Synthesis and Properties of a Polyamine-Cumulene/Carbon Nanotubes for Removing Harmful Substances from Aqueous Solutions

E A Neskoromnaya¹, A V Melezhik ¹, O V Alekhina ¹, I V Burakova¹*, E S Mkrtchyan, A E Burakov¹
¹Department “Technology and Methods of Nanoproduct Manufacturing”, Tambov State Technical University, Tambov, 392000, Russia
* iris_tamb68@mail.ru

Abstract. In the current work, a method for obtaining an effective adsorption material (nanocomposite) through polycondensation of hexamethylenetetramine in sulfuric acid in the presence of multi-walled carbon nanotubes as texture component is proposed, and the properties of this material are studied. The elemental composition of the material was determined by energy-dispersive X-ray analysis, and the morphology was evaluated by scanning electron microscopy. Its adsorption activity was estimated towards Cu(II) ions and synthetic dyes – methylene blue (MB) and methyl orange (MO). It was established that the adsorption capacity of the studied material for the dyes is 1,255 and 801 mg g⁻¹ (for MB and MO, respectively), whereas for Cu(II) ions, it is 24.5 mg g⁻¹. Besides, the kinetics of the adsorption of all those species was studied, thereby making it possible to determine the expediency of using the developed nanocomposite for purification of aqueous solutions.

1. Introduction
Authoritative research works in the field of synthesis and application of new types of carbon-nanomaterial-based adsorbents prove that graphene nanostructured materials are more effective in comparison with currently used commercial adsorbents [1-3]. Graphene-based adsorbents are assumed to become an alternative to the conventional materials such as rocks, clays, hydrated aluminosilicates, activated carbons, low-cost biosorbents prepared from agricultural waste, etc [4,5]. Among the existing physical and chemical processes of removal and subsequent isolation of harmful contaminants, a significant role is played by adsorption-desorption cycles. Their practical implementation allows removal, transfer and accumulation of toxic compounds with almost 100-% efficiency [2].

The synthesis of aminocumulene, a soluble polycondensation product of hexamethylenetetramine (HMTA) in anhydrous sulfuric acid, is described by the authors in [6]. This substance presumably contains cumulated double carbon-carbon bonds and amino groups. It was established that during the HMTA polycondensation in sulfuric acid at an elevated temperature (180-200 °C), a polymeric insoluble sulfur-containing product (polyamine cumulene - PAC) is formed, and it demonstrate high adsorption properties with respect to heavy metal ions and organic dye molecules. Considering this, herein, the authors study the adsorption properties of a PAC/carbon nanotubes (CNTs) nanomaterial regarding the removal of acidic and basic organic dyes – methylene blue (MB), and methyl orange (MO), respectively, as well as heavy metal ions – Cu(II).
2. Experimental Details
2.1. Material Synthesis
The nanocomposite was synthesized as follows. First, HMTA was slowly added to anhydrous sulfuric acid; after that, the mixture was stirred and cooled. Next, Taunit-M CNTs (NanoTechCenter Ltd., Tambov, Russia) were added to the resulting viscous solution with thorough stirring. The mixture was heated to 180 °C and held at 180-200 °C for 2 h. The product (PAC/CNTs) was washed with water until the sulfuric acid was completely removed, and dried in a drying oven at 110 °C. The CNT content in this material was 14-15 wt.%.

2.2. Kinetic Study
1,500 mg L⁻¹ stock (initial) solutions were separately prepared by dissolving 1.5 g of MO and MB (both – reagent grade, Laverna Ltd., Moscow, Russia) in 1 L of distilled water and standing for several hours. To determine kinetic parameters of the MO and MB adsorption, experiments were carried out in tubes containing 0.03 g of PAC/CNTs and 30 mL of the 1,500 mg L⁻¹ MO and MB solutions. To calculate kinetic parameters of the Cu(II) adsorption, tests were performed with 30 mL of a 100 mg L⁻¹ Cu(NO₃)₂ 3H₂O solution (Laverna Ltd.) and 0.03 g of the adsorbent. All the tubes were shaken for equilibration at 100 rpm and room temperature on a Multi Bio RS-24 programmable end-over-end rotator (Biosan, Riga, Latvia). After that, the suspensions were centrifuged at 10,000 rpm for 10 min using a 5810 R device (Eppendorf, Hamburg, Germany). After the adsorption procedure, dye amounts were determined spectrophotometrically on a PE 5400V instrument (Ekros, St. Petersburg, Russia) at 400 nm (MO) and 570 nm (MB), whereas equilibrium Cu(II) adsorption concentrations were determined by atomic absorption spectrometry (AAS) on an MGA-915MD instrument (Atompribor Ltd., Saint-Petersburg, Russia). The adsorbent morphology was elucidated by scanning electron microscopy (SEM) using a Neon 40 equipment (Carl Zeiss AG, Oberkochen, Germany). The same instrument was employed for energy-dispersive X-ray elemental analysis of the material.

3. Results
3.1. Material Characterization
According to the SEM image of the PAC/CNTs nanocomposite shown in Figure 1, it can be seen that the HMTA polycondensation polymeric product is formed on the CNT surface, resulting in the spongy structure favorable for using this material as an adsorbent.

![Figure 1. SEM image of the PAC/CNTs material.](image-url)
there should be 3 or 4 oxygen atoms per sulfur atom. It can be supposed that the material contains sulfide sulfur, which may have an affinity for heavy metal ions and organic matters.

3.2. Kinetic Results
Based on the results of the experimental studies, kinetic dependences of the dye and Cu(II) adsorption on the nanocomposite were constructed (Figure 2).

![Figure 2. Kinetics dependences of the dye adsorption (a) and of the copper ions (b) on the PAC/CNTs nanocomposite.](image)

It should be noted that the studied material exhibited a high sorption capacity for both the MB (1,255 mg g\(^{-1}\)) and the MO (801 mg g\(^{-1}\)). At the same time, equilibrium was achieved much faster (within 5 min) in comparison with the conventional materials (e.g., for activated carbons – within 30-50 min). The Cu(II) adsorption proceeded with the following parameters: capacity 24.5 mg g\(^{-1}\), and equilibrium time 50 min.

The experimental data obtained were fitted to the diffusion, pseudo-first-order, pseudo-second-order and Elovich models (Figures 3 and 4).
The adsorption interaction of the material under study with the organic dyes can be described quite well by almost all the mathematical models implemented herein. Analyzing the data using these models makes it possible to reveal a significant contribution of the chemisorption to the dye removal process (Figure 3b) (high correlation of the data with the pseudo-second-order equation), as well as chemical affinity of the adsorbent surface for the compounds being removed (data approximation using the Elovich model) (Figure 3c). Table 1 below presents the basic calculated parameters of the kinetic equations implemented.

**Table 1. Kinetic parameters of the adsorption of the dyes and Cu(II) ions on the PAC/CNTs nanocomposite.**

| Model             | Pseudo-first-order: | Pseudo-second-order: |
|-------------------|---------------------|----------------------|
|                   | log(Q_e - Q_t) = log Q_e - k_1 t / 2.303 | t/Q_t = 1/k_2 Q_e^0.5 + 1/Q_e |
| Adsorbate         | Q_e                | k_1                  | R^2 | Q_e | k_2 | R^2 |
| MO                | 107.28             | -0.0965              | 0.9665 | 833.33 | 0.0018 | 1  |
| MB                | 66.53              | -0.0702              | 0.86 | 1250 | 0.0032 | 1  |
| Cu(II)            | 17.73              | -0.0055              | 0.6737 | 27.47 | 0.00796 | 0.999 |

| Model             | Elovich:           | Intraparticle diffusion: |
|                   | Q_t = \frac{1}{\beta} \ln (\alpha \beta t) + \frac{1}{\beta} \ln t | Q_t = k_{id} t^{0.5} + C |
| Adsorbate         | \alpha | \beta | R^2 | k_{id} | C | R^2 |
| MO                | 6·10^{10} | 0.03 | 0.9113 | 13.969 | 733.11 | 0.8199 |
| MB                | 1.2·10^{26} | 0.04 | 0.9525 | 10.322 | 1205.3 | 0.9056 |
| Cu(II)            | 1.52·10^{2} | 0.324 | 0.9386 | 1.859/0.291 | 129/22.93 | 0.909/0.9646 |

*Q_e – adsorbate amount adsorbed onto the adsorbent surface at equilibrium (mg g^{-1}); Q_t – adsorbate amount adsorbed onto the adsorbent surface at time t (mg g^{-1}); k_1 - pseudo-first-order adsorption rate constant (min^{-1}); k_2 - pseudo-second-order adsorption rate constant (mg g^{-1} min^{-1}); α, β - Elovich model constants; C – intercept of intraparticle diffusion model.*
– pseudo-second-order adsorption rate constant (g mg\(^{-1}\) min\(^{-1}\)); \(\alpha\) - initial adsorption rate constant (min\(^{-1}\) mg g\(^{-1}\)); 
\(\beta\) - degree of surface coverage and activation energy of chemisorption (g mg\(^{-1}\)); \(k_{\text{id}}\) - internal diffusion coefficient (mg g\(^{-1}\) min\(^{-0.5}\)); C - boundary layer thickness (mg g\(^{-1}\)).

It should also be noted that a high correlation of the experimental data with the \(Q_t\) vs. \(t^{1/2}\) approximation (Figure 3d) indicates a contribution of the intraparticle diffusion into the porous adsorbent structure to the dye removal (Table 1).

As for the Cu(II) adsorption, Figure 4a shows the approximation straight line constructed from the pseudo-first-order model. A sufficiently low value of the correlation coefficient \(R^2=0.6737\) suggests that the studied process depends little on the film diffusion of the Cu(II) ions. The pseudo-second-order model (Figure 4b, Table 1) implemented shows the best correlation with the experimental data (\(R^2=0.9999\)). The results obtained indicate a significant contribution of the chemical reaction to the Cu(II) adsorption from the aqueous solution. Heterogeneity of the adsorption sites available on the nanocomposite surface, which is due to the existence of various types of the chemical affinity for the adsorbate, can be evidenced by a good correlation of the experimental data with the Elovich model; in this case, \(R^2=0.9386\) (Figure 4c, Table 1). Besides, the Cu(II) adsorption on the PAC/CNTs nanocomposite can successfully be described by the diffusion model, the calculated data of which are presented in Table 1. The removal process proceeds in two steps, thereby indicating the mixed-diffusion nature of the interaction. High values of the correlation coefficient (\(R^2=0.9093\) and 0.9646)

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**Figure 4.** Kinetic models used to fit the data obtained for the Cu (II) adsorption: a) – pseudo-first-order, b) – pseudo-second-order, c) – Elovich models, and d) – intraparticle diffusion.
demonstrate a significant contribution of both the external and intraparticle diffusion to the Cu (II) adsorption (Table 1).

4. Conclusion
The possibility of using the adsorption material (PAC/CNTs) based on a CNT matrix modified with an organic ligand for selective removal of impurities of different chemical nature from aqueous media is considered herein. Kinetic curves describing the peculiarities of the interaction between the contaminants and the PAC/CNTs nanocomposite were constructed. The time of the organic dye adsorption was found to be 5 min at the adsorption capacity of the material being equal to 1.255 mg g\(^{-1}\) (MB) and 801 mg g\(^{-1}\) (MO), and 50 min at 24.5 mg g\(^{-1}\) (Cu(II) ions). The experimental results were processed using the known mathematical equations describing of adsorption kinetics. The analysis of the approximation straight lines elucidated the significant contribution of the chemisorption and the intraparticle diffusion of the studied contaminants into the material structure to the adsorption process (in the case of the organic compounds). The data obtained unequivocally indicate the prospect of using the material proposed as a highly effective universal adsorbent.

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