UDC 628.16:544.723

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STUDY OF THE ADSORPTION CAPACITY OF KAOLIN CLAY AND ITS COMPOSITE FOR REMOVING METHYL GREEN DYE FROM AN AQUEOUS MEDIUM

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Water pollution from industrial waste, particularly dye contaminants such as methyl green, is a major problem. One promising approach involves using kaolin clay and its composite with palmitic acid. The materials were characterized using X-ray diffraction, scanning electron microscopy, and Fourier-transform infrared spectroscopy. The adsorption efficiencies of kaolin clay and its compounds for methyl green were 86% and 97%, respectively, indicating that the modification improved the adsorption performance of the clay.

Keywords: adsorption, kaolin, methyl green, palmatic acid, modified clay.

DOI: 10.32434/0321-4095-2026-164-1-22-29

Introduction

For a long time, environmental pollution has threatened and affected life at different levels, including humans. The increase in population growth during the period 2000–2020 requires development in life standards in various fields, which in turn leads to an increase in the use of chemicals, especially dyes, in the industrial sector. As a result, its impact on the aquatic environment has increased, making it an existing problem that requires solutions [1,2]. Three groups (physical, chemical, and biological) of methods are used for treating dyes from their aqueous solutions [3].

One of these methods is the adsorption technique, which was proposed by German physicist Heinrich Kayser years ago (1881), and has contributed significantly to environmental adsorption studies through the removal of pollutants from the aqueous phase. It is preferred over other methods for the ease of its design, effectiveness, and low cost [4,5]. Each adsorbent has its own characteristics, such as porosity, pore structure, surface area, and structural specificity [6].

Among the adsorbent surfaces are clays, especially kaolin clay, which is considered to have a lower adsorption efficiency than similar ones, such as bentonite and activated charcoal, so it has been improved through various processes, such as intercalation, columns, thermal activation, and acid or basic activation [7]. We will present a number of studies in this field, where a specific study dealt with the adsorption of cationic dyes from their aqueous solutions by raw kaolin clay and activated kaolin clay with different concentrations of sulfuric acid. The experimental data were analyzed using kinetic methods to track the pseudo-second-order kinetic model, and the isotherm followed the Langmuir model for both dyes. The activation process led to an increase in the adsorption efficiency of both dyes [8].

Another study dealt with removing Direct Brown 1 (DB 11) dye from wastewater using raw kaolin clay and comparing it with kaolin clay modified with an

organic compound (hexadecyltrimethylammonium bromide, HDTMA). The modified surfaces were characterized by different techniques, such as X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FT-IR). The effect of a number of factors on the adsorption process was studied, and the optimal conditions for the process were determined using batch technology. This resulted in the modified clay being several times more efficient than the crude clay under these conditions [9]. The aim of this study is to improve the efficiency of kaolin clay in the adsorption of cationic dye through its modification with an organic compound.

Materials and methods

Kaolin clay preparation (kao)

Kaolin clay consists of pure white blocks prepared from the Akashat area in the Western Desert by the General Company for Geological Survey and Mining, Baghdad, Iraq. The samples were collected and separated from stones and other heavy particles, then ground, washed, dried, crushed, and sieved through a 200-mesh sieve to obtain a certain volume of raw kaolin clay (kao) particles. The clay powder was washed seven times with a sufficient quantity of distilled water to remove exotic substances soluble in water and then dried in an oven (Daihan Labtech Oven LDO-060E) at a temperature of 80^{0}C for about 72 hours.

Kaolin clay modification (kao/P)

Kaolin clay modification (kao/P) was carried out by adding a certain amount of kaolin clay to a 0.05 M solution of sodium hydroxide (CDH) in a 100 ml reaction flask with continuous stirring (Hotplate, Daihan Labtech Co., LTD, Stirrer) for 1 hour at a certain temperature. The mixture was then transferred to an ultrasonic device (Ultrasonic Cleaner POWER SONIC-0405S) with the gradual addition of a certain amount of palmitic acid, $CH_3(CH_2)_{14}COOH$ (Fluka), for 1 hour at 30^{0}C, and then filtered, washed, and dried in an oven (Daihan Labtech Oven LDO-060E) for 10 hours at 100^{0}C to obtain the modified kaolin clay (kao/P).

Adsorbate and adsorption experiment

Methyl green (MG) is a cationic dye and belongs to the triphenylmethane family of pigments. Its molecular weight is M.wt.=458.47 g·mol^{-1}, and the formula of MG dye is $C_{26}H_{33}Cl_2N_3$ (Fig. 1).

Batch adsorption experiments were conducted in the following way. A known dose of slurry was introduced into 10 ml of colored water at certain MG concentrations. The solution was placed in a constant agitation shaker (Shaking Water Bath, Labtech) at a fixed speed of 120 rpm for time intervals of 1–180 min. Samples were centrifuged at 6000 rpm using a Hettich EBA-20 centrifuge. The residual concentration of MG dye was analyzed using a UV-vis spectrophotometer (Shimadzu 1800, Japan), and the remaining MG dye concentrations were measured at λ_{max}=632 nm. The amount of MG dye adsorbed was determined by the following equation [10]:

$$q_e = \frac{(C_i - C_f)V}{M}$$

where q_e is the adsorption capacity at equilibrium (mg/g); C_i and C_f (mg/L) are the initial and final concentrations, respectively; V (L) is the solution volume; and M (g) is the amount of kao or kao/P used.

The dye removal ratio was calculated using the following equation [11]:

$$\text{Removal},\% = \frac{C_i - C_e}{C_i} \cdot 100\%$$

Results and discussion

Characterization of the kaolinite clay surfaces (kao, kao/P)

XRD characterization

Kaolin clay surfaces were characterized before and after modification (kao, kao/P) using X-ray diffraction (XRD) in the 2θ range of 10–80^0 (Figs. 2 and 3). It was shown that the palmitic acid modification process led to relative changes in the diffraction angles, intensities, and shapes of the peaks, which indicates that the modification occurred without deforming or breaking the clay's composition or losing its crystalline structure [8,12].

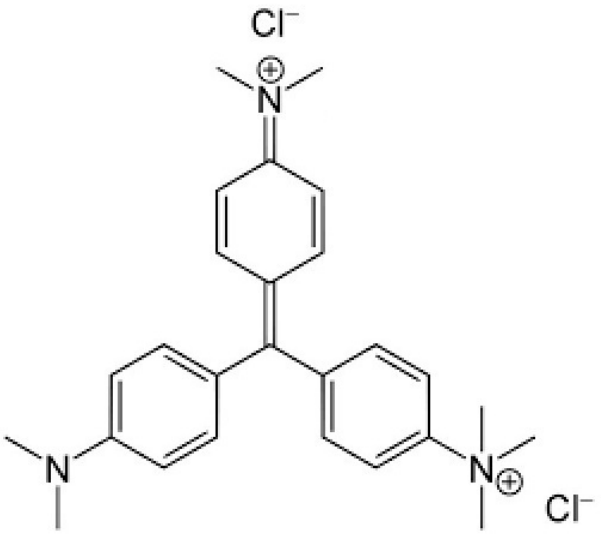

Fig. 1. Structure of the MG dye molecule

FT-IR spectroscopy characterization (FT-IR)

Kaolin clay surfaces were characterized before and after modification (kao and kao/P) through FT-IR spectra in the range of 400–4000 cm^{-1}, as shown in Figs. 4 and 5. The strongest characteristic bands of kao are recorded as follows. The bands in the wavenumber region ≥3000 cm^{-1} correspond to the hydroxyl groups at the ends of the clay platelets on the surface of the octahedral layers that interact with the oxygen atoms of the adjacent tetrahedral layers, as well as the internal hydroxyl groups. The bands at 910 cm^{-1} are due to stretching of Al–OH groups. The bands within the range of 790–550 cm^{-1} correspond to the vibrations of Si–O–Al groups. The bands within the range of 1500–1000 cm^{-1} correspond to the stretching of Si–O–Si; all these bands are typical of the kaolinite clay mineral. Figure 5 for the kao/P surface also shows that the modification process led to a relative displacement in the positions of all characteristic peaks of the spectrum, except the bands at 2800 and 2900 cm^{-1}, which are attributed to symmetric and asymmetric stretching of C–H groups. This indicates that the FT-IR results agree with the X-ray diffraction results [13,14].

Scanning electron microscopy (SEM)

The surface morphology of these two adsorbents (kao and kao/P) was observed by SEM analysis (Figs. 6 and 7). These images show the crust shapes of the kaolin clay surface with heterogeneous surfaces of different sizes, with an approximate size of about 27 nm, while the images of the surface of the clay modified with aluminum oxide show crust shapes that are more homogeneous and larger, within about 72 nm. This confirms the occurrence of the modification process (kao/P) [13,15].

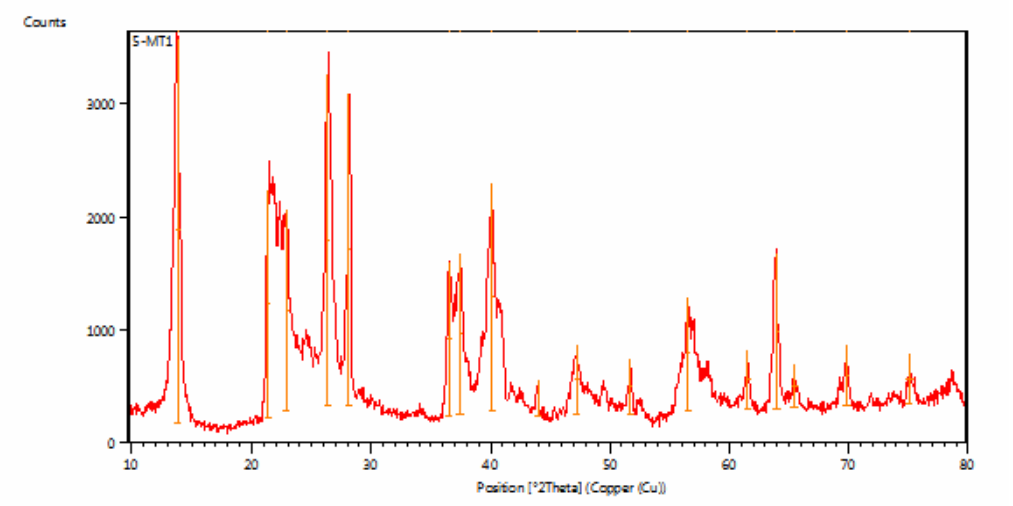

Fig. 2. XRD spectrum of the kao surface

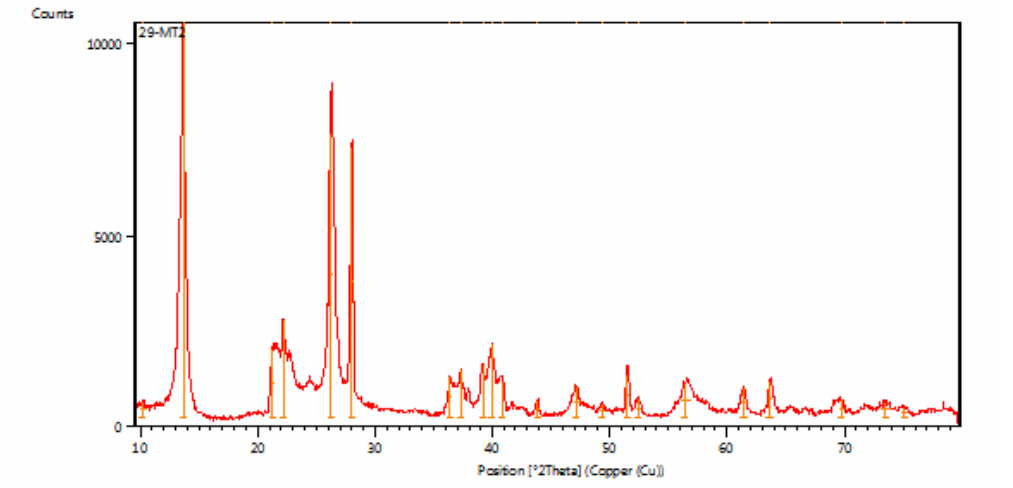

Fig. 3. XRD spectrum of the kao/P surface

Adsorption efficiency

In order to show that the modification process led to an improvement in the surface properties after modification, the surface efficiency (kao and kao/P) for the adsorption of methyl green dye was tested under certain laboratory conditions. The amount of adsorption is shown in Figs. 8 and 9, and the adsorption percentage is shown in Figs. 10 and 11. It can be noted that the surface efficiency after modification (kao/P) increased to reach 97%, with an adsorption amount of 16.2 mg/g at an initial concentration of 50 mg/L, compared to the original surface (kao), which showed an adsorption amount of 8.8 mg/g and an adsorption percentage of 86% at an initial concentration of 30 mg/L. This may be due to the increase in adsorption sites and the change in surface morphology after modification with palmitic acid [16,17].

The improvement in adsorption efficiency after modification with palmitic acid can be attributed to changes in the surface morphology and chemical composition of the kaolin clay. The modification increased the number of active adsorption sites and enhanced the interaction between the cationic MG dye molecules and the clay surface. The presence of functional groups from palmitic acid likely contributed

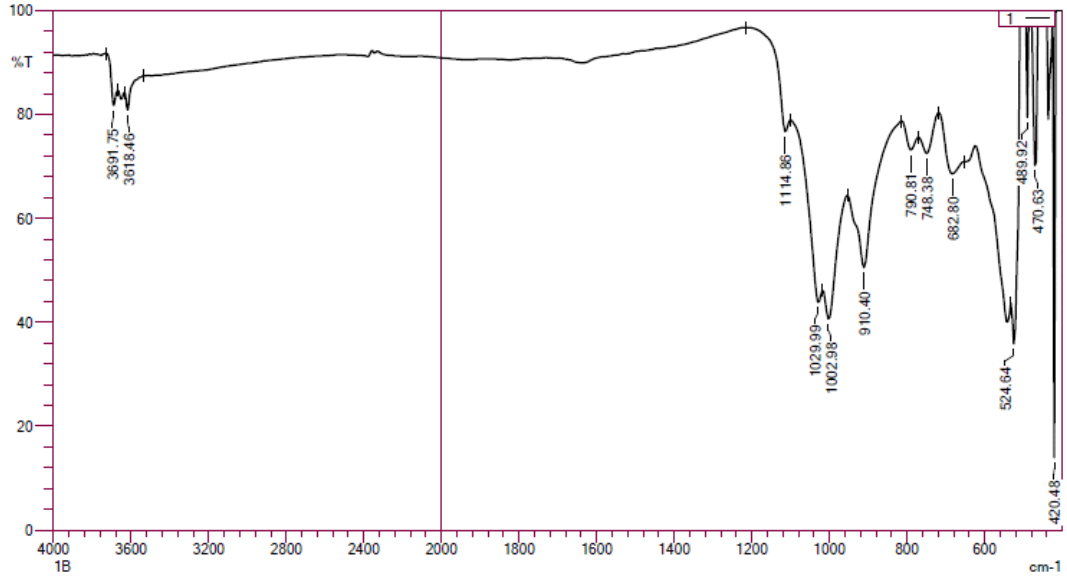

Fig. 4. FT-IR spectrum of the kao surface

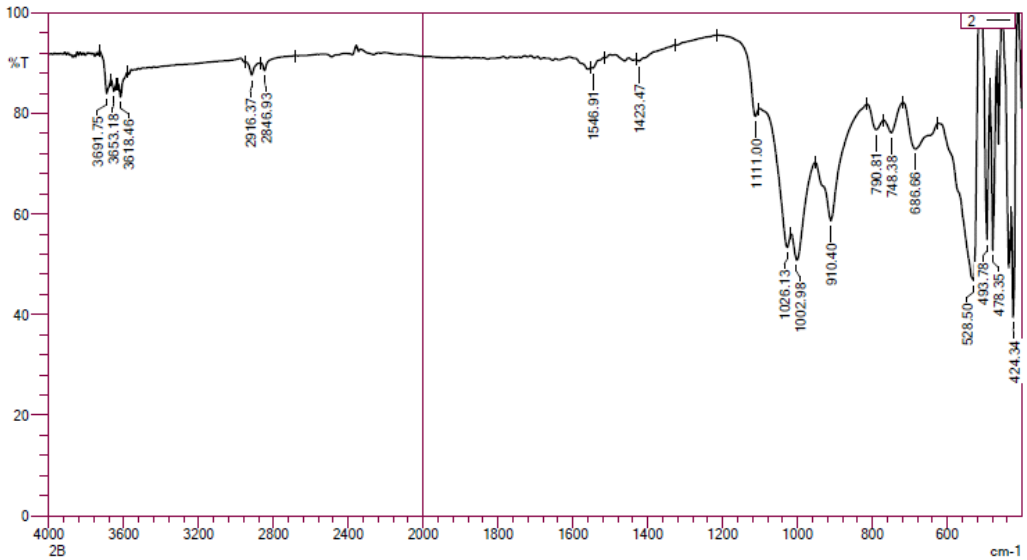

Fig. 5. FT-IR spectrum of the kao/P surface

to stronger electrostatic and van der Waals interactions, facilitating greater dye uptake. These results demonstrate that surface modification effectively enhances the adsorption capacity of kaolin clay by altering both its structural and chemical properties.

Conclusions

Based on FT-IR, XRD, and SEM analyses, the modification of kaolin clay with palmitic acid particles (kao/P) effectively altered the surface morphology and chemical composition of the clay. These changes increased the number of active adsorption sites and enhanced interactions between the cationic MG dye molecules and the clay surface. As a result, the adsorption capacity of the modified clay increased from 8.8 mg/g for raw kaolin clay to 16.2 mg/g for kao/P at an initial dye concentration of 50 mg/L. The findings indicate that surface modification with palmitic acid significantly improves the adsorption performance of kaolin clay and demonstrates its potential as an efficient adsorbent for the removal of cationic dyes from aqueous solutions.

Acknowledgements

The authors would like to acknowledge the College of Education for Pure Science (Ibn Al-Haitham), University of Baghdad.

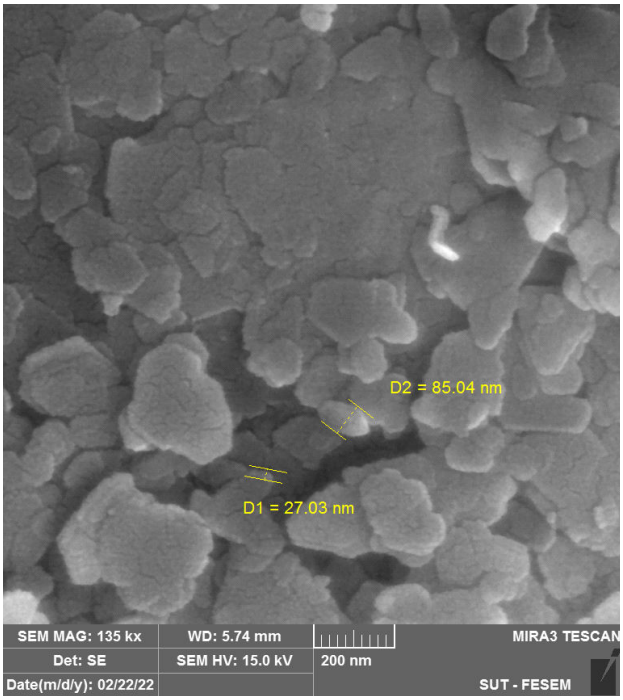

Fig. 6. FESEM image of the kao surface

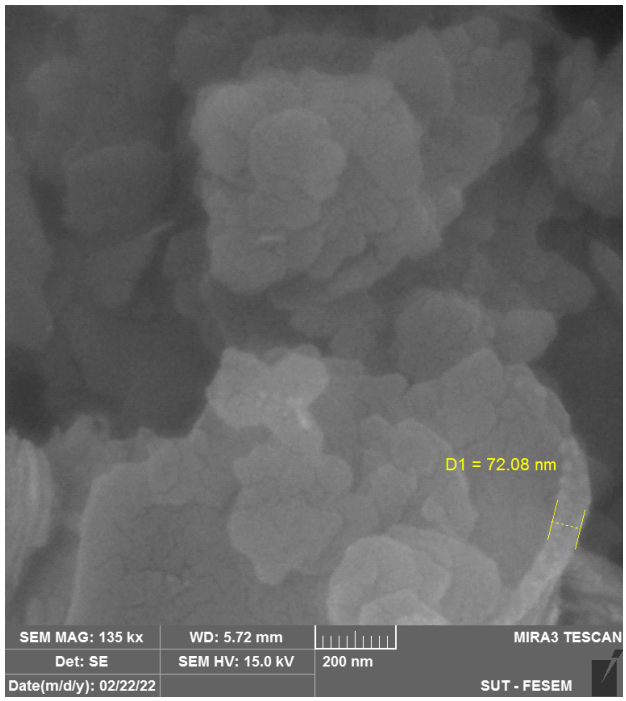

Fig. 7. FESEM image of the kao/P surface

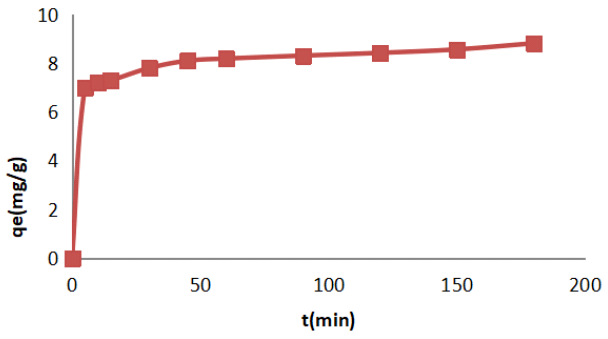

Fig. 8. Quantity of MG dye adsorption on the kao adsorbent (0.03 g) at 298 K, 30 mg/L during different time periods

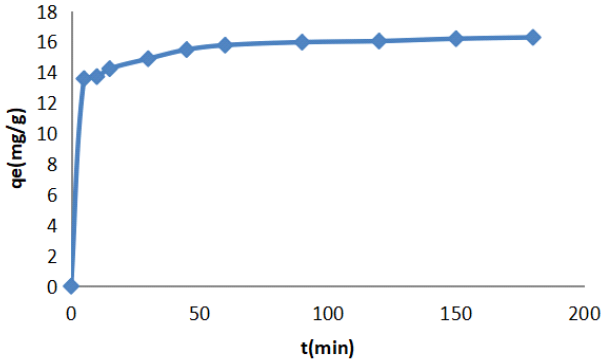

Fig. 9. Quantity of MG dye adsorption on the kao/P adsorbent (0.03 g) at 298 K, 50 mg/L during different time periods

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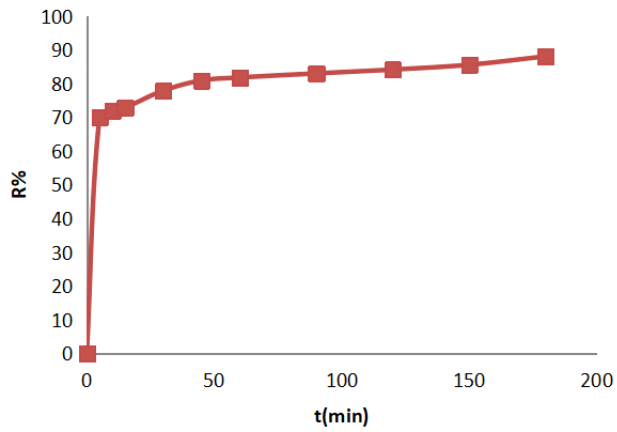

Fig. 10. Adsorption efficiency of MG dye by the kao adsorbent (0.03 g) at 298 K, 30 mg/L during different time periods

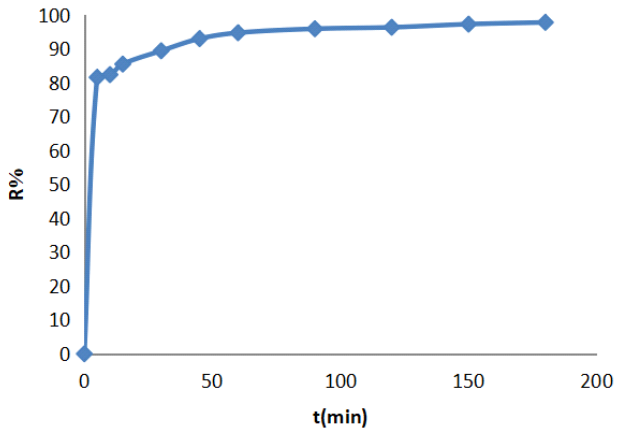

Fig. 11. Adsorption efficiency of MG dye by the kao/P adsorbent (0.03 g) at 298 K, 50 mg/L during different time periods

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Received 21.05.2025
Accepted 03.12.2025
Published 25.02.2026

ДОСЛІДЖЕННЯ АДСОРБЦІЙНОЇ ЗДАТНОСТІ КАОЛІНОВОЇ ГЛИНИ ТА ЇЇ КОМПОЗИТУ ДЛЯ ВИДАЛЕННЯ БАРВНИКА МЕТИЛОВИЙ ЗЕЛЕНИЙ З ВОДНОГО СЕРЕДОВИЩА

М.С. Казем, А.М. Аббас

Забруднення води промисловими відходами, зокрема барвниками, такими як метиловий зелений, є серйозною проблемою. Одним із перспективних підходів є використання каолінової глини та її композиту з пальмітиновою кислотою. Матеріали були охарактеризовані за допомогою рентгенівської дифракції, сканувальної електронної мікроскопії та інфрачервоної спектроскопії з Фур'є-перетворенням. Адсорбційна ефективність каолінової глини та її композиту щодо метилового зеленого становила відповідно 86% і 97%, що свідчить про те, що модифікація покращила адсорбційну здатність глини.

Ключові слова: адсорбція; каолін; метиловий зелений; пальмітинова кислота; модифікована глина.

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