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SOME DEFINITIONS ABOUT THE MECHANISM OF PUBLIC-PRIVATE PARTNERSHIP AND ITS ROLE IN STRENGTHENING THE ACTIVITIES OF BUSINESS ENTITIES AND SMALL BUSINESSES

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Abstract: This paper examines the kinetic parameters of the adsorption of methylene blue and Congo red on various modified carbon adsorbents (RU, BSH, and UO). An analysis was conducted on the effectiveness of different kinetic models (pseudo-first and pseudo-second order) to describe the adsorption process. The results indicated that the pseudo-second order model most accurately reflects the adsorption kinetics, as evidenced by high correlation coefficients ($R^2 > 97\%$) and positive values of adsorption capacity (As) for all investigated systems. This suggests that the adsorption process is governed by chemical sorption (chemisorption), resulting in strong bonds between the adsorbate and active sites on the carbon surface. RU carbon exhibited the highest adsorption activity compared to BSSH and OXC, which can be attributed to its developed porous structure and a greater number of available active sites. The obtained data can be utilized to optimize adsorption process conditions and select the most effective adsorbents for the removal of organic dyes from wastewater.

Keywords: adsorption, methylene blue, Congo red, carbon adsorbents, kinetic model, pseudo-second order, chemisorption, wastewater treatment.

Introduction. Research on the adsorption of dyes on carbon sorbents is becoming increasingly relevant in the context of environmental protection and ensuring water quality. Synthetic dyes, widely used in industries such as textiles, leather, food, and pharmaceuticals, eventually enter wastewater streams. These organic dyes, such as

methylene blue (MB) and congo red (CR), are highly resistant to biodegradation and can have toxic effects on aquatic ecosystems and human health. Therefore, their effective removal from wastewater has become a priority in the field of water treatment [1-4].

Among the various methods for removing dyes from wastewater, adsorption on carbons—activated and modified—has proven to be one of the most effective and economically feasible approaches. Carbon sorbents possess high adsorption capacity, large specific surface area, and porous structure, making them ideal candidates for removing organic pollutants. However, despite these known advantages, the successful implementation of adsorption on an industrial scale requires a deep understanding of adsorption kinetics and the mechanisms of interaction between dyes and carbon sorbents [5-8].

The study of adsorption kinetics plays a crucial role in optimizing wastewater treatment processes. Kinetic analysis allows for the assessment of the rate and mechanism of adsorption, which is essential for selecting the most suitable carbon sorbent and its application conditions. In particular, pseudo-first-order and pseudo-second-order kinetic models are commonly used to describe adsorption processes. These models help to understand how adsorption depends on dye concentration, contact time, temperature, pH, and other parameters. Choosing the correct kinetic model helps predict the behavior of the system and develop efficient and cost-effective water treatment technologies [9-13].

Thus, the relevance of research in the field of dye adsorption on carbons is associated with the need to develop sustainable and highly efficient methods for removing organic pollutants from wastewater. Studying kinetic parameters and their modeling allows for optimizing adsorption conditions, improving efficiency, and reducing the costs of water purification [14-16].

The primary aim of this research is to study the kinetic parameters and select an appropriate adsorption model, such as pseudo-first or pseudo-second order, which is crucial for developing effective and sustainable water treatment technologies. Special attention is given to the adsorption of MB and CR on various carbon adsorbents, enabling a better understanding of their sorptive properties and determining conditions under which adsorption is maximally effective.

Methodology & empirical analysis. The objects of the study were selected as natural coals from the Angren deposit: ordinary coal (OC), «BSSH» grade coal, and oxidized coal (OXC). These coals underwent preliminary physical purification, which included grinding, sieving, and magnetic separation to remove impurities and ensure sample uniformity.

After purification, the coals had the following characteristics:

ordinary Coal (OC): moisture content of 13%, ash content of 12.2%, volatile matter content of 35%, humic acid content of 2%, carboxyl group (COOH) content of 0.1 mg*eq/g, and hydroxyl group (OH) content of 0.5 mg*eq/g;

«BSSH» Grade Coal: moisture content of 12%, ash content of 26.4%, volatile matter content of 36%, humic acid content of 5%, carboxyl group (COOH) content of 0.3 mg*eq/g, and hydroxyl group (OH) content of 1.7 mg*eq/g;

oxidized Coal (OXC): moisture content of 11%, ash content of 40%, volatile matter content of 45%, humic acid content of 50%, carboxyl group (COOH) content of 2.1 mg*eq/g, and hydroxyl group (OH) content of 1.4 mg*eq/g.

To assess the adsorption activity, model solutions of cationic dye (methylene blue, MB) and anionic dye (Congo red, CR) were prepared within a concentration range from 1 to 100 mg/L. Quantitative determination of dye concentrations was performed using scanning spectrophotometry in a wavelength range from 190 to 700 nm with a UV/V-5100 spectrophotometer (Shanghai Metash Instruments Co.). The adsorption capacity was determined by measuring optical density at specific wavelengths: 660 nm for MB and 505 nm for CR [8]. Calibration curves were constructed based on solutions of varying dye concentrations.

Subsequently, 0.05 g of powdered aluminosilicates was added to each 50 mL solution. After reaching equilibrium, defined by kinetic adsorption curves, optical density measurements were conducted, and concentrations were calculated.

The dye adsorption process was investigated under static conditions at various contact times between the adsorbent and solution to determine kinetic characteristics. Kinetic parameters were analyzed using pseudo-first (1) and pseudo-second (2) order models described by the respective equations:

$$ln(A_s - A_t) = ln(A_s) - k_1 t. \quad (1)$$

$$\frac{t}{A_t} = \frac{1}{k_2 A_s^2} + \frac{t}{A_s}, \quad (2)$$

where: k1 is the rate constant for the pseudo-I order equation, expressed in g/mg*min; As and At are the amounts of adsorption upon reaching equilibrium and at time t, respectively; k2 is the rate constant for the pseudo-II order equation, also expressed in g/mg*min. The kinetic dependencies of the sorption of MG and KK dyes on coals were analyzed using the above-mentioned kinetic models.

Results. This section presents the findings of the study on the adsorption of cationic and anionic dyes (methylene blue and Congo red) onto various carbon adsorbents. The kinetic parameters obtained during the experiments are discussed, along with their interpretation based on pseudo-first-order and pseudo-second-order models. The influence of dye concentration, contact time, and the properties of the adsorbents on the efficiency of dye removal from solutions is analyzed. Special attention is given to how different parameters affect the adsorption capacity, as well as the selection of optimal conditions for conducting adsorption processes. The data obtained from the kinetics of dye adsorption onto carbon materials are illustrated in Figures 1 and 2.

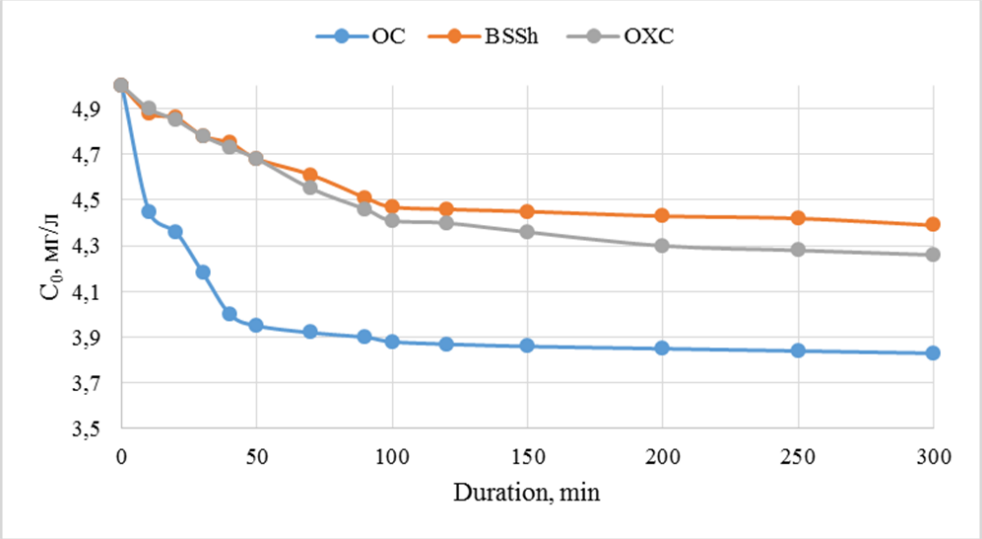


Fig. 1. The process of decreasing the concentration of methylene blue

The change in the residual concentrations of MB in the solution during adsorption on OC, BSSh and OXC carbons demonstrates the differences in the sorption activity of these materials. During the experiment, OC carbon shows the most significant decrease in the concentration of MB - from 5 mg / l to 3.83 mg / l in 300 minutes. In the first 50 minutes, the concentration of MB on OC quickly decreases, after which the adsorption process slows down, which may indicate a gradual saturation of the active centers of the carbon.

BSSh carbon also reduces the concentration of MB in the solution, but this process is slower compared to OC carbon. After 300 minutes, the residual concentration of MB on BSSh is 4.39 mg / l, which is higher than on RU. This may indicate a lower availability of active centers or a smaller number of pores involved in adsorption.

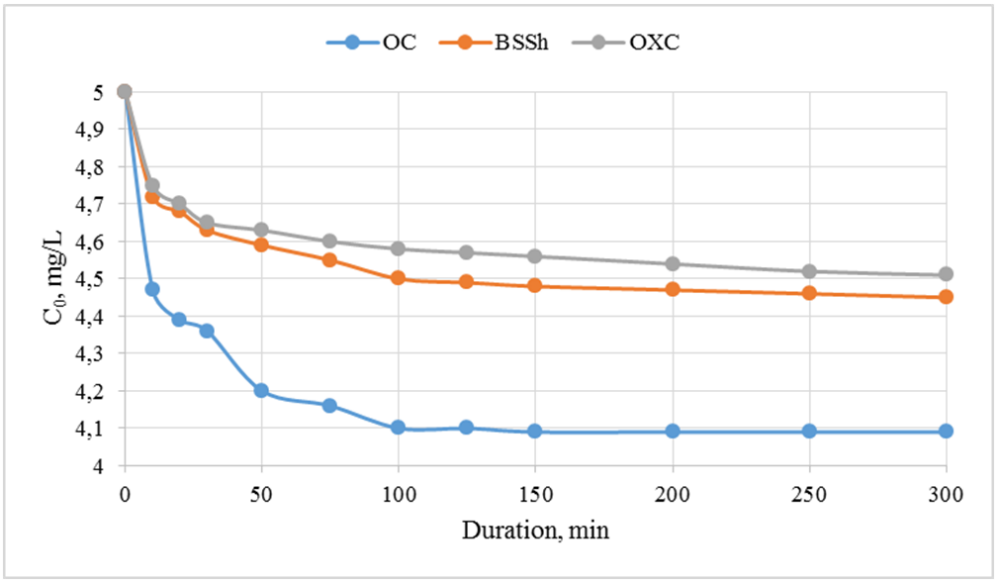
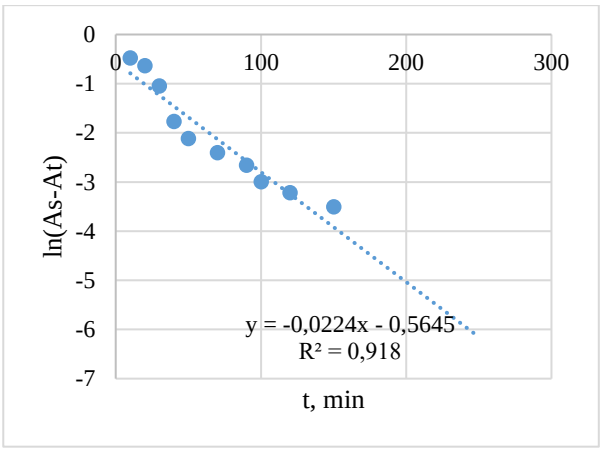


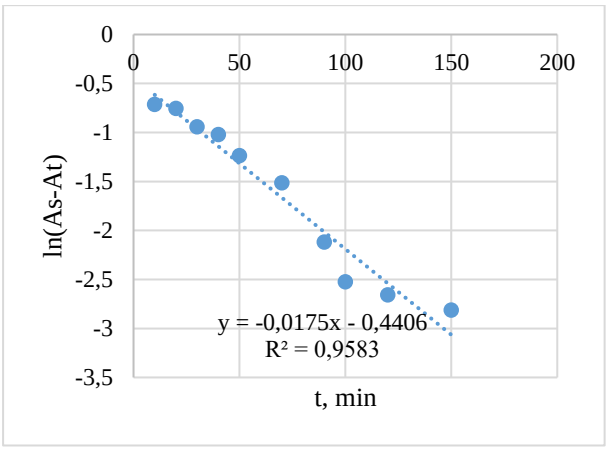
Fig. 2. Kinetics of the decrease in the concentration of CR.

OXC carbon also contributes to a decrease in the residual concentration of MB, reaching 4.26 mg/l after 300 minutes. At the initial stages (up to 50 minutes), the concentration of MG in the OXC decreases faster, but then the process slows down and reaches a stable level.

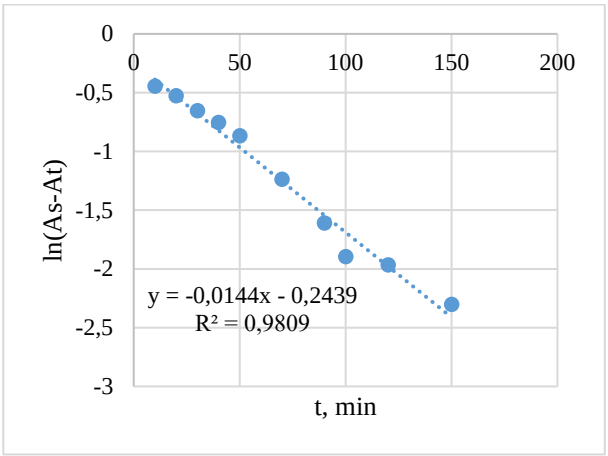
The study of the kinetics of the decrease in the concentration of Congo red (CR) in the solution revealed that the OC carbon has the greatest adsorption capacity, reducing the concentration of CR from 5 to 4.09 mg/l within 300 minutes. At the same time, the BSSh and OXC carbons showed a slower decrease in concentration - to 4.46 mg/l and 4.51 mg/l, respectively, which indicates their lower adsorption efficiency. This difference may be due to the fact that OC has a more developed porous structure and a greater number of active centers compared to BSSh and OXC.



OC



BSSH



OXC

Fig. 3. Linear dependence of ln(As - At) on time t for determining the pseudo-first order adsorption rate constant for coals by MG adsorption.

Analysis of the data on the adsorption of methylene blue (MB) and Congo red (CR) on activated carbons OC, BSH and OXC allows us to conclude that there are oxygen-containing functional groups (carboxyl, phenolic, quinoid) on their surface, which provide adsorption of cationic dyes, such as MB, by ion exchange. A decrease in the adsorption of the anionic dye CR indicates the predominance of negatively charged groups, which prevent interaction with anionic particles.

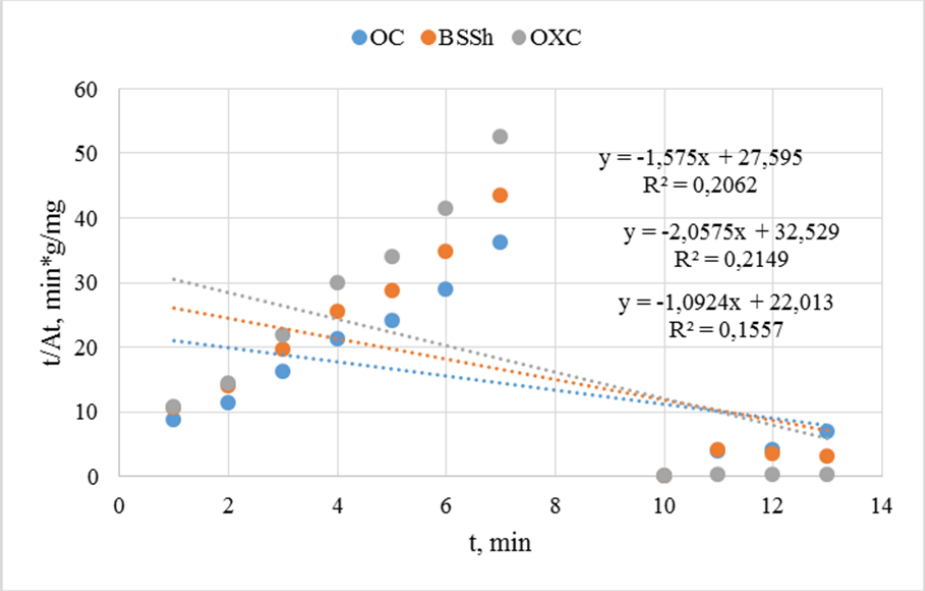


Fig. 4. Determination of the adsorption rate constant using the pseudo-II order model based on the linear dependence of t/At on time t for various modified carbons and MB adsorption.

Table1. Kinetic parameter modeling for adsorption processes.

Carbon	k_1	R^2	As	k_2	R^2
OC	-0,0144	91,80	1,22	0,07	99,90
BSSH	-0,0224	95,83	0,76	0,02	97,77
OXC	-0,0175	98,09	1,02	0,01	97,67
OC	0,229	9,82	0,99	0,10	99,63
BSSH	0,308	98,72	0,60	0,10	99,78
OXC	0,221	95,67	0,51	0,14	99,75

The analysis of kinetic parameters of MG and KK adsorption on various carbon sorbents shows which of the kinetic models describes the system behavior better. The correlation coefficient (R^2) for the pseudo-I order model is below 99% for all coals, both for MG and KK, which indicates insufficient accuracy of this model. Particularly low R^2 values are observed for KK adsorption on OC and OXC coals — 9.82 and 95.67, respectively, which confirms the poor applicability of this model. Additionally, negative values of adsorption capacity (As) for KK on all coals also indicate the inadequacy of the pseudo-I order model.

In turn, the pseudo-II order model demonstrates high values of correlation coefficients (R^2) for all coals, both for MG and KK (more than 97%). The highest R^2 values (99.90 for MG on OC and 99.78 for KK on BSSh) confirm that this model describes the adsorption kinetics in the studied systems better. Positive values of adsorption capacity (As) and acceptable values of rate constants (k2) additionally support the compliance of

the pseudo-second order model. Thus, the pseudo-second order model turns out to be more suitable for describing the adsorption kinetics of both methylene blue (MG) and Congo red (KK) on OC, BSSh and OXC coals. High R^2 values and positive values of adsorption capacity (As) indicate that the adsorption kinetics in these systems are better described by this model.

The second order model assumes that the adsorption process is controlled by chemical sorption (chemisorption) or interactions associated with the exchange of substances between the adsorbate and the active sites on the coal surface. According to the obtained data, the high correlation for the pseudo-second order model ($R^2 > 99\%$) for most carbons indicates that the adsorption rate is determined not only by the dye concentration in the solution, but also by the number of available active sites on the carbon surface that are capable of participating in chemical interactions with the adsorbate molecules.

The adsorption rate in the second-order model depends quadratically on the adsorbate concentration, which means that doubling the adsorbate concentration can increase the adsorption rate fourfold if the active sites on the adsorbent surface remain unsaturated. This model also assumes the formation of an adsorbate monolayer, which indicates a chemisorption mechanism and the presence of strong interactions that ensure strong binding of the adsorbate molecules to the adsorbent surface.

Conclusions. As a result of the study, the kinetic parameters of methylene blue (MB) and Congo red (CR) adsorption on various carbons (OC, BSSh and OXC) were studied. Data analysis showed that the pseudo-second-order adsorption model most accurately describes the adsorption kinetics for all the studied systems. High values of the correlation coefficients ($R^2 > 97\%$) and positive values of the adsorption capacity (As) indicate that the adsorption process is controlled by chemical interactions between the adsorbate and active sites on the carbon surface. The second-order model assumes that adsorption occurs as a monolayer formation, which confirms the chemisorption mechanism, which ensures strong binding of dye molecules to the carbon adsorbent.

The study also showed that differences in the adsorption efficiency of MB and CR on different carbons are associated with their porous structure and the presence of oxygen-containing functional groups. The OC coal demonstrated the highest adsorption activity, which is explained by the developed porous structure and a large number of active centers capable of effectively binding dye molecules. While the B BSSh SH and OXC coals showed a slower decrease in dye concentrations, which is due to the lower availability of active centers. The obtained results confirm that the selection of a suitable carbon adsorbent and optimal conditions of the adsorption process plays a key role in the development of effective technologies for wastewater treatment from organic dyes. Future research can be aimed at modifying the surface of carbon sorbents and studying their interaction with other types of pollutants to further improve their adsorption efficiency and stability under various conditions.

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