Kinetics of the Adsorption of Synthetic Dyes on a Polyhydroquinone/Graphene Carbon Nanocomposite

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Abstract. The paper considers the possibility of applying the innovative p-benzoquinone-modified graphene-oxide-based nanocomposite material – polyhydroquinone/graphene- as an adsorbent of organic compounds of different nature on the example of synthetic dyes. The graphene content in the composite is about 30-40 %, whereas the polyhydroquinone content is 60-70 %. The kinetics of the adsorption of the dyes - methyl orange (MO) and methylene blue (MB) - from aqueous solutions was studied. The adsorption capacities towards the MB and MO were found to be 890 and 601 mg g⁻¹, respectively, for the contact time of 10 min. Kinetic dependencies were constructed, and the expected mechanisms of the adsorption on the carbon nanocomposite were described.

1. Introduction
The adsorption of organic compounds of various origins is widely studied throughout the world. The problem of complete purification of industrial effluents from water-soluble organic substances is one of the most important and, at the same time, difficult-to-solve issues. Adsorption is a universal technique that makes it possible to extract almost all impurities from the liquid phase. It is based on preferential removal of contaminant molecules under the action of a force field in adsorbent pores and due to chemically active adsorption sites [1,2].

To purify water from molecularly dissolved organic substances, activated carbons are usually used as conventional material [3]. The other conventional materials include synthetic zeolites such as NaX [4], plant-origin waste such as wheat straw, sawdust, shell husks, etc. [5], carbon nanomaterials such as carbon nanotubes (CNTs) and their functionalized forms [6-8].

The maximum degree of purification can be achieved by increasing time of the contact between the solution and the adsorbent up to 30-50 min [5]. However, under modern conditions, it is required to develop new types of adsorption materials capable of removing hard-to-remove impurities at a higher degree of adsorption and a short contact time. These requirements are met by using carbon nanomaterials such as nanotubes and graphene, both in their native or modified form. A wide range of publications are known to confirm the prospects of employing nanomaterials for the adsorption of dyes like methylene blue (MB) and methyl orange (MO).

The authors of the present work synthesized a nanocomposite material (polyhydroquinone (PHQ)/graphene) based on graphene oxide (GO) and modified with p-benzoquinone - an organic compound, the chemical formula of which is C₆H₄O₂. To assess the adsorption capacity of this material for organic substances, kinetic studies on the adsorption of the cationic (methylene blue - MB) and anionic (methyl orange - MO) dyes from aqueous solutions were carried out.
2. Experimental Details

2.1. PHQ/Graphene Nanocomposite

The adsorbent proposed herein was synthesized by polymerization of p-benzoquinone in an aqueous solution in the presence of a GO dispersion. Simultaneously, a partial reduction of GO to graphene occurs during the process, so that the product obtained probably represents PHQ molecules chemically bonded to few-layered graphene sheets (as elucidated by the X-ray diffraction data). In this material, the graphene content is about 30-40 %, the rest is PHQ. The PHQ weight content can be varied by choosing ratios of the initial reagents. Due to the presence of phenolic groups and the well-developed surface (at the expense of the texture-forming properties of graphene nanoplatelets), this material could be an effective adsorbent of organic substances and heavy metals.

2.2. Adsorbent Characterization

To analyze the crystalline structure of the PHQ/graphene nanocomposite, Raman spectra were recorded by a DXR™ Raman microscope using Array Automation software (Thermo Fisher Scientific Inc., Waltham, MA USA).

To qualitatively determine the phase composition of the PHQ/graphene nanocomposite, a Difrey 401 X-ray diffractometer (Scientific Instruments CJSC, St. Petersburg, Russia) was used.

2.3. Kinetic Study

To carry out experiments on the organic dye removal, 30 mL of 1,500 mg L\(^{-1}\) MO and MB aqueous solutions were separately added in tubes containing the weighed amount of the adsorbent (0.03 g), then shaken on a Multi Bio RS-24 programmable rotator (Biosan, Riga, Latvia) at time intervals of 5, 15, 30, and 60 min. Next, the solutions were passed through paper filters, and optical density measurements were made on a PE 5400V spectrophotometer (Ekros, St. Petersburg, Russia) at 400 (for the MO) and 570 (for the MB) nm, followed by calculating concentration (“after-adsorption”) values.

3. Results and Discussion

3.1 Characterization

Figure 1 shows the spectra with individual peaks indirectly confirming the availability of structured carbon.

![Figure 1. Raman spectra recorded for the PHQ/graphene nanocomposite.](image)

The spectra of the synthesized nanocomposite have characteristic peaks at two frequencies: \(\sim 1,587\) cm\(^{-1}\) representing the G band related to sp\(^2\)-hybridized carbon atoms possessing higher energy, and
$\sim$1,346 cm$^{-1}$ representing the D band associated with sp$^3$-hybridized carbon atoms having lower energy. These peak frequencies are identical with those ones fixed for the GO. The synthesized nanocomposite is also characterized by the absence of peaks typical of deformation vibrations of the C-H bonds in the benzene ring probably related to the oxidation of polymerized quinone particles during the modification of the GO surface. High intensity of the spectral bands can be observed at a frequency of $\sim$ 1,420 cm$^{-1}$ typical of vibrations of the double C=C bonds in the molecular structure of the benzene ring.

Figure 2. X-ray diffraction pattern recorded for the PHQ/graphene nanocomposite material.

The X-ray diffraction pattern presented in Figure 2 shows the availability of few-layered graphene in the studied sample (the band at $2\theta$ = 38.0°). The bands at $2\theta$ = 20.0-27.0° indicate the presence of organic compounds in the composite structure, which are most likely formed as a result of the chemical interaction between the PHQ and the GO surface functional groups. The unidentifiable peaks in the X-ray pattern presumably correspond to an amorphous phase formed by p-benzoquinone decomposition products.

3.2 Kinetic results

After the experiments, kinetic dependencies of the MO and MB adsorption on the PHQ/graphene nanocomposite were constructed (Figure 3). According to the data obtained, the adsorbent exhibited high adsorption activity towards the organic molecules (890 and 601 mg g$^{-1}$ in the cases of the MB and MO, respectively). Adsorption equilibrium was reached within 10 min in both cases.
Figure 3. Kinetic of the dyes adsorption on the PHQ/graphene nanocomposite.

The adsorption proceeding in the adsorbate-adsorbent system represents a multi-stage process, which makes its description rather difficult. To calculate the kinetic parameters and elucidate possible dye adsorption mechanisms taking place on the PHQ/graphene nanocomposite, the following known models were implemented to process the experimental data: pseudo-first- and pseudo-second order, Elovich, and intraparticle diffusion.

Figure 4. Kinetic models: pseudo-first-order (a), pseudo-second-order (b), Elovich (c), and intraparticle diffusion (d).
Figure 4a shows the straight line of the experimental data approximation using the pseudo-first-order model. Given sufficiently low determination coefficient ($R^2$) values for both data sets ($R^2=0.5954$ – for the MB, and $R^2=0.5332$ – for the MO), it can be assumed that the process under study is not limited by the film diffusion of the contaminant molecules, which determines the process rate during the initial period of time. As a rule, such a model can be used when the concentration of the contaminant on the adsorbent surface is much lower than that of the adsorbent surface groups, which is possible only at the initial adsorption stage. Table 1 below presents the main calculated parameters of the kinetic equations.

| Table 1. Kinetic parameters of the organic dyes adsorption onto PHQ/graphene*. |
|-------------------------------------------------|
| **Pseudo-first-order:**                        | **Pseudo-second-order:** |
| $\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303}t$ | $t = \frac{1}{Q_e}k_2Q_e^2 + \frac{1}{Q_e}t$ |
| $Q_e$ | $k_1$ | $R^2$ | $Q_e$ | $k_2$ | $R^2$ |
| MO    | 34.39 | -0.052 | 0.595 | 625   | 0.0032 | 0.9999 |
| MB    | 35.22 | -0.058 | 0.533 | 909.1 | 0.0024 | 0.9997 |
| **Elovich:**                                   | **Intraparticle diffusion:** |
| $Q_t = \frac{1}{\beta} \ln (\alpha t) + \frac{1}{\beta} \ln t$ | $Q_t = k_{id} t^{0.5} + C$ |
| $\alpha$ | $\beta$ | $R^2$ | $k_{id}$ | $C$ | $R^2$ |
| MO    | $1.16 \times 10^{10}$ | 0.039 | 0.7459 | 38.25/1.18 | 456.5/599 | 0.984/0.507 |
| MB    | $1.16 \times 10^{10}$ | 0.02 | 0.5207 | 99.57/2.64 | 545.3/921.4 | 0.909/0.588 |

* $Q_e$ – dye amount adsorbed onto the adsorbent surface at equilibrium (mg g$^{-1}$); $Q_t$ – dye 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 (g mg$^{-1}$ min$^{-1}$); $\alpha$ – initial adsorption rate constant (min$^{-1}$ g mg$^{-1}$); $\beta$ – degree of surface coverage and activation energy of chemisorption (g mg$^{-1}$); $k_{id}$ – intraparticle diffusion coefficient (mg g$^{-1}$ min$^{-0.5}$); $C$ – boundary layer thickness (mg g$^{-1}$).

In its turn, the pseudo-second-order model is applicable to the description of the entire contaminant removal process, and indicates chemical adsorption. In the case considered herein (Figure 4b), the determination coefficient values of the approximation straight line for the MO and MB dyes are $R^2=0.9999$ and 0.9997 (Table 1), respectively, thereby confirming the chemical interaction between the dye molecules and the functional phenolic groups of the nanocomposite.

In order to evaluate the adsorption and desorption contributions, the well-known Elovich model was applied. The classical definition of the determination coefficient by the data linearization method makes it possible to evaluate the suitability of the model for using in a particular process. A low coefficient indicates the absence of heterogeneous chemisorption on the surface of the material synthesized, or it shows that this type of interaction is not limiting and does not determine the kinetics of adsorption removal (Figure 4c, Table 1).

Furthermore, to describe the kinetics of the adsorption of the organic substances on the nanocomposite under study, the diffusion model, was used herein. Fig. 4d shows the experimental data approximation in the corresponding coordinates. The trend of the dependence constructed indicates impossibility of an unambiguous interpretation of the process nature. The adsorption proceeds in a mixed diffusion mode, which confirms the stepwise variation of the approximation straight line slope.

4. Conclusion
In the present research, the innovative p-benzoquinone-modified graphene-oxide-based material – PHQ/graphene nanocomposite – is proposed as an adsorbent for removing dye molecules from
aqueous media. The analysis of the kinetic mechanisms of the dye adsorption on this nanocomposite was carried out in accordance with the commonly accepted methods allowing evaluation of the material functional characteristics. The results obtained show a significant superiority of PHQ/graphene over the existing analogs (e.g., those ones reported in [3-7]). The comprehensive study on the physical and chemical characteristics of the material made it possible to identify the crystalline structure of carbon, similar to that of graphene in type and energy, and to establish the presence of characteristic peaks related to the vibrations of constituent elements in the molecular structure of the organic modifier. The mathematical analysis of the experimental kinetic dependencies allows elucidation of the mixed diffusion mechanism of adsorption removal affected by the chemical interaction between the dye molecules and the phenolic groups of the adsorbent.

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