

Liquid-Phase Adsorption of an Organic Dye on Non-Modified and Nanomodified Activated Carbons: Equilibrium and Kinetic Analysis

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Abstract

The present paper reports on a study of kinetic parameters of the adsorption of the Methyl Orange organic dye from aqueous solutions on nanomodified and non-modified carbon materials under static conditions. Commercially available NWC coconut shell-based activated carbon was used as a pristine adsorbent. It was modified with multi-walled carbon nanotubes to obtain a nanomodified material. These carbon nanotubes were synthesized via chemical vapor deposition over a metal-oxide catalyst prepared by a citrate sol-gel method. A spectrophotometric method was used to determine Methyl Orange concentrations (at wavelength of 400 nm). For each type of adsorbents (nanomodified and non-modified activated carbon), chemical interactions between its surface functional groups and the dye were observed. The adsorption kinetics for both types of activated carbons were analyzed by pseudofirst and pseudosecond-order models, which were well-described by the pseudosecond-order model with a correlation coefficient of about 0.99. Besides, adsorption rate constants were calculated using kinetic models. It was found that equilibrium of the Methyl Orange adsorption on the nanomodified carbon is achieved 1.5 times faster than that of the Methyl Orange adsorption on the pristine carbon, and the adsorption capacity of the former is 2.1 times higher than that of the latter one. These findings suggested that the activated carbons could be regarded as a promising adsorbent for the removal of the organic dye – Methyl Orange – from wastewaters.

Keywords

Liquid-phase adsorption; activated carbon; organic pollutants; carbon nanotubes; kinetics; adsorption rate constants.

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1. Introduction

Adsorption processes taking place on carbon surfaces play a key role in the production of synthetic graphite, carbon-carbon composites, heterogeneous catalysts, etc. when removing contaminants from gaseous and liquid media after burning solid carbonaceous fuels. The nature and profundity of these processes are determined by the size, chemical composition and structural features of the carbon surface.

Among other physical and chemical processes, adsorption is probably the most promising method to be potentially applied for treating drinking water and industrial wastewater. Complex organic compounds such as organochlorine pesticides and dioxins appear to be some of the most dangerous and persistent substances in aqueous solutions [1–3].

There is a variety of adsorbents for removing organic pollutants [4–11]. It should be noted that activated carbons have been widely used in this field, since their surface has a high binding affinity for organic matter due to the presence of surface functional groups.

In many cases, to qualitatively and quantitatively assess the adsorption and better understand the kinetic mechanism of removing organic compounds (external diffusion, internal diffusion or chemical interaction) from aqueous media, the limiting stage of this process must be identified. Besides, based on kinetic data obtained, it is possible to determine the time required to reach adsorption equilibrium in the adsorbent-adsorbate system.

Dyes and heavy metals are two types of contaminants commonly found in the wastewater of several industries [12–14].

Specifically, heavy metals are discharged by industries such as agrochemical, petrochemical and fertilizers, whereas dyes are found principally in effluents of dye manufacturing industries, electroplating factories, distilleries and food companies [15, 16]. It was further reported that an anionic dye favored the electrostatic interactions with heavy metals or might create new specific sites for the adsorption process [17].

Adsorption can be employed efficiently for removal of organics at trace level with low cost. It is a mass transfer process that involves contact of a solid (adsorbent) with a fluid containing the target solute (adsorbate) [18–21]. The surface area of the adsorbent generally governs adsorption efficiency and selectivity as a result of accumulation of the adsorbate on the surface of the adsorbent. Among the potential adsorbent materials are carbon-based compounds which are hydrophobic and non-polar, including materials such as carbon nanotubes (CNTs) and activated carbons (ACs). Carbonaceous materials such as CNTs and ACs are characterized by their extraordinary large specific surface area, well-developed porosity and tunable surface-containing functional groups. As a result, these materials are widely used as adsorbents for the removal of solutes/pollutants from water and wastewater [22–24]. Activated carbon in particular is extensively used for the removal of both organic and inorganic compounds from aqueous solutions. CNTs, on the other hand, have recently been utilized for the removal of heavy metals from solution. However, little information is available in literature regarding its capacity to remove organics from liquid medium.

Considering the aforementioned, the kinetic parameters (contact time, adsorption rate constants) and the capacity of Methyl Orange (MO) adsorption on pristine and nanomodified activated carbons were estimated herein.

2. Materials and Methods

2.1. Materials

In the present research, the synthetic dye – MO (chemical formula: $C_{14}H_{14}N_3O_3SNa$) – was used as organic adsorbate, whereas the commercially available NWC coconut shell-based activated carbon was employed as pristine (original) adsorbent. The latter was modified with multi-walled carbon nanotubes (MWCNTs) to get a nanomodified material.

The MWCNTs were synthesized via chemical vapor deposition (CVD) over a metal-oxide catalyst prepared by a citrate sol-gel method, as described in [25]. The structure of the nanomodified NWC activated carbon is presented in Fig. 1.

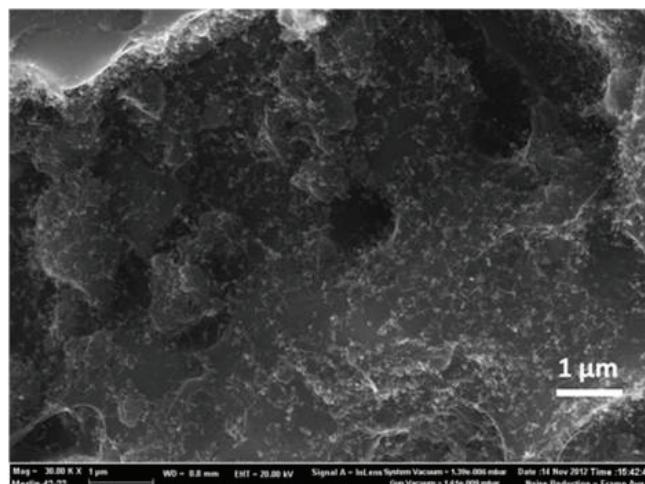


Fig. 1. The structure of the nanomodified (NWC-N) activated carbon; CNTs obtained over a (Ni,Co)/MgO catalyst by pyrolysis of a propane-butane mixture

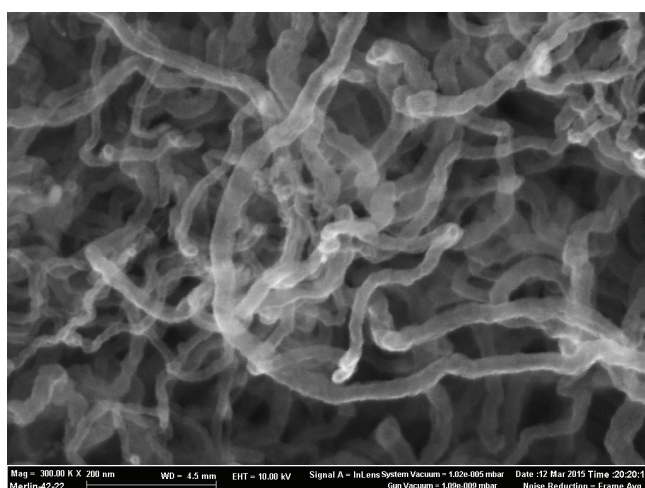


Fig. 2. The multi-walled CNTs synthesized on the activated carbon surface

The SEM-images of the CNTs structure can be seen in Fig. 2. The average diameter of the nanotubes is 25–40 nm, and the diameter of catalyst particles is 50 nm.

2.2. Kinetic Study

To study the kinetics of the MO adsorption on two adsorbent materials, samples (0.1 g each) of the pristine (NWC) or the modified (NWC-N) activated carbon were treated in a drying oven at 100–120 °C for 1 h. After that, they were equilibrated by end-over-end shaking at 100 rpm and room temperature for 1 h in a Multi Bio RS-24 programmable rotator (Biosan, Riga, Latvia). The suspensions were then centrifuged at 10,000 rpm for 10 min using a 5810 R device (Eppendorf, Hamburg, Germany). The adsorption capacity of the materials was determined every 15 min.

2.3. Adsorption Study

Adsorption experiments were conducted with 0.1 g of the adsorbent and 25 mL of MO solutions at fixed temperature (21 °C). The initial concentrations of the solutions ranged from 50 to 1500 mg·L⁻¹. The systems were equilibrated by end-over-end shaking at 100 rpm and room temperature for 45 min (in the case of NWC-N) or 120 min (in the case of NWC) in a Multi Bio RS-24 rotator. After that, the suspensions were centrifuged at 10,000 rpm for 10 min using a 5810 R centrifuge. MO concentrations were measured on a PE-5400VI spectrophotometer (Ecokhim, Saint Petersburg, Russia) at 400 nm.

3. Results and Discussion

TG and DSC plots of NWC and NWC-N can be seen in Fig. 3 *a, b*.

Activated carbons NWC started to burn at 350 °C (Fig. 3 *a*). The 50 % of NWC burned at 750 °C. Nanomodified NWC-N started to burn at 300 °C and the 50 % of NWC-N burned at 700 °C (Fig. 3 *b*).

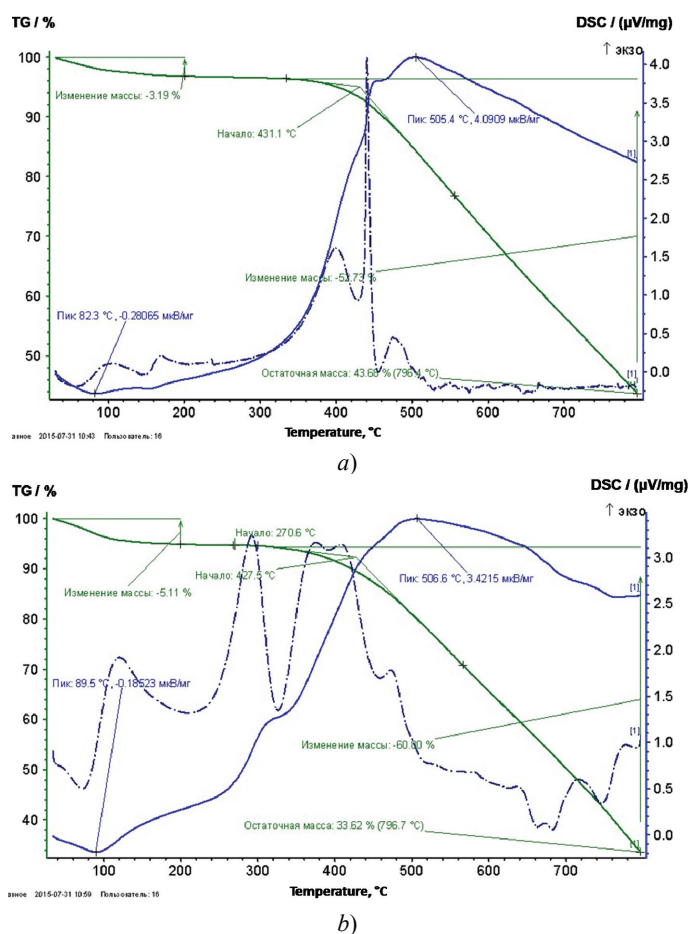


Fig. 3. TG and DSC plots of NWC (*a*) and NWC-N (*b*)

Raman spectroscopy has been a major experimental technique to obtain data about the microstructure of various carbon materials.

Highly ordered graphite shows only one band in the region of 1100 and 1700 cm⁻¹ and shows second order features between 2400 and 3300 cm⁻¹. The Raman spectra change significantly for disordered carbons and show *D* band at around 1350 cm⁻¹.

Therefore the characteristic Raman spectra for synthetic graphite show peaks at around 1350 cm⁻¹ for disordered carbon (*D* band) and 1580 cm⁻¹ for graphitized carbon (*G* band). The degree of graphitization may be estimated by examining the Raman spectra for a specimen.

Relative intensity between *G* band and *D* band could be changed by heat treatment, crystallite size of the disordered carbon, and crystallinity [26].

In all the cases (Fig. 4) the spectra exhibited the same appearance, that is, two well-resolved bands, namely *D* (~1330 cm⁻¹) and *G* (~1580 cm⁻¹) band.

The ratio of *G* and *D* bands allows to estimate the quantity of various defects. For good samples *D* band is several orders of magnitude smaller than *G*. The samples have quite a large number of defects if the intensity of these bands is proportionate.

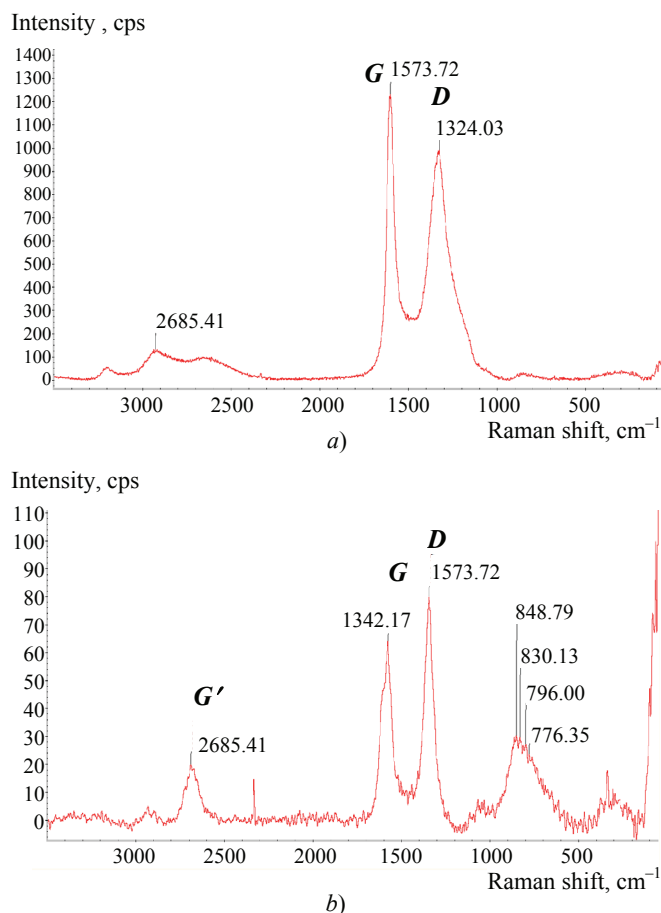


Fig. 4. Raman spectrum of the original (*a*) and nanomodified activated carbons (*b*)

The nanomodification process affects the position and intensity of the Raman bands. There were no significant differences between the positions of *D* bands. However *G* band positions were slightly changed. For the nanomodified materials (Fig. 4 *b*) the intensity of *D* band is higher than for the standard activated carbon (Fig. 4 *a*). This can be possible due to the poor organization of carbon materials (i.e., more disorder) [27, 28].

Based on the experimental data obtained, the kinetic curves were constructed for both materials (Fig. 5).

It can be seen that although the adsorption on NWC and NWC-N is initially fast, the adsorption rate becomes slower over time, and equilibrium is reached after 75 min and 120 min for NWC-N and NWC, respectively. The initial adsorption may be due to the availability of unsaturated surface sites, since the adsorption kinetics depends on the surface area of the adsorbent.

In the past decades, several mathematical models have been proposed to describe adsorption data, which can generally be classified as adsorption reaction models and adsorption diffusion models. Both models are applied to describe the kinetic process of adsorption; however, they are quite different in nature [29].

Adsorption diffusion models are always constructed on the basis of three consecutive steps [30]: (1) diffusion across the liquid film surrounding the adsorbent particles, i.e., external diffusion or film diffusion; (2) diffusion in the liquid contained in the pores and/or along the pore walls, which is so-called internal diffusion or intra-particle diffusion; and (3) adsorption and desorption between the adsorbate and active sites, i.e., mass action.

However, adsorption reaction models originating from chemical reaction kinetics are based on the whole process of adsorption without considering these steps mentioned above.

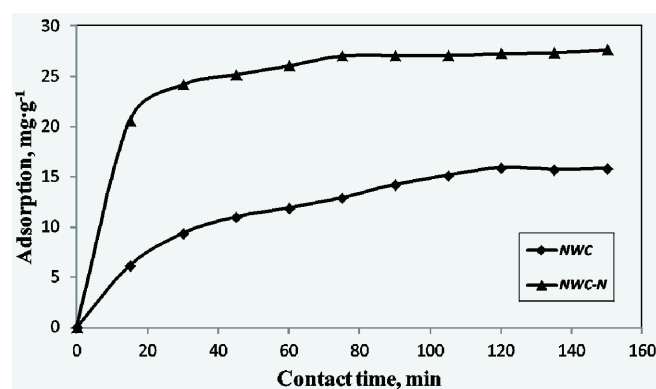


Fig. 5. The contact time effect on the MO adsorption on the non-modified (NWC) and nanomodified (NWC-N) carbon adsorbents; initial concentration: 150 mg·g⁻¹

To elucidate the mechanism of the MO adsorption process, the following kinetic models were employed herein: external diffusion, pseudo-first-order (Lagergren), and pseudo-second-order.

The external (film) diffusion model suggests that the diffusion of the adsorbate from the liquid phase to the solid phase is the rate-determining step [31, 29]. It can be expressed by the following equation:

$$F = q_t / q_e, \quad (1)$$

where q_t and q_e are the MO adsorption capacity at time t and at equilibrium, respectively (mg·g⁻¹), and F is the fraction attainment at equilibrium.

Fig. 6 demonstrates the linear plots of $-\lg(1 - F)$ versus t (in the case of NWC-N, more linearity is achieved compared with NWC). Based on this figure, it can be assumed that the kinetics of the MO adsorption on the activated carbons is controlled by diffusion of the liquid film surrounding each adsorbent over a particular (often initial) time interval.

The pseudo-first-order (Lagergren) model assumes first-order kinetics for the MO adsorption [31] and can be expressed according to the following equation:

$$\lg(q_e - q_t) = \lg(q_e) - k_1 t / 2.303, \quad (2)$$

where k_1 is the rate constant of pseudo-first-order adsorption (min⁻¹).

Fig. 7 presents the graphical interpretation of this model. It can be seen that the plots of $\lg(q_e - q_t)$ versus t are almost linear, especially in the case of NWC-N, thereby confirming the suitability of this model for describing the MO adsorption on the carbon materials.

The pseudo-second model assumes that the surface adsorption involving physicochemical interactions (i.e., chemisorption) is the rate-limiting step [29]. It is usually presented as:

$$t / q_t = 1 / k_2 q_e^2 + t / q_e, \quad (3)$$

where k_2 is the rate constant of pseudo-second-order adsorption, g·mg⁻¹·min⁻¹.

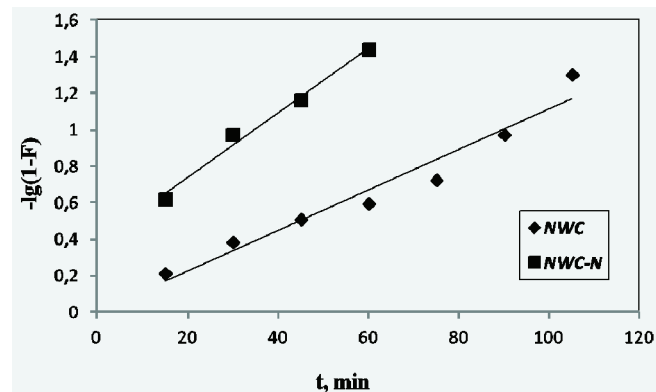


Fig. 6. Linear plots of $-\lg(1 - F)$ versus contact time t obtained for the MO adsorption on the non-modified (NWC) and nanomodified (NWC-N) carbon adsorbents

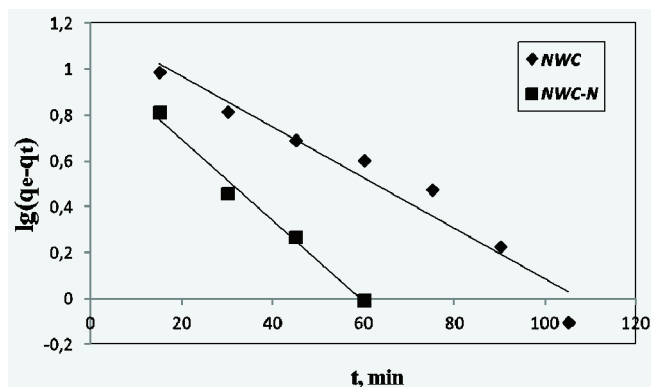


Fig. 7. Linear plots of $\lg(q_e - q_t)$ versus contact time t obtained for the MO adsorption on the non-modified (NWC) and nanommodified (NWC-N) carbon adsorbents

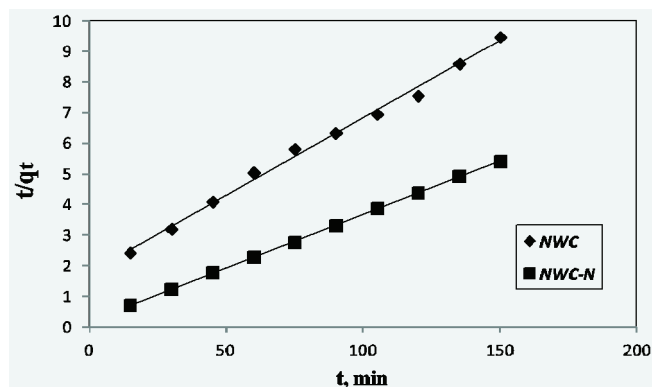


Fig. 8. Linear plots of $\lg(q_e - q_t)$ versus contact time t obtained for the MO adsorption on the non-modified (NWC) and nanommodified (NWC-N) carbon adsorbents

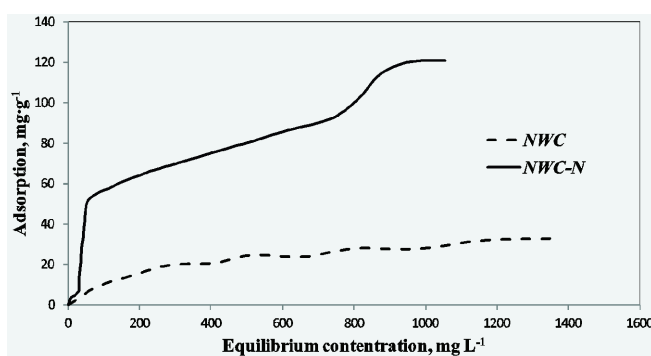


Fig. 9. The isotherms of the MO adsorption on NWC and NWC-N; $T = 21^\circ \text{C}$

The graphical interpretation of this model is given in Fig. 8. Since the plots are linear for both adsorbents, the model can adequately describe the MO adsorption.

The adsorption characteristics obtained experimentally and the parameters calculated for the pseudo-first- and pseudo-second-order equations are presented in Table 1. It can be seen that both models provide a good fit to all the experimental data, according to the correlation coefficient R^2 values, but the pseudo-second-order model presents higher values, thereby confirming the chemical nature of the MO adsorption.

These suggest that the adsorption data are well represented by pseudo-second-order kinetics and supports the assumption that the rate-limiting step of cadmium adsorption on rice husk may be chemical

sorption. In chemisorption, the metal ions stick to the adsorbent surface by forming a chemical (usually covalent) bond and tend to find sites that maximize their coordination number with the surface [32].

The pseudo-second-order kinetic analysis reveals that the values of the initial adsorption rates increase with an increase in the initial MO concentration. At higher concentrations, the competition for the surface active sites is high and, consequently, lower sorption rates are obtained [33]. The equilibrium adsorption capacity, however, increased with an increase in initial cadmium concentration because a large number of MO molecules are adsorbed at the available adsorption sites.

Among the adsorbents studied, a better fit is achieved for the nanommodified activated carbon. Furthermore, comparing the equilibrium time and adsorption capacity (q_e) values for NWC and NWC-N (Table 1), it was found that the MO adsorption on the nanommodified adsorbent is 1.5 times faster compared to the pristine material, and the adsorption capacity of the former is 2.1 times higher than that of the latter one. These phenomena can also be confirmed by the adsorption isotherms shown in Fig. 9.

The adsorption capacity for MO treated by nanommodified activated carbons increased by 3.5 times from the initial concentration of $200 \text{ mg} \cdot \text{L}^{-1}$ in comparison with standard materials and by 6 times from the initial concentration of $3000 \text{ mg} \cdot \text{L}^{-1}$.

Table 1

Adsorption characteristics and kinetic model parameters obtained for the MO adsorption on the activated carbons (non-modified – NWC and nanommodified – NWC-N); initial concentration – $150 \text{ mg} \cdot \text{g}^{-1}$; R^2 – correlation coefficients

Adsorbent	Experimental $q_e, \text{mg} \cdot \text{g}^{-1}$	Equilibrium time, min	R^2		k_1, min^{-1}	$k_2, \text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$
			Lagergren first-order	Pseudo-second order	Lagergren first order	Pseudo-second order
NWC	12.9	120	0.9504	0.9946	0.0256	0.0033
NWC-N	27.1	75	0.9875	0.9998	0.0407	0.0069

Thus, nanomodified activated carbons using carbon nanotubes have good adsorption properties and high capacity for organic dye MO and can be applied for the purification of this element in aqueous solutions.

4. Conclusion

1. In the present research, a novel material representing MWCNTs-modified activated carbon was studied as adsorbent for removing organic pollutants (i.e, Methyl Orange dye) from aqueous solutions.

2. Kinetic and adsorption characteristics of the nanomodified and pristine activated carbons were obtained.

3. The experimental data were analyzed by implementing three kinetic models – external diffusion, pseudo-first-order (Lagergren), and pseudo-second-order. These models adequately describe the MO adsorption process, but a better fit is provided by the pseudo-second-order equation, thereby confirming that the chemisorption is the rate-limiting stage.

4. Based on the external diffusion model (i.e, the linearity of its plots), it is assumed that kinetics of the MO adsorption on both materials is controlled by diffusion of the liquid film surrounding each adsorbent.

5. Among the adsorbents used, better characteristics were obtained for the nanomodified activated carbon: equilibrium of the Methyl Orange adsorption on the nanomodified carbon can be achieved 1.5 times faster than that of the Methyl Orange adsorption on the pristine carbon, and the adsorption capacity of the former is 2.1 times higher than that of the latter one.

6. The results obtained demonstrated a great potential of the nanomodified activated carbon for removing organic pollutants from water.

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