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ENHANCED PHOTOCATALYTIC AND ADSORPTİVE REMOVAL OF METHLENE BLUE AND CONGO RED BY GRAPHENE OXİDE DOPED ZnAl-LDH NANOCOMPOSITES

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In the research work, graphene oxide (GO) was initially synthesized by Hummers'method, and GO/ZnAl-LDH samples were prepared with different concentrations (50 mL, 25 mL, 12.5 mL, and 5 mL) of pre-synthesized ZnAl-LDH nanocomposite. The samples were measured by ultraviolet-visible (UV-Vis) spectroscopy, and the band gap width was calculated for each sample. The crystal structure of GO/ZnAl-LDH samples was confirmed by X-ray diffraction (XRD). Methylene blue (MB) and Congo red (CR) solutions were prepared with the GO/ZnAL-LDH composite. After the prepared solutions were stored for 24 hours, the adsorption process was initially studied for methylene blue, and in the next stage, the photodegradation process was carried out under ordinary lamp light for 2, 4, and 6 hours. The sorption and photodegradation rates, as well as the rate constants, were calculated for each sample. The strongest photodegradation for methylene blue samples was observed in sample 1, and for Congo red in sample 4. Based on the results, we can note that the removal of Congo red was faster and more efficient than that of methylene blue. This is explained by the fact that Congo red is an anionic dye, as it forms a strong electrostatic interaction with the positive charges of the ZnAl-LDH nanocomposite.

Keywords: Graphene oxide (GO), ZnAl-LDH nanocomposite, Methylene blue (MB), Congo red (CR), Photodegradation

INTRODUCTION

Water is one of the main components that is vital for the growth, development, and survival of all living organisms. Studies have shown that although 71.1% of the earth's surface is covered by water and 28.8% by land, only 2.5% of this is freshwatersuitable for drinking [1]. Rapid population growth, urban growth, excessive use of chemical fertilizers in agriculture, and the direct discharge of dyes used in the textile industry into freshwater bodies without treatment are among the main causes of waterpollution [2]. The exact amount of dyes used per year is not known, but studies have shown that approximately 7×10^5 tons of dyes are produced per year, and 1.4×10^5 tons of them are discharged directly into freshwater bodies without treatment [3]. Heavy metal ions such as cadmium, lead, chromium, and mercury are required in the production of dye pigments for dyeing clothes in the textile industry [4].

These chemicals, especially dyes, remain in the soil for a long time, causing a decrease in theamount of oxygen and a decrease in the efficiency of the photosynthesis process,

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which negatively affects all aquatic and terrestrial organisms. Dyes can be divided into 2 main groups: cationic and anionic. An example of a cationic dye is methyleneblue, and an example of a benzene-based azoic anionic dye is Congo red [6]. Azo dyes are considered dangerous for the environment because toxic aromatic amines are released when N=N bonds are broken [7]. Methylene blue and Congo red dyeshave a toxic effect, are highly resistant to decomposition and heat, and can remain in water for a long time. They cause cardiovascular diseases, skin problems, hallucinations, muscle paralysis, and sometimes fatal diseases in people who consume thiswater. Therefore, it is important to clean both heavy metal ions and dyes from polluted water sources in order to improve the vital activity of all living organisms.

There are various physical, chemical, and biological methods for the removal of methylene blue, Congo red, and other pollutants from the aquatic environment: chemical methods include oxidation [8], flocculation [9], and photodegradation [10], biological methods include biodegradation [11], and physical methods include adsorption [12-14]. One of the most effective methods for the effective removal of both heavy metal ions and dyes from contaminated water sources is adsorption. This methodhas the main advantages of simplicity, low energy requirements, reusability, and rapid implementation of the processes. The efficiency of the adsorption process also depends on the correctly selected adsorbent. The main quality of the adsorbent depends on its large surface area, multifunctional groups, porosity, and chemical composition [15].

Graphene oxide is an oxidized form of graphene with a carbon-based, dihedral structure (2D), rich sp^2 hybridization with functional groups (-COOH, -OH). Layered double hydroxides have recently been used for the mechanical strengthening of polymer nanocomposites.

The main purpose of this work is to synthesize the GO/ZnAl-LDH nanocomposite and its removal from water sources contaminated with dyes such as methylene blue and Congo red, mainly consisting of studying the cleaning efficiency bysorption and photodegradation.

EXPERIMENTAL

Graphene oxide was synthesized by the Hummers method, which is the most widely used and efficient method. First, 3 g of graphite and 1.5 g of $NaNO_3$ were added to a 500 ml flask. In the next step, 69 ml of H_2SO_4 was slowly added to the mixture and stirred in an ice bath for 1 hour. Over 15–20 min, 9 g of $KMnO_4$ was gradually added to the mixture, and the temperature was kept below 20 °C. The color of the solution turned dark green, which is an indication of the successful oxidation of graphite to graphene oxide. The mixture was then stirred for 1 h on a magnetic stirrer at 35 °C. 70 ml of DI water was carefully added to the mixture and, since the process was exothermic, the temperature was increased to 98 °C. The resulting thick paste was kept at this temperature for 30 min. Then, DI water was added, and the color of the solution changed from brown to yellow. The mixture was filtered through filter paper, and a solution of HCl: H_2O = 1:10 was added to the mixture to remove metal ions. Graphene oxide was washed 3–4 times with HCl and deionized water. The resulting graphene oxide suspension was stirred at room temperature for 1 hour and precipitated by centrifugation. For the next stage, the synthesized graphene oxide material was used to prepare GO/ZnAl-LDH nanocomposite samples. A total of five samples were prepared, and the amount of ZnAl-LDH nanocomposite in each sample was 0.005 g. 50, 25, 12.5, and 5 ml of GO were added to the first four samples, respectively, and the fifth sample consisted of only ZnAl-LDH composite. After storing the prepared solutions for 24 hours, they were measured by UV-Vis spectroscopy, and the band gap of the samples was calculated by the Tauc method.

The main objective of the study was to study the adsorption and photocatalytic ability of GO/ZnAl-LDH nanocomposite in the removal of dyes such as methylene blue (MB) and Congo red (CR) from aqueous solutions. For this purpose, 50 ml of 100 ppm (100 mg/L) methylene blue and Congo red solutions were prepared. To carry out the adsorption and photodegradation process, the previously synthesized GO/ZnAl-LDH nanocomposite was added to 10 ml of 10 ppm methylene blue and Congo red solutions. The solutions were kept at room temperature for 24 hours. The photodegradation process was carried out under ordinary lamp light for 2, 4, and 6 hours.

The adsorption efficiency R (%) (1) and photodegradation efficiency FD (%) (2) of methylene blue (MB), and Congo red (CR) were calculated using the following equations

$$R(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

$$FD(\%) = \frac{A_0 - A_t}{A_0} \times 100 \quad (2)$$

where C_t is the concentration after irradiation, C_0 is the initial concentration of the dye, A_t is the absorbance after irradiation and A_0 is the initial absorbance.

The adsorption capacity (q_e) was calculated using the following equation [17]:

$$q_e = \frac{(C_0 - C_t)}{m} \times V \quad (3)$$

where C_0 is the initial MB and CR concentration (mg/L), q_e is the adsorption capacity (mg/g), C_e is the equilibrium concentration (mg/ L), and m is the mass of the adsorbent (g), V is the volume of MB and CR solution (L)

According to the first-order kinetic model, the rate constant k (min^{-1}) was determined using the following equation [18]:

$$\ln \frac{C_t}{C_0} = k \cdot t \quad (4)$$

where C_0 and C_t are the concentrations at the initial and at time t, respectively, and t is the irradiation time.

RESULTS AND DISCUSSION

The optical adsorption coefficients of GO/ZnAL-LDH samples prepared using graphene oxide (GO) synthesized by the Hummers method were measured using an ultraviolet- visible (UV-Vis) spectroscopy device. According to the results obtained, the bandgap widths of the samples with 50%, 25%, 12.5%, and 5% GO doping were 3.31 eV, 3.28 eV, 3.22 eV, and 3.67 eV, respectively.

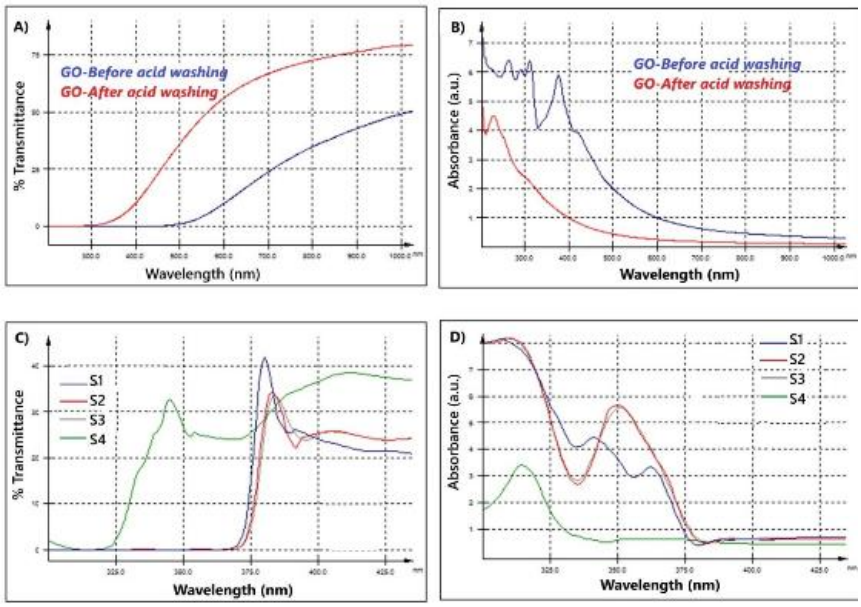

Figure 1. Absorption and transmittance spectra of GO (A, B) and GO-doped ZnAl-LDH/PVA samples (C, D) mixed with 50% (S1), 25% (S2), 12.5% (S3) and 5% (S4) graphene oxide.

In sample 4, although the amount of graphene oxide is the lowest (5%), the band gap width has the highest value (3.67 eV). Graphene oxide is a carbon-based, two-dimensional

structure, rich in functional groups. Having a large surface area facilitates the movement of electrons, and therefore the width of the band gap decreases. Reducing the amount of graphene oxide weakens this effect. The band gap in the ZnAl-LDH composite is large, while the low amount of graphene oxide makes it difficult for electrons to move, and it becomes difficult for them to pass from one band to another [19, 20]. As a result, the band gap remains large.

Table 1. Adsorption and photodegradation performance of the obtained samples for Methylene blue dye.

Irradiation Time (min)	**Sample I**	**Sample II**	**Sample III**	**Sample IV**	**Sample V**
Adsorption capacity mg/g)	3.2	1.2	2	0.4	1
Adsorption efficiency (R, %)	16%	6%	10%	2%	5%
120 (min)	29%	21%	26%	23%	10%
240 (min)	44%	31%	51%	42%	36%
360 (min)	61%	50%	61%	55%	58%
Rate constant (k, min^{-1})	0.0023	0.0024	0.0024	0.0023	0.0024

Table 2. Adsorption and photodegradation performance of the obtained samples for Congo red dye.

Irradiation Time (min)	**Sample I**	**Sample II**	**Sample III**	**Sample IV**	**Sample V**
Adsorption efficiency (R, %)	58	64	51	63	45
120 (min)	81	86	83.5	89	85
240 (min)	89	96	92	96	95
360 (min)	95.7	98.7	98.2	98.8	98.2
Rate constant (k, min^{-1})	0.0087	0.0128	0.0112	0.0124	0.0112

According to the results, although the amount of graphene oxide in sample 1 was the highest (50 mL) and in sample 4 the least (5 mL), the band gap value of sample 1 was 3.31 eV, and in sample 4 the band gap increased to a maximum value of 3.67 eV. This means that the band gap value is not directly determined by the amount of GO alone. The width of the forbidden band is explained by the amount of GO, the homogeneity of the nanocomposite, the synergistic interaction between GO and ZnAl-LDH, and the presence of active functional groups.

Based on the experiments conducted for methylene blue, the results obtained show that the adsorption and photodegradation capacity of the samples mainly depend on the amount of graphene oxide and the composition of the nanocomposite. Sample 1 showed the highest adsorption capacity (3.2 mg/g, 16%). This is due to the highest amount of graphene oxide in sample 1 (50 mL), because graphene oxide has a large surface area and many functional groups (–OH, –COOH), which significantly increases the adsorption capacity compared to other samples. Sample 4 showed the lowest adsorption capacity (0.4 mg/g, 2%) because the amount of graphene oxide is minimal, and as a result, the surface area is reduced, and the number of active centers is not sufficient. The photodegradation results increased over time. For example, after 360 minutes, sample 1 demonstrated the highest removal efficiency (61%).

This increase is explained by the longer-range interaction between methylene blue molecules and the active centers of the nanocomposite and the efficiency of electron-hole separation.

The efficiency of the photodegradation process increased over time. After 120 minutes, the photodegradation efficiency of the samples was 81–89%, after 240 minutes it was 89–96%, and after 360 minutes it was 95–98.8%. Based on these results, we can note that the photodegradation efficiency of Congo red was faster and more efficient than that of methylene blue. This is explained by the fact that Congo red is an anionic dye, as it formed a strong electrostatic interaction with the positive charges of the ZnAl-LDH nanocomposite.

In addition, the crystal structure of the synthesized GO/ZnAl-LDH nanocomposites was studied by X-ray diffraction (XRD). The obtained diffraction peaks indicated that the nanocomposite was successfully synthesized and that there was a structural interaction between GO and ZnAl-LDH.

As a result of XRD analysis of graphene oxide (GO), the main peak was observed at the angle 2θ = 8.83°. This peak is characteristic of GO and indicates that the interlayer distance increases as a result of the oxidation of graphite. The fact that the distance d is about 10.00 Å confirms that the layers are further apart compared to the graphite structure and that oxygen-containing functional groups (–OH, –COOH, etc.) are included. At the same time, a weak peak was also observed at the angle 2θ ≈ 26.67°, which indicates that the residual structure of graphite is not completely oxidized. In addition, the peaks observed at the angles 32.10° and 42.3° can be explained by some degree of disorder in the structure or the presence of additionalphases.

As a result of XRD analysis of graphite, a very sharp and intense peak was observed at the angle 2θ = 26.52°. This peak corresponds to the (002) crystal plane of graphite, indicating that it has a highly ordered and crystalline structure. The d distance corresponding to this peak is approximately 3.35 Å, which confirms the existence of a layered structure of graphite. In addition, other peaks observed at angles of 12.31°, 36.51°, 54.64°, and 87.03° indicate that graphite has a polycrystalline structure. However, the main and dominant peak is located at 26.52°, which is the main indicator of the structure of graphite. Overall, the XRD results confirm that graphite has a high crystallinity and a well-formed layered structure.

CONCLUSION

In this work, graphene oxide (GO) was synthesized by the Hummers method, and GO/ZnAl-LDH nanocomposites with different concentrations were synthesized. X-ray diffraction (XRD) analysis confirmed the successful oxidation of graphite tographene oxide to form LDH nanocomposites. Using UV-Vis analysis, it was determined that the width of the forbidden band varied in the range of 3.22-3.67 eV as a result of varying the amount of graphene oxide. Photodegradation experiments showedthat the degradation efficiency of dye contaminants strongly depends on the composition of the nanocomposite. The highest photodegradation efficiency for methylene blue was observed in sample I for 360 min, which was explained by the highestamount of graphene oxide (50 mL) and the large number of active sites in sample I. On the contrary, for Congo red dye, the highest photodegradation efficiency was observed in sample IV.

The image constants for both dyes were calculated. The imageconstants for methylene blue varied in the range of 0.0023-0.0024, and for Congo red in the range of 0.0087-0.0128. Overall, the obtained results show that GO/ZnAl-LDH nanocomposites are promising materials for the efficient removal of organic dyepollutants from aqueous media and have strong potential for application in water treatment processes.

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