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Kinetics of the Cu(II) sorption from aqueous solutions by carbon nanomaterials

A. V. Babkin, I. V. Burakova, A. E. Burakov, E. A. Neskoromnaya,
A. E. Kucherova, D. A. Kurnosov

Tambov State Technical University, Tambov, Russia

flex_trol@mail.ru, iris_tamb68@mail.ru, m-alex1983@yandex.ru, lenok.n1992@mail.ru,
anastasia.90k@mail.ru, ozikimoziki@mail.ru

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The present paper contains comprehensive studies on the adsorption properties of graphene oxide (GO), coconut activated carbon (AC) and "Taunit-M" carbon nanotubes (CNTs). Cu(II) ions served as extracted component. Measurements of the Cu(II) content in water were performed using electrothermal atomization atomic absorption spectroscopy. The obtained experimental data indicate high adsorption capacity of the GO along with CNTs and AC. Kinetic parameters of the adsorption process on the graphene oxide were calculated using standard models (pseudo-first- and pseudo-second-order, external and intraparticle diffusion, and Elovich models). The presented results demonstrate the prospects of using the GO in selective extraction of heavy and rare-earth metal ions from aqueous media.

Keywords: sorption, graphene oxide, kinetic study, copper.

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1. Introduction

Along with carbon nanotubes (CNTs) and materials on a similar basis, graphene oxide and its modifications have become widespread. Like any carbon nanomaterial, graphene possesses a number of unique physical and chemical properties, to which its two-dimensional structure and the corresponding thermal, electroconductivity (zero width of the forbidden band) and optical characteristics, as well as high specific surface, can be related. The latter opens great prospects for using graphene oxide (GO) in selective extraction of harmful impurities of different chemical nature from gaseous and aquatic media. CNTs and GO are currently one of the promising materials in the field of extraction of heavy metal ions from aqueous solutions [1].

In the present work, the adsorption of Cu(II) ions from aquatic media using carbon nanostructures such as CNTs and GO, along with conventional materials such coconut activated carbon (AC) was studied.

Table 1 gives comparative results reported elsewhere for the Cu(II) adsorption on both the nanostructured and commercially available adsorbents. From this table, it can be seen that the CNTs exhibit the adsorption characteristics similar to those of the commercial materials, but the adsorption time in their case is reduced by 2- to 3-fold.

TABLE 1. The Cu(II) adsorption on different materials

Adsorbent	Adsorption capacity (mg/g)	$C_{init.}$ (mg/L)	Adsorption time (min)
Activated carbon (chemical activation) [2]	7	40	210
Activated carbon [2]	11.5	40	200
Activated carbon from hazelnut husks [3]	6.65	200	60
CNT sheets [4]	6	100	70
CNT sheets (oxidized) [4]	14	100	70
As-produced CNTs [5]	8.92	50	1440

2. Materials

Nanocarbon materials – "Taunit-M" CNTs and GO as nanoplatelet aggregates obtained via thermal oxidation of pyrolytic graphite (both – NanoTechCenter Ltd., Tambov, Russia) – were used as adsorbent samples for testing. The diameter of the CNTs is 15–20 nm, the orientation of graphene layers is cylindrical. The main characteristics of AC (AQUACARB 207C, Chemviron Carbon, UK) used as reference materials are as follows: surface area 1150–1350 m^2/g, adsorption capacity regarding methylene blue 230–270 mg/g, and bulk density 0.47–0.51 g/cm^3.

3. Research methods

To determine the adsorption kinetic parameters, experiments were carried out with 0.02 g of the CNTs, 0.1 g of the GO, and 1.0 g of the AC. The volume of aqueous solutions was 30 mL at the initial concentration of $Cu(NO_3)_2 \cdot 3H_2O$ (Laverna Ltd., Moscow, Russia) equal to 100 mg/L. Each solution and each adsorbent were equilibrated by agitating on an end-over-end rotator (Multi Bio RS-24, Biosan, Riga, Latvia) at 120 rpm for 1 h, and then centrifuged on a centrifuge (5810 R, Eppendorf, Hamburg, Germany). The Cu(II) equilibrium concentration was determined by electrothermal atomization atomic absorption spectrometry on an MGA-915MD instrument (Atompribor Ltd., Saint Petersburg, Russia).

4. Result and discussion

To identify characteristic features of the Cu(II) adsorption process, kinetic studies aimed at determining the time required to achieve equilibrium in the systems under study were performed.

As seen in Fig. 1, for the GO, at the initial stage, the adsorption rate is sufficiently high, and about 90 % of the adsorbate is extracted during the first 5–10 min. It can be clearly observed that the Cu(II) maximum adsorption capacity of the GO is superior to that of the other materials studied. To describe kinetic mechanisms of the adsorption, the well-known mathematical models (pseudo-first- and pseudo-second-order, external and intraparticle diffusion, and Elovich models) – were implemented herein (Figs. 2, 3).

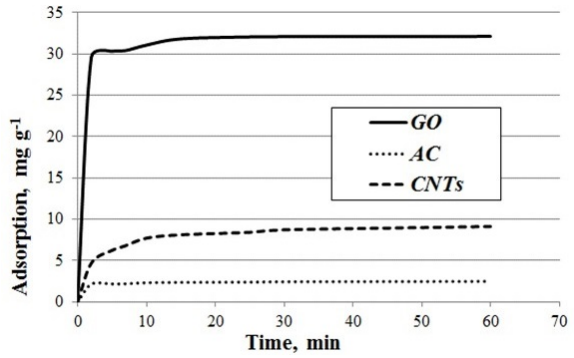

FIG. 1. Kinetic curves constructed for the Cu(II) adsorption on the GO

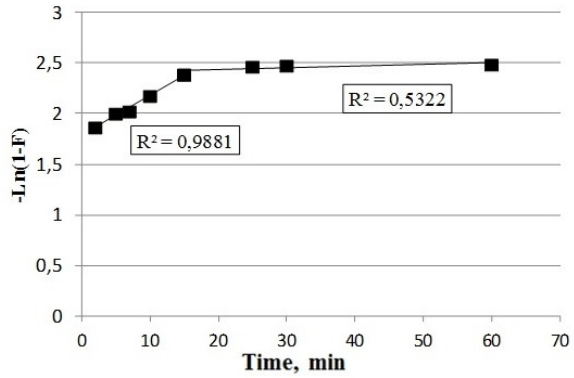

FIG. 2. External diffusion curve constructed for the Cu(II) adsorption on the GO

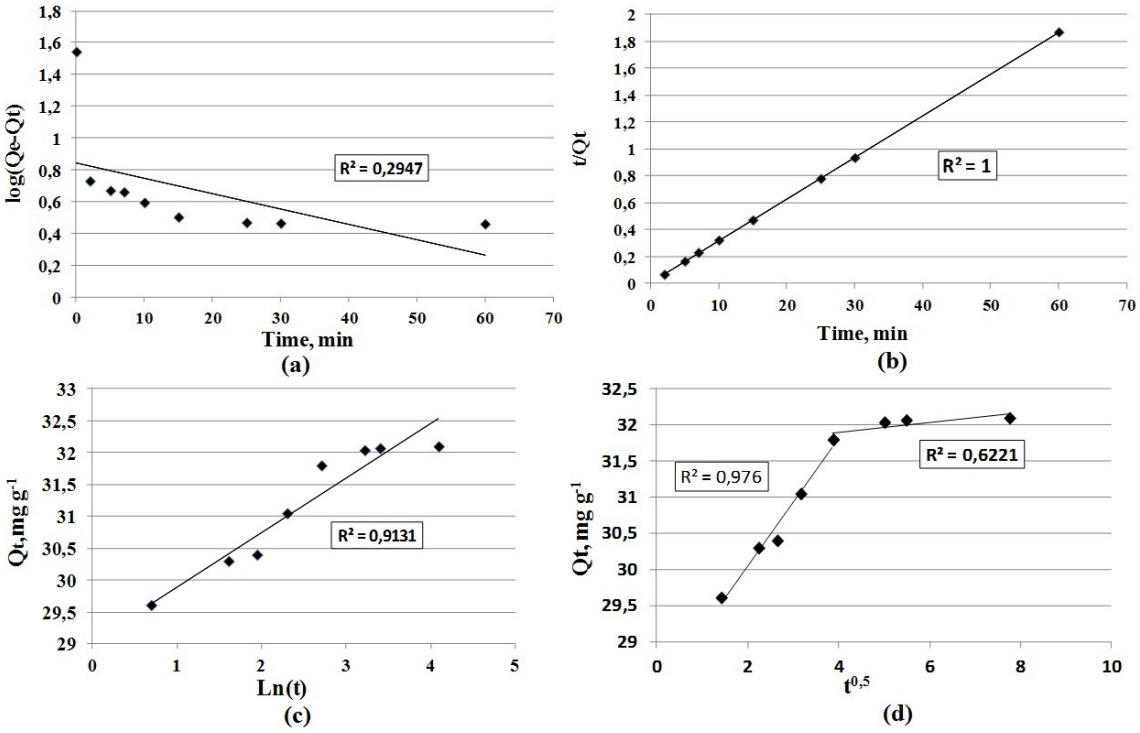

FIG. 3. Kinetic models of the Cu(II) adsorption on the GO – a) pseudo-first order; b) pseudo-second order; c) Elovich model; d) intraparticle diffusion

Figure 2 demonstrate chemical interactions during the adsorption process (F is the fraction attainment at equilibrium, $F = \dfrac{Q_t}{Q_e}$; Q_e – Cu(II) amount adsorbed onto the adsorbent surface at equilibrium; Q_t – Cu(II) amount adsorbed onto the adsorbent surface at time t) (Fig. 3b). It can be seen that the results of the experimental data are mostly fitted to the pseudo-second-order model, thereby indicating that the rate of chemical bond formation is limited by the interaction of the adsorbate ions with each other. The adsorption process is of the complex nature, and it is affected by both the structure of the adsorption material and the features of its chemical interaction with the extracted component.

5. Conclusion

Within the framework of the present paper, the kinetic mechanisms of Cu(II) adsorption from aqueous solutions using the nanostructured and conventional materials were studied. The results of the comparative kinetic tests demonstrate a 10-fold superiority of the GO over the commercially available coconut AC regarding the maximum Cu(II) adsorption capacity.

Acknowledgements

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