acetates salts solutions both NDs and charcoal don't adsorb Cu^{2+} and adsorb acetate ions weakly. The adsorption efficiency of I6, I6COOH and charcoal in respect to all ions in acetate salt solutions is practically equal. On the basis of the IR and Raman spectroscopy results, we propose a hypothesis about adsorption mechanisms of nitrate and acetates anions and copper cations on the surface of the NDs. According to this hypothesis the main mechanism of adsorption of Cu^{2+} cations is a physical adsorption, and the main mechanism of nitrates and acetates anions is a chemical adsorption.

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REFERENCES

1. A.M. Schrand, S.A. Ciftan Hens, O.A. Shenderova, *Critical Rev. Solid State Mater. Sci.* **34**, 18 (2009).
2. V.N. Mochalin, O. Shenderova, D.Ho.Y. Gogotsi, *Nat. Nanotechnol.* **7**, 11 (2012).
3. B.V. Spitsyn, S.A. Denisov, N.A. Skorik, A.G. Chopurova, S.A. Parkaeva, L.D. Belyakova, O.G. Larionov, *Diamond Related Mater.* **19**, 123 (2010).
4. T.A. Dolenko, S.A. Burikov, K.A. Laptinskiy, T.V. Laptinskaya, J.M. Rosenholm, A.A. Shiryaev, A.R. Sabirov, I.I. Vlasov, *J. Alloy. Compd.* **586**, S436 (2014).
5. O. Shenderova, A.M. Panich, S. Moseenkov, S.C. Hens, V. Kuznetsov, H.M. Vieth, *J. Phys. Chem. C* **115**, 19005 (2011).
6. T.A. Dolenko, S.A. Burikov, J.M. Rosenholm, O.A. Shenderova, I.I. Vlasov, *J. Phys. Chem. C* **116**, 24314 (2012).
7. S.A. Dolenko, S.A. Burikov, T.A. Dolenko, I.G. Persiantsev, *Pattern Recognition and Image Analysis* **22** No4, 550 (2012).