Kinetic of the dyes adsorption on a polyhydroquinone/graphene nanocomposite under dynamic conditions

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Abstract. Conducting adsorption experiments in a dynamic mode makes it possible to simulate process parameters as close to real conditions as possible. In the present work, the kinetics of the adsorption of some organic dyes (methylene blue, alizarin red S, and malachite green) on a novel polyhydroquinone/graphene nanocomposite, developed by the authors, were studied. It was established that the equilibrium of the adsorption system is achieved within 40, 120 and 57 min for methylene blue, alizarin red S and malachite green, respectively. Data processing using kinetic models showed that chemical interactions take place between the dye molecules and the active sites of the adsorbent during the adsorption. Besides, the contribution of the diffusion through the film on the adsorbent surface was also marked. The maximum adsorption capacity of the adsorbent was found to increase in the following sequence: malachite green (688.1 mg g⁻¹) < methylene blue (2.610 mg g⁻¹) < alizarin red S (2.923 mg g⁻¹).

1. Introduction

Contaminated water is one of the factors of human viral diseases [1]. Due to rapid urbanization growth rates, the process of environment all pollution is increasing fast [2]. Improper disposal of waste water coming from various enterprises is one of the fundamental causes of water contamination. The textile, rubber, plastic and pulp and paper industries use organic dyes in their production activities [3], thereby being the main sources of organic pollution.

Methylene blue (MB; C₁₆H₁₈ClN₃S; thiazine dye), alizarin red S (ARS; C₁₄H₂NaO₇S; anthraquinone dye) and malachite green (MG; C₂₃H₂₅N₂; N-methylated diaminotriphenylmethane dye), used particularly for textile purposes, belong to synthetic (basic) dyes. They are persistent pollutants and can cause permanent damages to the eyes, skin and gastrointestinal tract of living beings [3].

At present, various methods of removing organic molecules from aquatic media are used – e.g., adsorption, membrane filtration, oxidation, and biological treatment [1]. Among these waste water/water purification techniques, adsorption is considered to be one of the promising options from both economic and process instrumentation points of view.
Different researchers have employed adsorbents of various chemical nature, including carbon nanomaterials, to extract MB, ARS and MG from contaminated wastewater. The brief overview on using some of these materials for the adsorption of the above-mentioned species (conditions and adsorption capacity) is given in table 1.

**Table 1.** An overview of carbon materials used for the adsorption of organic molecules (ARS, MB, MG), their adsorption capacity, and experiment conditions.

| Material                                         | $C_{in}$ | $t$ | $m$ | $T$ | $Q_e$ |
|--------------------------------------------------|----------|-----|-----|-----|-------|
| **ARS**                                           |          |     |     |     |       |
| Oxidized pentaerythritol-modified MWCNTs** [4]    | 50-400   | 2   | 0.005 | 35 | 257.7 |
| SWCNTs** [5]                                      | 100-1.000 | 1.08 | 0.03 | 45 | 312.5 |
| MWCNTs[5]                                         | 100-1.000 | 1.67 | 0.03 | 45 | 135.2 |
| AC** synthesized by carbonization and chemical activation of zinc [6] | 100 | 9 | 0.005 | 25 | 74 |
| Magnetic AC-based nanocomposite [7]               | 1000     | 4   | 0.01 | -  | 108.7 |
| **MB**                                            |          |     |     |     |       |
| Reduced GO**-hybridized polydopamine-kaolin composite [1] | 500     | 24  | 0.04 | 27 | 39.7  |
| Magneticalginate-functionalized MWCNTs [8]       | 30-230   | 0.66 | 0.01 | 25 | 905.5 |
| Regenerated cellulose/GO airgel [9]              | 20       | 0.5 | 0.05 | 25 | 68    |
| Graphene-like porous carbon nanostructure [10]    | 100      | 0.25 | 0.05 | 50 | 469   |
| MWCNTs filled Fe$_3$O$_5$ particles [11]         | 500      | 1   | 0.05 | 25 | 42.3  |
| Mesoporous carbon capsules with magnetic nanoparticles [12] | 50      | 0.16 | 0.005 | 20 | 608   |
| A- COx/G nanofilamentous membrane [13]            | 20       | -   | -   | -  | 95%   |
| HDPy-clay [14]                                    | 150      | 1   | 0.1 | 25 | 142.5 |
| HDTMA-clay [14]                                   | 150      | 1   | 0.1 | 25 | 142.22|
| **MG**                                            |          |     |     |     |       |
| Oxidized mesoporous carbon [15]                  | 700      | 6   | 0.01 | 40 | 963.1 |
| Hyberbranched polyamine-functionalized MWCNTs [16] | 40      | 2   | 0.005 | - | 78.7  |
| AC/Fe$_2$O$_4$ composite [17]                    | 15       | -   | 0.002 | 20 | 20.13 |
| Carbon nanoparticles with large pores [18]       | 500      | -   | 0.01 | 25 | 1.892 |
| GO [19]                                           | 200      | 7   | 0.05 | -  | 476.2 |
| Zeoliticimidazolate-modified GO/MWCNTs composite [20] | 100     | -   | 0.03 | 20 | 3,300/2.034 |
| 3D porous graphene hydrogel [21]                 | 140      | 12  | 0.008 | - | 738.1 |
| HDPy-clay [14]                                    | 150      | 1   | 0.1 | 25 | 145.5 |
| HDTMA-clay [14]                                   | 150      | 1   | 0.1 | 25 | 147.99|

* $C_{in}$ – initial concentration of sorbate in solution, mg L$^{-1}$; $t$ – adsorption time, h; $m$ – adsorbent weight, g; $T$ – the solution temperature, °C; $Q_e$ – adsorbate concentration in the adsorbent at equilibrium, mg g$^{-1}$.
** MWCNTs – multi-walled carbon nanotubes; SWNTs – single-walled carbon nanotubes; AC – activated carbon; GO – graphene oxide.
As can be seen, only a few materials showed the high adsorption capacity the organics being considered. In this regard, there is a need for developing new adsorbents that could efficiently purify wastewater from such pollutants.

Considering the aforementioned, in the present study, a novel material, polyhydroquinone/graphene (PHQ/G) nanocomposite, was used for the removal of MB, ARS and MG. Besides, the kinetics of the dye adsorption processes was studied. The studies were carried out using the original dynamic setup based on the spectrophotometric method for determining concentrations in solution. Adsorption studies were carried out for a number of organic dyes (methylene blue, alizarin red, malachite green) of various chemical nature and, accordingly, the nature of the adsorption interaction with the studied adsorbent.

![Figure 1. SEM images of the surface structure of the PHQ/G nanocomposite. Magnification:100.00 KX (a) and 30.00 KX (b).](image)

The morphology of the developed PHQ/G nanocomposite is shown in figure 1. At various image magnifications (100.00 and 30.00 KX), one can observe a graphene-like structure of the material in the form of flakes of carbon layers.

2. Experimental part

2.1. Material and reagents

The PHQ/G nanocomposite, herein employed as adsorbent, represents an organic ally modified graphene oxide. Its production technology is described in [22]. The material was developed at the Research Department “Technology and Methods of Nanoproducts Manufacturing” (Tambov State Technical University, Tambov, Russia). Solutions of MB, ARS and MG all acquired from Laverna Lab Ltd., Moscow, Russia, were used as adsorbates.

2.2. Kinetic study

Experiments, the scheme of which is presented in figure 2, were performed in a dynamic mode, i.e. aqueous solutions of the organic dyes continuously passed through an adsorption cell (figure 2). In real conditions, the adsorption proceeds dynamically, since this is more acceptable for automation of the production process and its continuity.

100 mL of 1500-mgL⁻¹ initial solutions of the MB, ARS and MG were separately fed from a container R to an adsorption cell (filled with 0.03 g of the adsorbent) along a loop 1.1 using a peristaltic pump, and then returned to the container R along a feedback loop 1.2.
Figure 2. A scheme of experiments on studying the dye adsorption in a dynamic mode (R-container with the initial solution, 1- adsorption cell, 2 - spectrophotometer, and 3 - peristaltic pump).

The parallel loop 2 was intended for feeding the solutions to a cuvette located in a spectrophotometer 2 (PE 5400V instrument, Ekros, St. Petersburg, Russia). The optical density of the solutions was recorded every 180 s at the wavelengths of 570, 660 and 710 nm (for the MB, ARS and MG, respectively).

3. Results and discussion

The integral kinetic curves obtained for the adsorption of the MB, ARS and MG on the PHQ/G nanocomposite are presented in figure 3. It can be seen that the adsorbent material is characterized by a high adsorption rate during the initial period (up to 25 min). With a further increase in the contact between the adsorbent and the solutions, the removal rate monotonously decreases. The adsorption equilibrium of the systems is achieved within 40 (MB), 120 (ARS) and 57 (MG) min. The maximum adsorption capacities ($Q_{eq}$) were found to be as follows: 2.610 mg g$^{-1}$ (MB), 2.923 mg g$^{-1}$ (ARS), and 688.1 mg g$^{-1}$ (MG). Comparing these values with those ones reported for the materials used as adsorbents by the other researchers ($Q_{eq}$, table 1), it can be observed that in the case of the MB and ARS, the adsorption capacity of the PHQ/G nanocomposite is the highest, whereas in the case of the MG, the capacity is lower than that of the other graphene-based materials and mesoporous carbon.
Figure 3. Integral kinetic curves obtained for the dye adsorption on the PHQ/G adsorbent.

The experimental data obtained were adjusted to equations of the known kinetic and diffusion models (pseudo-first and pseudo-second order, Elovich, and intraparticle diffusion) (table 2). The results are presented in figure 4 and tables 3 and 4.

Table 2. Kinetic model equations implemented [23].

| Model                | Equation*                                      |
|----------------------|------------------------------------------------|
| Pseudo-first-order   | \( \lg(Q_e - Q_t) = \lg(Q_e) - \frac{k_1 t}{2.303} \) |
| Pseudo-second-order  | \( t = \frac{1}{k_2 \cdot Q_e^2} + \frac{1}{Q_e} \cdot t \) |
| Elovich              | \( Q_t = \frac{1}{\beta} \ln(a \beta) + \frac{1}{\beta} \ln(t) \) |
| Intraparticle diffusion | \( Q_t = k_{id} \cdot t^{0.5} + c \) |

* t - adsorption time, min; \( Q_e \) - adsorption capacity at equilibrium, mg g\(^{-1}\); \( Q_t \) - adsorption capacity 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\(^{-1}\); \( k_{id} \) - intraparticle diffusion coefficient, mg g\(^{-1}\) min\(^{-0.5}\); \( c \) - boundary layer thickness constant, mg g\(^{-1}\); \( a \) - initial flow rate, min\(^{-1}\)mg g\(^{-1}\); \( \beta \) - desorption constant (degree of surface coverage and activation energy of chemisorption), g mg\(^{-1}\).
Figure 4. Kinetic and diffusion models fitted to the experimental data obtained for the dye adsorption on the PHQ/G nanocomposite: pseudo-first-order (a), pseudo-second-order (b), Elovich model (c), and intraparticle diffusion (d).

Table 3. Parameters of the kinetic models fitted to the data on the dye adsorption on the PHQ/G nanocomposite.

| Dye  | $Q_e^{exp}$, mg g$^{-1}$ | $Q_e$, mg g$^{-1}$ | $k_1$, min$^{-1}$ | $R^2$ | $Q_e$, mg g$^{-1}$ | $k_2$, min$^{-1}$ | $R^2$ | $\alpha$, min$^{-1}$, mg g$^{-1}$ | $\beta$, g mg$^{-1}$ | $R^2$ |
|------|-----------------|-----------------|-----------------|------|-----------------|-----------------|------|-------------------------------|---------------|------|
| MB   | 2.610           | 1.558           | 0.0012          | 0.921| 3.333           | 9 $\cdot$ 10$^{-7}$ | 0.9985| 35.71                         | 0.0020        | 0.8663|
| MG   | 688.1           | 948.7           | 0.0016          | 0.944| 840.3           | 1.78 $\cdot$ 10$^{-6}$ | 0.9970| 2.63                          | 0.0054        | 0.9803|
| ARS  | 2.923           | 2.826           | 0.0626          | 0.996| 3.333           | 2.25 $\cdot$ 10$^{-5}$ | 0.9899| 516.9                         | 0.0013        | 0.9713|
Table 4. Parameters of the intraparticle diffusion model fitted to the data on the dye adsorption on the PHQ/G nanocomposite.

| Dye | Intraparticle diffusion | | | |
|---|---|---|---|---|
| | Section 1 | Section 2 | | |
| | $k_{id} \cdot 10^{-0.5}$ | $c_i$ | $R^2$ | $k_{id} \cdot 10^{-0.5}$ | $c_i$ | $R^2$ |
| MB | 86.25 | 304.4 | 0.9674 | 7.74 | 1.91 | 0.7864 |
| MG | 14.55 | 15.50 | 0.9774 | 3.43 | 491.3 | 0.9441 |
| ARS | 75.37 | 476.08 | 0.9825 | 15.32 | 1.917 | 0.9462 |

It can be seen (judging by the highest determination coefficients $R^2$) that, in general all the models adequately describe the dye adsorption kinetics, but the best correlation to the experimental data is provided by the pseudo-second-order model (figure 4b, table 3): $R^2=0.9985$ (MB), 0.9899 (ARS) and 0.9973 (MG).

Based on the pseudo-first- and pseudo-second-order models (figures 4a and 4b), it can be assumed that chemical interactions occur between the adsorbent functional groups and the dye molecules. Theoretically, these interactions are stoichiometric, i.e. a single molecule occupies a single position on the adsorbent surface.

The Elovich model (figure 4c) implies heterogeneity of adsorption sites available on the material surface, meaning that these sites possess different binding energies and chemical affinities for the adsorbates.

The dependence describing the intraparticle diffusion (figure 4d) represents a multilinear curve consisting of two linear sections. Since the approximating lines do not pass through the origin, the effect of the boundary diffusion layer takes place; the diffusion is not a limiting stage, and the superficial adsorption stage is superimposed on the diffusion process.

4. Conclusion

As a result of the kinetic studies conducted in the dynamic mode, a comparative analysis was made for the adsorption capacity of the PHQ/G nanocomposite material regarding the removal of the dye organic molecules – MB, ARS, and MG. The following adsorption capacity values were found: 2.923, 2.610 and 688.1 mg g$^{-1}$ for the ARS, MB and MG, respectively. In the case of the ARS and MB adsorption, the novel material demonstrated the highest adsorption capacity among the adsorbents presented in table 1.

Besides, it was established that the adsorption equilibrium is achieved within 40, 120 and 57 min for the MB, ARS and MG, respectively. Moreover, the kinetic and diffusion models implemented to fit the experimental data adequately describe the dye adsorption processes. Based on those models, it was elucidated that in the course of the adsorption, chemical interactions take place between the dye molecules and the active sites of the material surface, and the diffusion through the film on the adsorbent surface also occur.

Thus, the PHQ/G nanocomposite proposed herein can be efficiently used in purifying wastewater from some dyes. However, further studies are required to investigate the dye adsorption based on adsorption isotherm construction.

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