Adsorption of the Methylene Blue Dye on Carbon Nanocomposites Under Dynamic Conditions: A Kinetic Study

I V Burakova¹, A V Babkin¹, E A Neskornaya ¹, A E Burakov¹, D A Kurnosov¹, A G Tkachev¹
¹Department “Technology and Methods of Nanoproducts Manufacturing”, Tambov State Technical University, Tambov, 392000, Russia

Abstract. The present paper describes kinetic regularities of the removal of the typical synthetic dye, methylene blue (MB), from aqueous solutions by two graphene-organic composites, polyhydroquinone (PHQ)/graphene and polyamine-cumulene (PAC)/carbon nanotubes (CNTs). To study the adsorption kinetics under dynamic conditions simulating the real industrial environment, a column method was implemented using the facility developed. The MB adsorption capacity of the studied nanocomposites was found to be very high (2,938 mg g⁻¹ for the PAC/CNTs at the contact time of 75 min, and 2,610 mg g⁻¹ for PHQ/graphene at 40 min). Finally, the kinetic parameters of the process were determined, and the mechanisms proceeding during the dye adsorption on the carbon nanocomposites were elucidated.

1. Introduction
Currently, in Russia, about 20% of water samples taken from various water supply sources does not correspond to the maximum permissible concentration limits set for hazardous biological and chemical components. In fact, every second Russian citizen, in one way or another, consumes water containing a huge number of harmful components, thereby inevitably subjecting himself/herself great health risks [1].

In modern wastewater treatment processes, more and more attention is being paid to controlling the content and efficient removal of synthetic organic dyes. This is due to their negative impact on the human body - almost all of them are harmful and possess different degrees of toxicity (allergens, carcinogens, mutagens). Thus, the removal of these contaminants is a very important and urgent issue.

Adsorption removal appears to be one of the main techniques of purifying aqueous media from dyes down to practically zero levels. Wastewater treatment facilities are the ones most widely used for this purpose; their functioning is based on adsorption processes. This is due not only to the efficiency of the purification technology, but also to the simplicity of their technological implementation and equipment design. It is worth noting that high adsorption capacity of materials used to remove contaminants allows effective implementation of selective purification of aqueous and even gaseous media [2-4].

The authors of the present research have studied the kinetics of the adsorption of methylene blue (MB), representing a basic thiazine dye, on graphene nanocomposites synthesized under laboratory conditions at the Research Department “Technology and Methods of Nanoproduct Manufacturing”, (Tambov State Technical University, Tambov, Russia). Nanomaterials seem to be good adsorbents due to their small size, catalytic potential, high reactivity, ease of separation, and a large number of active sites to interact with different contaminants [5-8].
Laboratory kinetic studies are usually carried out by mixing the adsorbent with a limited volume of the solution (“batch” tests). However, under real conditions, the purification process is implemented by pumping the solution through a fixed-bed column containing the adsorbent (“column” dynamic tests). In this regard, the authors have developed a facility for conducting adsorption studies in a dynamic mode.

2. Experimental Details

2.1. A Column Facility for Studying Adsorption Under Dynamic Conditions

To determine equilibrium time in the adsorbent-solvent-sorbate system, kinetic studies were performed in a dynamic mode using a laboratory facility, the scheme and photo of which are presented in Figure 1.

The solution (100 mL) is transported from the initial solution container along two loops (1.1) and (2) through control valves. The liquid is circulated by means of a peristaltic pump. The first loop supplies the aqueous solution to adsorption cell (1) containing the porous adsorbent sample, and then, the purified liquid is returned into the initial solution container along loop (1.2).

Figure 1. A laboratory facility to study the dynamic adsorption (R – initial solution container, 1- adsorption cell, 2- spectrophotometer, peristaltic pump).

Along the parallel loop, the liquid is supplied into a cuvette of spectrophotometer (2) to record optical density values at predetermined intervals, and then it is returned.

2.2. Adsorbent

Two nanocomposites – polyhydroquinone (PHQ)/graphene and polyamine-cumulene (PAC)/carbon nanotubes (CNTs) - were synthesized and used as adsorption materials. PHQ represents a molecule chemically bonded to few-layered graphene sheets, whereas PAC is a product of hexamethylenetetramine polycondensation in sulfuric acid in the presence of CNTs as texture component. The energy-dispersive X-ray analysis shows the availability of significant amounts of sulfur, presumably as sulfide groups.

2.3. Kinetic study

The initial MB solution (concentration 1,500 mg L⁻¹, and volume 100 mL) was supplied by means of the peristaltic pump into the adsorption cell containing the adsorbent (weight 0.03 g), and then was returned into the initial solution container along the reverse loop, where the concentrations were mixed. Along the parallel loop, the solution was supplied into the cuvette located in a PE 5400V spectrophotometer (Ekros, St. Petersburg, Russia) (wavelength 570 nm). The optical density of the solutions was recorded every 180 s.
3. Results and Discussion
The results of the kinetic studies under the dynamic conditions are graphically presented in Figure 2.

![Figure 2](image-url)

**Figure 2.** Kinetics of the dye adsorption on the PAC/CNTs and PHQ/graphene nanocomposites.

Due to the implementation of the adsorption process as a flow, very high adsorption capacity values were achieved for the MB removal: 2.938 mg g\(^{-1}\) at the contact time of 75 min (in the case of PAC/CNTs), and 2.610 mg g\(^{-1}\) at 40 min (in the case of PHQ/graphene). The experimental data were fitted to the following kinetic models: pseudo-first- and pseudo-second-order, Elovich, and intraparticle diffusion (Table 1).

Figure 3 shows the model fits with the correlation coefficients, the values of which indicate the applicability of each models to describe the adsorption on the materials under study. The pseudo-second-order model, with \(R^2=0.9985\) and 0.9972 determined for PHQ/graphene and PAC/CNTs, respectively (Figure 3b) shows a better correlation with the experimental data, in comparison with the pseudo-first-order model, with \(R^2=0.9210\) and 0.8617 for PHQ/graphene and PAC/CNTs, respectively (Figure 3a). Based on the results obtained, a chemical interaction between the adsorbent functional groups and the dye molecules can be assumed. Theoretically, this interaction is stoichiometric, meaning that one molecule occupies only one position on the adsorbent surface.
Figure 3. Experimental data fitted to the following kinetic models: a) – pseudo-first-order, b) – pseudo-second-order, c) – Elovich models, and d) – intraparticle diffusion.

The experimental data can also be described quite well by the Elovich model (Fig. 3c), which implies inhomogeneity of adsorption sites (having different energy and chemical affinity for the extracted compound) on the material surface. High correlation coefficients indicate the possibility of employing this model to describe the experiment under the conditions selected.

Table 1. Kinetic parameters of the MB adsorption.

|                | Pseudo-first order: | Pseudo-second order: |
|----------------|---------------------|----------------------|
|                | \(\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303} t\) | \(\frac{t}{Q_e} = \frac{1}{k_2 Q_e^2} + \frac{1}{k} t\) |
| \(Q_e\) | \(k_1\) | \(R^2\) | \(Q_e\) | \(k_2\) | \(k\) | \(R^2\) |
| PHQ/graphene   | 1558 | -0.0012 | 0.921  | 3333.3 | 9·10⁻⁷ | 0.9985 |
| PAC/CNTs       | 7962 | -0.0014 | 0.8617 | 3333.3 | 3·10⁻⁷ | 0.9972 |
The intraparticle diffusion model constructed from the experimental data represents a multi-linear dependence (Figure 3d). As can be seen, the adsorption removal consists of two distinct stages, which indicates its mixed-diffusion mechanism. High correlation coefficients determined for the initial region on the curve indicate a significant contribution of the external diffusion to the total process time.

From the analysis of the adsorption rate constant values (Table 1) calculated for the diffusion and chemical kinetic models, it can be found that the adsorption on PHQ/graphene proceeds several times faster than on PAC/CNTs. Besides, the chemical interaction between the dye molecules and the adsorbent functional groups is the limiting stage of the process.

4. Conclusions
The parameters of the organic dye (MB) adsorption by the composite materials based on graphene structures modified with organic products - PHQ/graphene and PAC/CNTs - are analyzed herein. To study the adsorption capacity under dynamic conditions, the authors developed a laboratory facility allowing for continuous measurement of solution optical density values using a spectrophotometer. The maximum MB adsorption capacity was experimentally found to be 2,610 (at 40 min) and 2,938 mg g\(^{-1}\) for PHQ/graphene (at 40 min) and PAC/CNTs (at 75 min), respectively. With the kinetic data approximation using the diffusion and chemical kinetic equations, it was established that the mixed-diffusion-contributed chemical interaction stage limits the process.

Acknowledgment
The research was funded by the Ministry of Education and Science of the Russian Federation (Project No. 16.1384.2017/PCh).

References
[1] Information available at http://www.water.ru/bz/likbez/regionalnye__problemy_kachestva.shtml.
[2] Wang H J, Zhou A L, Peng F [et al.] 2007 Mater. Sci. Eng., A 466 201-206.
[3] Han R, Lu Z, Zou W [et al.] 2006 J. Hazard. Mater B 137 480.
[4] Mohan D, Pittman C U 2006 J. Hazard. Mater. B 137 762.
[5] Wenhao Wu, Wei Chen, Daohui Lin [et al.] 2012 Environ. Sci. & Technol. 46 5446-5454.
[6] Liu X Y, Ji Y S, Zhang Y H [et al.] 2007 J. Chromatogr. A 1165 10-17.
[7] Kaur A, Gupta U 2009 Mater. Chetu. 19 8279-8289.
[8] Yang K, Wu W, Jing Q [et al.] Environ. Sci. Technol. 2008, 42(21), 7931-7936.