

**THE STUDY OF ADSORPTION OF COPPER AND NICKEL IONS  
BY POLYANILINE AND ITS NANOCOMPOSITE  
WITH CARBON NANOTUBES**

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**Key words and phrases:** carbon nanotubes; copper; nickel; polyaniline.

**Abstract:** The adsorption of copper and nickel ions by polyaniline (PANI) and its nanocomposite with carbon nanotubes (CNTs) in various conditions of preparation of the initial samples (deprotonation with ammonia, reduction with hydrazine) has been investigated. It is shown that deprotonation has little effect on the absorption of copper and nickel from solutions of acetates of these metals. Preliminary reduction of PANI and PANI/CNTs strongly increases absorption of copper, presumably due to redox reaction of copper ions with PANI leuco-base.

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### **Introduction**

Polyaniline (**PANI**) is an electrically conductive polymer [1, 2], which is also capable of producing composite materials with various organic and inorganic nanoscale components. There are created and intensively investigated numerous nanocomposite material containing polyaniline and metal ions or nanoparticles of metal compounds [3–12], carbon nanotubes [5, 13–17]. These materials are used as adsorbents, catalysts, sensors, electrodes in chemical power sources, for electromagnetic radiation shielding. In particular, great attention is drawn to polyaniline nanocomposites with compounds of catalytically active metals such as copper and nickel [18–33]. In a number of studies metal-nanocomposites containing polyaniline and carbon nanotubes have investigated [5, 20, 25, 29].

Previously, we have synthesized and investigated nanocomposite materials based on polyaniline and multi-walled carbon nanotubes (**CNTs**) Taunit-M, produced by NanoTechCenter Ltd (Tambov) [34–36].

The purpose of this paper is to study conditions for obtaining nanocomposite materials of the type [M]/PANI, [M]/PANI/CNTs, where M – copper or nickel ions at different conditions of pretreatment of PANI.

### **Experimental**

The nanocomposites PANI/CNTs which were studied in this paper were synthesized by oxidative polymerization of aniline in presence of carbon nanotubes Taunit-M in medium of 0.1 M sulfuric acid using potassium permanganate as an

oxidizer in accordance with the method described previously [36]. In these nanocomposites polyaniline forms a layer on the surface of carbon nanotubes. The weight content of nanotubes in the final nanocomposite was 65 %, the rest was PANI in form of green emeraldine protonated with sulfuric acid.

For comparison, samples of pure polyaniline without CNTs were synthesized by the classical method of oxidation of aniline by ammonium persulfate in hydrochloric acid or acetic acid solution [2].

PANI-S was obtained by oxidative polymerization of aniline in 0.1 M hydrochloric acid using ammonium persulfate as an oxidant at room temperature.

PANI-Ac was obtained by oxidative polymerization of aniline by ammonium persulfate in 0.4 M acetic acid at 0 °C for 5 hours.

Aqueous solutions of copper or nickel acetates were used as the initial metal compounds. Preliminary treatment of samples of PANI and PANI/CNTs was carried out as follows.

**Deprotonation:** a sample of 1 g PANI or PANI/CNTs was placed into a glass, 30 ml of water was added and stirred. In the resulting suspension it was added 50 ml of 25 % ammonia, stirred and left to stand in a closed beaker at room temperature for day and night. Then the material was filtered and washed with water. For the adsorption of metal ions resulting deprotonated material was used without drying.

**Deprotonation and reduction:** a sample of 1 g PANI or PANI/CNTs nanocomposite was placed into the glass and 50 ml of water was added, thoroughly mixed and 5 ml of hydrazine hydrate was added at stirring. The resulting mixture was placed in a closed beaker in boiling water bath for 2 h. After cooling 50 ml of ammonia was added and allowed to stand in a closed glass during the day and night at room temperature. The product was filtered, washed with water. For the adsorption of metal ions resulting deprotonated and reduced material was used without drying.

For adsorption of copper or nickel ions to the wet samples of PANI or PANI/CNTs, pre-treated as described above or without pre-treatment, 20 ml of 0.25 M copper or nickel acetate was added and the mixture was kept for 2 days at room temperature in a closed glass. The product was then filtered, washed with water and dried at 80 °C.

To determine the content of metals the samples were burned in a muffle furnace at 800 °C. The mineral residue was dissolved in concentrated hydrochloric acid and after dilution with water the metals were determined photometrically according to the standard analytical techniques (copper in the form of ammonia complex, nickel with dimethylglyoxime in presence of ammonium persulfate as an oxidant).

## Results and discussion

Macromolecules of polyaniline can be in different redox states (non-conductive leuco-base, electrically conductive green and blue emeraldine, pernigraniline) and with varying degrees of protonation of nitrogen atoms, depending on the acidity of the medium [1, 2]. Obviously, these factors may influence the complexing ability of the nitrogen atoms in the molecule of PANI with respect to metal ions, particularly copper and nickel. Thus, in a reduced form of PANI, the electron density on the nitrogen atoms should be higher and, therefore, we can assume that the strength of the complexes with metal ions should be larger.

To determine the effect of redox state of PANI on its ability to bind metal ions, we have investigated the amount of copper and nickel, absorbed by the initial PANI and its nanocomposites with carbon nanotubes (PANI in the protonated form of green emeraldine) under different conditions of preliminary treatment (no treatment, with the deprotonation of ammonia, with the restoration of hydrazine and ammonia deprotonation). The results are shown in Table.

**The weight content of copper and nickel in the samples of PANI and PANI/CNTs after treatment with metal acetate solution under different conditions of pretreatment**

Starting sample	Pretreatment of the starting sample (PANI or PANI/CNTs)	Mass content of metal in the material after treatment with a solution of metal acetate, %	
		copper	nickel
PANI/CNT	No	0.41	0.19
	Deprotonation	1.43	0.31
	Reduction and deprotonation	3.50	0.23
PANI-S	No	1.8	
	Deprotonation	1.8	–
	Reduction and deprotonation	4.1	
PANI-Ac	No	5.4	0.26
	Deprotonation	5.3	0.24
	Reduction and deprotonation	8.0	0.06

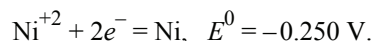
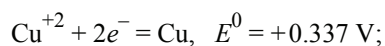
The data obtained show that the preliminary deprotonation of PANI/CNTs and PANI with ammonia increases the adsorption of copper by the PANI/CNTs and has virtually no effect on it in the case of PANI-S and PANI-Ac. On the adsorption of nickel ions on PANI/CNTs, PANI-S and PANI-Ac preliminary deprotonation has little or no effect. It can be assumed that, since the adsorption of metal ions is conducted from solutions of metal acetates, acetate ion itself, being a weak base, acts as a deprotonating reagent and therefore preliminary deprotonation does not give a pronounced effect.

Preliminary reduction of the starting PANI or PANI/CNTs with hydrazine for all samples leads to a significant increase in the adsorption of copper ions. There are two possible mechanisms to explain this phenomenon:

1) increase of the basicity of nitrogen atoms after transformation of conjugated forms of PANI with double bonds at nitrogen atoms into leuco-base, which is accompanied by an increase in their affinity to copper ions;

2) the redox reaction of PANI leuco-base with with copper ions.

In the case of nickel ions preliminary reduction of the initial samples of PANI and PANI/CNTs with hydrazine has little or leads to a decrease in the adsorption of nickel. This difference in adsorption of ions of copper and nickel may be due to differences in their redox potentials, namely:



Apparently, the nickel ions, in contrast to copper ions, are not able to be reduced with leuco-base of PANI.

### Conclusions

PANI and its nanocomposites with carbon nanotubes absorb copper and nickel from aqueous solutions of acetates of these metals. Reduction of the original PANI with hydrazine leads to significant increase in the absorption of copper, probably due to the redox reaction of copper ions with leuco-base of PANI.

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### **Исследование поглощения ионов меди и никеля полианилином и его нанокомпозитом с углеродными нанотрубками**

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**Ключевые слова и фразы:** медь; никель; полианилин; углеродные нанотрубки.

**Аннотация:** Исследовано поглощение ионов меди и никеля полианилином (ПАНИ) и его нанокомпозитом с углеродными нанотрубками (УНТ) в различных условиях предварительной подготовки исходных образцов (депротонирование аммиаком, восстановление гидразином). Показано, что депротонирование мало влияет на поглощение меди и никеля из растворов ацетатов этих металлов. Предварительное восстановление ПАНИ и ПАНИ/УНТ сильно увеличивает поглощение меди, предположительно, за счет окислительно-восстановительной реакции ионов меди с лейкооснованием ПАНИ.

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### **Forschung der Absorption der Ionen des Kupfers und des Nickels vom Polyanilin und vom seinen Nanokomposit mit den Kohlenstoffnanoröhren**

**Zusammenfassung:** Es ist die Absorption der Ionen des Kupfers und des Nickels vom Polyanilin (PANI) und vom seinen Nanokomposit mit den Kohlenstoffnanoröhren (KNR) in den verschiedenen Bedingungen der vorläufigen Vorbereitung der Ausgangsmuster (die Deprotonierung vom Ammoniak, die Wiederherstellung vom Hydrazine) untersucht. Es ist gezeigt, dass die Deprotonierung die Absorption des Kupfers und des Nickels aus den Lösungen der Acetate dieser Metalle wenig beeinflusst. Die Vorwiederherstellung von den PANI und PANI/KNR vergrößert stark die Absorption des Kupfers, vermutlich, auf Kosten von der Redox-Reaktion der Ionen des Kupfers mit der Leukobase vom PANI.

## Etude de l'absorption des ions du cuivre et du nickel par polyaniline et son composite avec les nanotubes carbonés

**Résumé:** Est étudiée l'absorption des ions du cuivre et du nickel par polyaniline (PANI) et son composite avec les nanotubes carbonés (NTC) dans de différentes conditions de la préparation préalable des échantillons initiaux (déprotonation par ammoniacale, régénération par hydrazine). Est montré que la déprotonation influence peu sur l'absorption du cuivre et du nickel à partir des solutions des acétates de ces métaux. La régénération préalable de PANI et de PANI/NTC augmente beaucoup l'absorption du cuivre probablement compte tenu de la redox-réaction des ions du cuivre avec une leucobase PANI.

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