

PHOTOCHEMISTRY, MAGNETOCHEMISTRY,
MECHANOCHEMISTRY

Application of TiO₂/ZnAl-Layered Double Hydroxide Photocatalysts for the Solar Photocatalytic Degradation of Food Dye

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Received May 8, 2022; revised September 8, 2022; accepted September 13, 2022

Abstract—Photocatalysis of food dye (tartrazine) was studied using TiO₂/ZnAl-LDH material derived from layered-double hydroxide structure, which were synthesized by co-precipitation method. The catalyst was characterized using Fourier-transform infra-red (FTIR) spectroscopy, X-ray diffraction (XRD) spectroscopy, Brunauer–Emmett–Teller (BET) analysis, and scanning electron microscope (SEM), combined with energy dispersive X-ray spectroscopy. The photodegradation experiments were carried out by varying different parameters such as initial dye concentration, pH, irradiation time, and dose photocatalyst. Tartrazine mineralization was also studied by calculating the degradation of chemical oxygen demand. The reusability of TiO₂/ZnAl-LDH catalysts was studied and its photocatalytic efficiency was found to be unchanged, even after six cycles of use. The degradation of food dye is achieved at a natural pH 6 and catalyst content of 1 g/L after 120 min under sun with a maximum percentage of degradation 82%. The results of kinetic studies correspond to the Langmuir–Hinshelwood model.

Keywords: food dye, tartrazine, layered double hydroxides (LDH), advanced oxidation processes

DOI: 10.1134/S0036024423040040

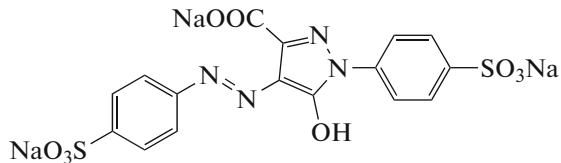
INTRODUCTION

Dyes are extensively used in the food and textile industry in Algeria. They are abundant source of colored organic pollutants emanating from the food and textile dyeing method [1]. The high concentration of organics in the wastewater effluents can make environmental problems, in addition the influence of the human life, as the greater part of them are cancer-causing and mutagenic and disrupt to aquatic life. The synthetic dyes most frequently used in the food industry are azo dyes (–N=N–). Of these, the most common is the tartrazine anionic dye which is used to color jellies, ice creams, soft drinks, and alcoholic drinks [2–4]. Tartrazine is chosen as the model pollutant for the present study. Tartrazine, also known as Acid Yellow 23 or the additive E102, it has a sulfonic group as an auxochrome that makes it highly water soluble and polar [2, 5]. Many studies published in the last few decades have reported the dangers of tartrazine dye, identifying its potentially deleterious effects, such as food allergies, mutagenicity, carcinogenicity, and phototoxicity [4, 6]. Various methods have been

suggested to handle the dye removal from water such as biological methods, flocculation, reverse osmosis, membranes process, adsorption, and solar wastewater treatment (SOWAT) methods are either expensive or ineffective for the complete color removal from wastewater [4, 7, 8].

Recently, advanced oxidative processes (AOP) can be applied to promote the degradation of a variety of organic compound, including dyes. AOPs include photocatalytic process as an environmentally friendly process and has considerable advantages over some existing technologies; usually leads to complete mineralization of organic pollutants into water and carbon dioxide, and inorganic salts by using atmospheric oxygen as oxidant and solar light as light source [9–11]. Advanced oxidation processes are based on the formation of the intensively reactive strong oxidizing agents such as hydroxyl radicals capable of mineralizing organic pollutants [12, 13]. As a catalyst, titanium dioxide is the most widely used photocatalyst for degradation of organic compounds due to its properties, such as non-toxicity, low cost and abundance, physical and chemical stability, superhydrophilicity, and

Table 1. Relevant characteristics of tartrazine [2–4]

Molecular, g/mol	Molecular structure	Solubility in water, g/L	λ_{\max} (absorption), nm	Color
534.36		200	427	Yellow 23

superior photocatalytic activity under UV radiation [3, 10, 11].

Recently, layered double hydroxides (LDH) have attracted considerable attention in recent years for water remediation due of its physicochemical properties such as larger surface area, high porosity, low-cost, and high anion exchange capacity [14–16]. Therefore, it is particularly advantageous to immobilize TiO_2 on appropriate materials in order to promote their separations and thus improve their regeneration, and to preserve their photocatalytic activities for possible practical applications in the field of wastewater depollution. In order to overcome this problem, some researches have been carried out with the aim of developing TiO_2 based photocatalysts support materials which include glass, cellulose, Hexagonal mesoporous silica (HMS), biopolymer chitosan, beads, polymers and its copolymers [4, 10, 11, 17]. Immobilization of TiO_2 particles on layered double hydroxides can leads to initiates the transfert of the photo-generated electrons to the surface of photocatalysts, which improve the photocatalytic activity. The $\text{TiO}_2/\text{ZnAl-LDH}$ has much high sedimentation velocities than TiO_2 particles facilitating their removal by physical process within minutes at the end of the photocatalytic degradation process [14]. Thus, the major focus of this work is to demonstrate TiO_2 immobilized on a layered double hydroxides (LDH) as being an efficient method for the degradation of tartrazine dye under sun.

EXPERIMENTAL

Materials

Tartrazine (TAR- $\text{C}_{16}\text{H}_9\text{N}_4\text{Na}_3\text{O}_9\text{S}$) was purchased to ACROS organics (USA). Relevant physico chemical properties of TAR are presented in Table 1. HCl and NaOH were obtained from HACH-COMPANY. All solutions were prepared with ultrapure water (Milli-Q).

Catalysts Preparation

The sample $\text{TiO}_2/\text{ZnAl-LDH}$ was synthesized by co-precipitation method similar to the procedure reported in previous studies [14, 16]. In a typical preparation, solution containing a fixed amount of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were added dropwise, to solution containing NaOH, Na_2CO_3 , and TiO_2 . The mixture was stirred until it was homogeneous, and then the resulting slurry was placed on oil bath at 60°C under magnetic stirring and reflux. The obtained solids were recovered by filtration, washed several times with distilled water, and then placed in the oven at 80°C for 24 h for drying (Fig. 1). Finally the samples were designated as $\text{TiO}_2(r)/\text{ZnAl-LDH}$, where r stands for the molar ratio of ($\text{Ti}^{4+}/\text{Al}^{3+}$) equal to 1.8, 3.6, and 5.4, with ratio ($\text{Zn}^{2+}/\text{Al}^{3+}$) equal to 2.

Photocatalytic Activity Experiments

The experiments were performed in a beaker of 250 mL with tartrazine solutions of desired concentra-

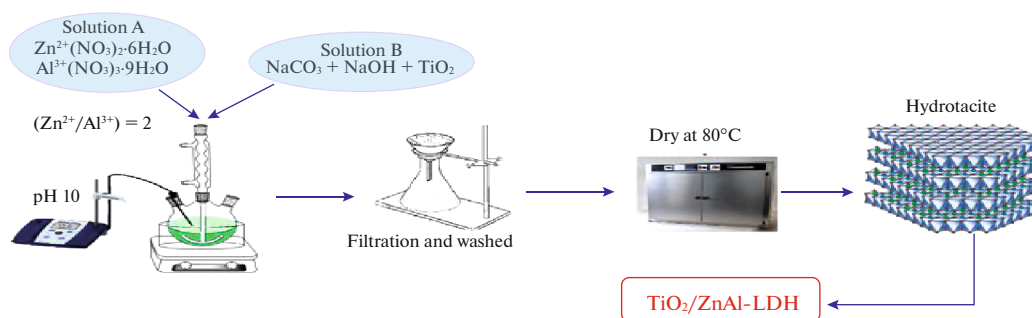
**Fig. 1.** Schematic preparation of $\text{TiO}_2/\text{ZnAl-LDH}$.



Fig. 2. Schematic representation of the experimental setup used for tartrazine; degradation assays under sunlight radiation.

tions are prepared by dissolving the corresponding amount of tartrazine in distilled water. The pH of the solution was adjusted by the addition of NaOH or HCl. To carry out the photochemical reaction, an appropriate amount of TiO₂/ZnAl-LDH is added to tartrazine solutions. All mixtures are magnetically stirred. Each sample is kept in the dark for 30 min. After ensuring the adsorption equilibrium, the experiments were then carried out under magnetic stirring for 2 h and under sunlight radiation. The solar flux was measured using a pyranometer (KIPP & ZONEN, CMP11) coupled to a data acquisition software. 4 mL of the aliquots were with draw not predetermined time intervals and centrifuged to separate the solid particles from the solution. The absorbance of the tartrazine solution at 427 nm is measured by UV-visible spectrophotometer (Shimadzu-1800) (Fig. 2). The percentage of degradation was estimated using the following equation [4, 12]:

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

where C_0 and C_t are the initial and concentration of tartrazine at time t , respectively.

Chemical Oxygen Demand (COD) Measurements

In order to confirm the mineralization of tartrazine the sample was taken before and after treatment and analyzed by COD based on the oxidation of organic materials by an excess of potassium dichromate in acidic medium and boiling, in the presence of silver sulfate and mercury sulfate. The COD reduction in percentage was calculated as follows [2, 10]:

$$\text{COD, \%} = \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0} \times 100,$$

where COD_0 and COD_t are the initial COD and COD at time t , respectively.

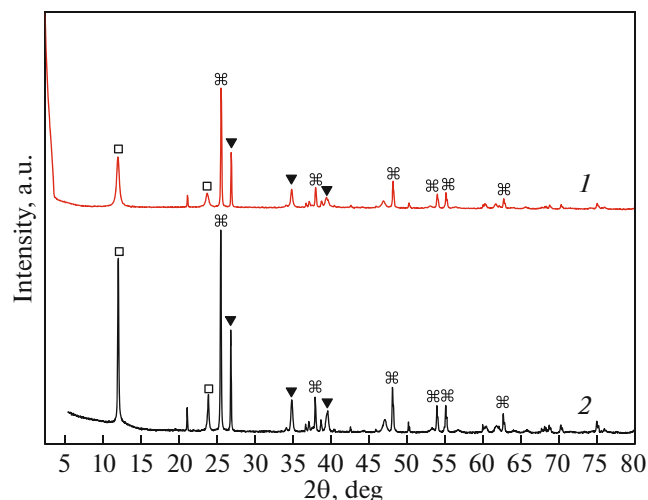


Fig. 3. XRD pattern of TiO₂/ZnAl-LDH before (1) and after (2) tartrazine degradation; (⊠) anatase, (▼) rutile, and (□) hydrotalcite.

Characterization

Powder X-ray diffraction patterns were recorded on a Siemens D500 diffractometer with CuK_α radiation in 2θ range from 5° to 70° were used to identify the crystalline phases of samples. The N₂ isotherms were used to determine the specific surface areas and pore volumes and diameters of the samples using the BET equation and BJH theory. FTIR spectra were recorded in a JASCO-460 plus model FTIR Spectrophotometer in the region of 400–4000 cm⁻¹ and the sample was prepared as KBr pellets under high pressure. The morphologies of the samples were studied using a JEOL JSM 5600 scanning electron microscope (SEM), combined with energy dispersive X-ray spectroscopy for the determination of materials composition.

RESULTS AND DISCUSSION

The XRD spectra obtained for TiO₂/ZnAl-LDH are shown in Fig. 3. The major peaks appeared at 2θ = 25.43°, 37.92°, 48.03°, 53.97°, 55.05°, 62.70°, 68.80°, 70.39°, and 75.05° corresponding to anatase phase (A) (JCPDS card no. 21-1272) and 2θ = 26.86°, 34.97°, and 36.60° corresponding to Rutile phase (R) similar to the standard spectra (JCPDS card no. 21-1276). We also observed a series of (00*l*) reflection peaks at low 2θ = 11.59° and 23.39° corresponding to reflection plane (003) and (006), respectively. Those patterns reflected the presence of a hydrotalcite-like LDH structure (JCPDS card no. 38-0486). These results suggest that the reconstructed phase is intercalated by carbonate anions and that TiO₂ is adsorbed on the surface of the LDH. These results are in good agreement with several works [16, 18].

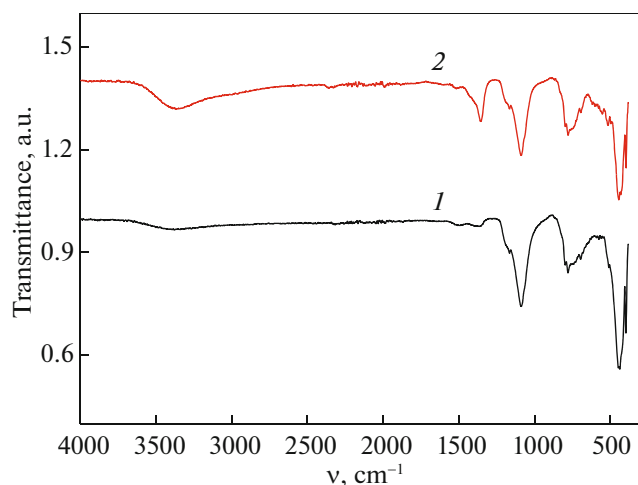


Fig. 4. FTIR spectra of TiO_2/ZnAl before (1) and after (2) tartrazine degradation.

Infrared spectroscopy of TiO_2/ZnAl -LDH samples before and after photocatalytic degradation are shown in Fig. 4. The spectrum of TiO_2/ZnAl -LDH sample illustrated the presence of peaks characterized to a hydroxalate and incorporation of TiO_2 the LDH matrix. Figure 4 shows a broad band at 3367 cm^{-1} related to the stretching vibration of the hydroxyl groups of the adsorbed water on their surface and interlayer space of the material. The band observed at about 1353 cm^{-1} is assigned to the asymmetric stretching mode of the carbonate anions. Absorption peak at 1086 cm^{-1} assigned to the O–H bending vibration due to the reabsorption of water from the atmosphere. The vibrations of metal–oxygen bonds related to the metallic cation used in the synthesis of the LDH components and TiO_2 which presents a band at 777 cm^{-1} due to the vibration of the Zn/Al–OH bond. On the other hand, the bands appearing at frequencies between $400\text{--}800\text{ cm}^{-1}$ assigned to Ti–O–Ti vibration, this results are on harmony with similar works [16, 19–21].

According to the IUPAC classification, the sample exhibit a typical type IV isotherms of mesoporous materials, with the presence of a hysteresis loop type H1. The results of the textural analysis of the synthesized solid: the BET surface area $S = 29.47\text{ m}^2/\text{g}$, average pore diameter $d = 14.10\text{ nm}$, and pore volume $V = 0.08\text{ cm}^3/\text{g}$ of the catalysts are confirmed the obtained mesopores ($2 < d < 50\text{ nm}$). These results are in agreement with previously reported findings by Aoudjit et al. [16].

Scanning electron microscopy (SEM) measurement are shown in Fig. 5 also confirm that the formation of agglomerates with a spongy appearance, which are responsible for the increased heterogeneity of the material, as reported by Aoudjit et al. [16]. The EDX results confirm the incorporation of TiO_2 particles in the LDH structure as shown in Fig. 6.

Photodegradation of Tartrazine

Assessment of treatment method on the degradation of tartrazine. During our study, three types of elimination procedures were tested for the efficiency of TAR degradation in contaminated water, photolysis (in the absence of our catalyst), adsorption and photocatalysis. The graph shown in Fig. 7 clearly illustrates the importance of photocatalysis in the elimination of TAR, while the effect of both adsorption and photolysis was minimum (22 and 4%) after 120 min of the reaction time. This results are on harmony with those obtained by Tayab et al. [2], where the photolysis of tartrazine does not exceed 5%. In the case of the photocatalysis process, the combined system of TiO_2/ZnAl -LDH and solar radiation increased the removal efficiency of the tartrazine up to 82% in compared to photolysis and adsorption methods. These results are in good agreement with similar works [3, 4, 13]. The results allowed concluding that the elimination of the dye is actually induced by the photocatalytic process with the participation of TiO_2/ZnAl -LDH.

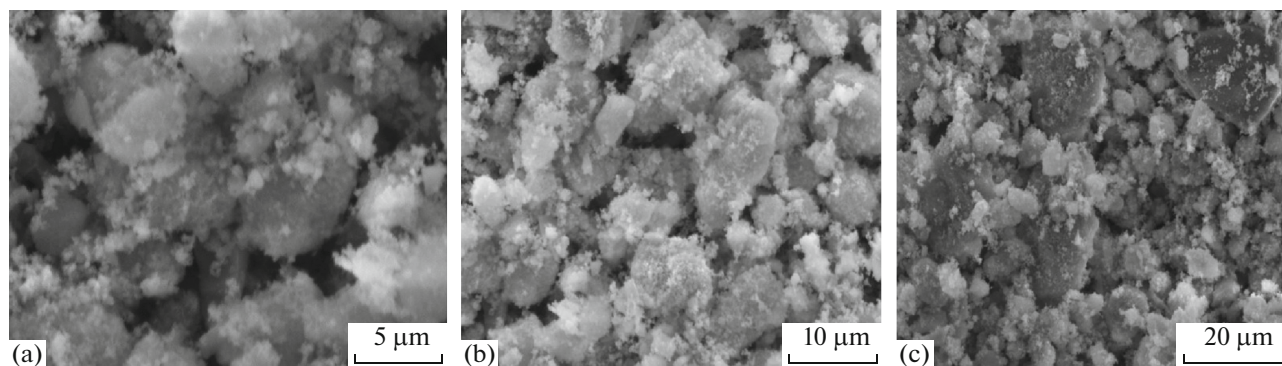


Fig. 5. SEM images of TiO_2/ZnAl material.

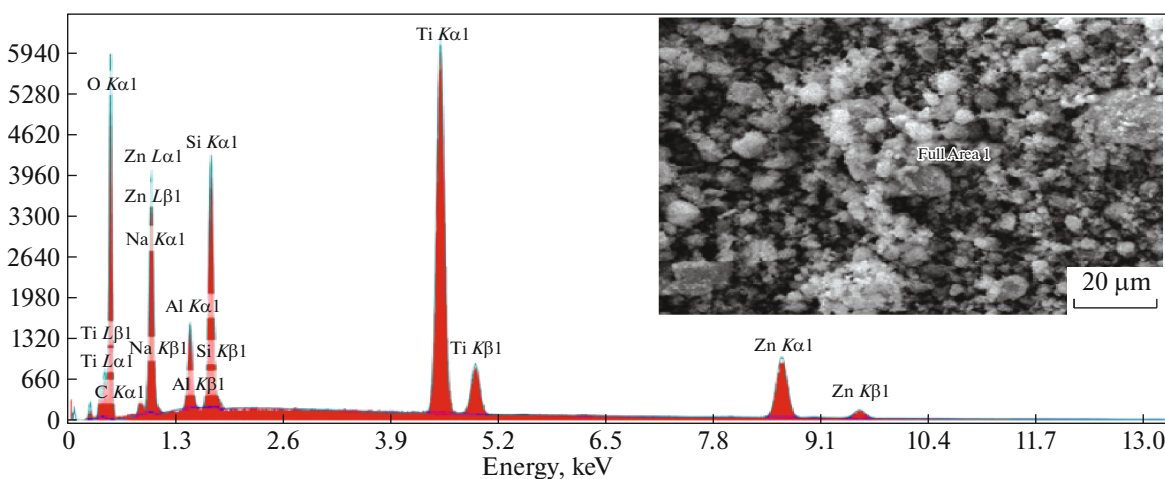


Fig. 6. EDX and mapping of TiO₂/ZnAl-LDH material.

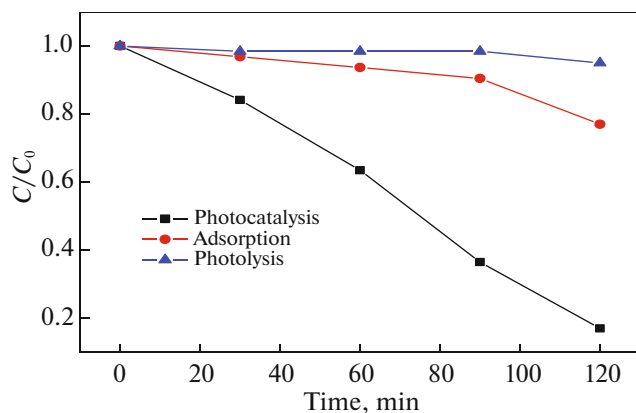


Fig. 7. Degradation of tartrazine under different processes ($C_{\text{TAR}} = 20 \text{ mg/L}$, $C_{\text{catalyst}} = 0.1 \text{ g/L}$, and free pH 6).

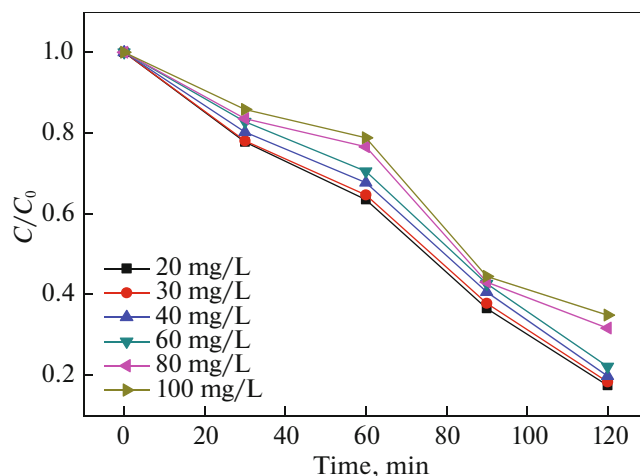


Fig. 8. Photodegradation of tartrazine with time at different concentrations in sunlight (free pH 6 and $[\text{catalyst}] = 0.1 \text{ g/L}$).

Effect of Initial Pollutant Concentration

The effect of initial TAR concentration on the rate of photodegradation has been studied by varying the initial TAR concentration from 20 to 100 mg/L with optimal catalyst (TiO₂-HDL) loading of 0.1 g/L at neutral pH 6 for a reaction time of 120 min (Fig. 8). As shown in Fig. 9, the photocatalytic degradation efficiency decreased with increasing the initial TAR concentration from 20 to 100 mg/L. After 120 min, 17.38% reduction in the degradation of the 100 mg/L tartrazine solution was observed. This could be because of insufficient quantity of generated OH⁻ radicals present in the solution, which influence the photodegradation process favorably [2]. On the other hand, the increasing in TAR concentration can lead to the decreases of the photon path length that penetrates the pollution solution [14], the optimal concentration is found to be 20 mg/L with a degradation yield of 82.53%. Figure 10 shows the absorption intensity of

TAR solar photocatalysis using of 0.1 g/L TiO₂-HDL as photocatalyst, the important change in the peak intensity at 427 nm is observed. Increasing the solar exposure time the absorption intensity decreased, the reduction of this peaks also indicates that the chromophoric groups of tartrazine are breakdown as reported by Aoudjit et al. [4].

Effect of Photocatalysts Dose of TiO₂

The effect of dose of TiO₂ on the degradation of TAR ($C_{\text{TAR}} = 20 \text{ mg/L}$, free pH) has been studied. The results are shown in Fig. 10. The photodegradation of TAR reaches 40, 79, and 82% for TiO₂ doses of 1, 3, and 5%, respectively, after 120 min under sun radiation. Therefore, it can be considered that in this chosen range, the photocatalytic efficiency is optimal for a dose of 5%. The difference between the amounts adsorbed for the three used percentages of TiO₂ is

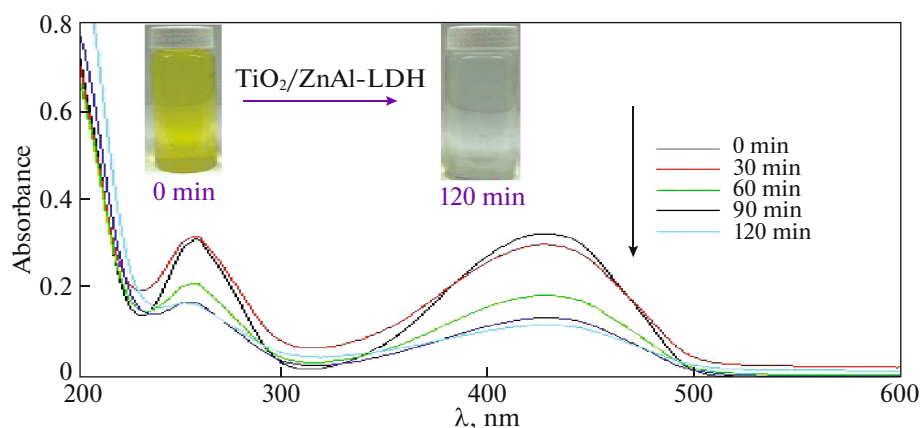


Fig. 9. UV-Vis spectra during degradation process with as-synthesized $\text{TiO}_2/\text{ZnAl-LDH}/\text{dye}$ systems.

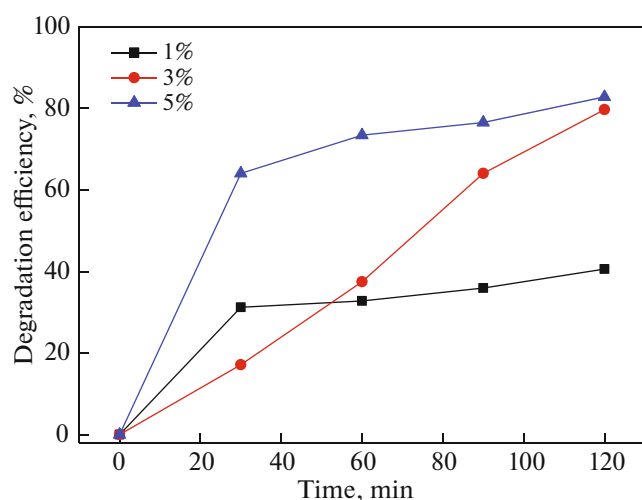


Fig. 10. Influence of the doses TiO_2 (1, 3, and 5%) in LDH- TiO_2 ($C_{\text{TAR}} = 20 \text{ mg/L}$, $C_{\text{catalyst}} = 0.1 \text{ g/L}$, and free pH 6).

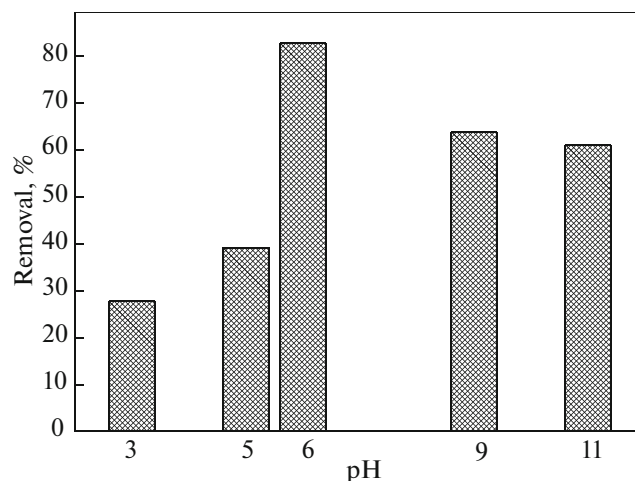


Fig. 11. The influence of the initial pH on tartrazine photocatalytic degradation ($C_{\text{TAR}} = 20 \text{ mg/L}$, $C_{\text{catalyst}} = 0.1 \text{ g/L}$).

probably due to the electrostatic interactions between TAR and the TiO_2 particles immobilized on the surface of the LDH sheets. This adsorption is more marked in the case of a percentage of 5%, which justifies the use of LDH as a support to promote the adsorption process and consequently the degradation of tartrazine.

Effect of pH

The degradation for TAR is studied as a function of pH of the solution (3, 5, 6, 9, and 11). The pH adjustment of the solutions was carried out before irradiation using dilute solutions of NaOH or HCl, as shown in Fig. 11. The results obtained indicate that the photocatalytic degradation is strongly related to the initial pH of the tartrazine solution. The highest removal efficiency, approximately 82%, was obtained at free pH 6, close to that of the natural aquatic environment,

such a result that has been reported by other authors [2, 4].

Kinetics of Tartrazine Solar Photocatalytic Degradation

The kinetics of photocatalytic degradation of tartrazine can be depicted using the first-order equation given by following equation [12, 14]:

$$\ln\left(\frac{C_0}{C_t}\right) = k_{\text{app}}t, \quad (2)$$

where k_{app} is the pseudo-first-order rate constant (min^{-1}); C_0 is the initial concentration; C_t is the concentration of tartrazine at time t (min).

The half-life time ($t_{1/2}$) of the photodegradation process is given as:

$$t_{1/2} = \ln 2/k_{\text{app}}. \quad (3)$$

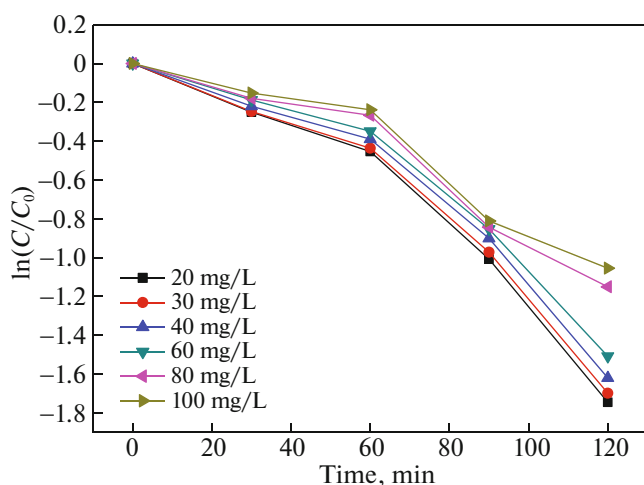


Fig. 12. $\ln(C/C_0)$ vs. time for different initial dye concentration (10, 20, 40, 60, 80, and 100 mg L⁻¹), with $C_{\text{catalyst}} = 1$ g/L, and free pH 6.

The apparent rate constant k_{app} and R^2 were calculated from the linear plot $\ln(C_0/C)$ vs. irradiation time (t) as shown in Fig. 12. With an increase in tartrazine concentration from 20 to 100 mg/L, the degradation rate constant decreases from 0.014 to 0.009 min⁻¹ and the half-life time ($t_{1/2}$) increases from 49.28 to 76.66 min when the value of TAR was increased from 20 to 100 mg/L. Consequently the pseudo first-order kinetic can really be used to describe the photodegradation of tartrazine onto the TiO₂/ZnAl-LDH catalyst in agreement with similar works [3, 4, 13].

Recyclability of TiO₂/ZnAl-LDH Catalyst

The reusability of TiO₂/ZnAl-LDH catalyst in the photodegradation of TAR ($C_{\text{TAR}} = 20$ mg/L) at free pH 6 was also studied under sunlight conditions over the course of 120 min (Fig. 13). The photocatalyst in any run was collected, washed with distilled water, dried and then used in a new experiment. The reduction in the activity (4%) of reused catalyst after 5 cycles may result from fouling of the photocatalyst due the deposition of hydroxide radicals on the surface of the catalyst. It result that the catalyst maintained good photodegradation capacity after fifth treatment cycles. This observation can be explained by the high stability of TiO₂-HDL catalyst, while its surface remained resistant to agglomeration or sintering under the stated experimental conditions. These results are in agreement with the results of DRX and FTIR obtained previously.

Mineralization of Tartrazine Dye by COD Analysis

Chemical oxygen demand (COD) experiment was carried out at fixed time (120 min), catalytic dosage

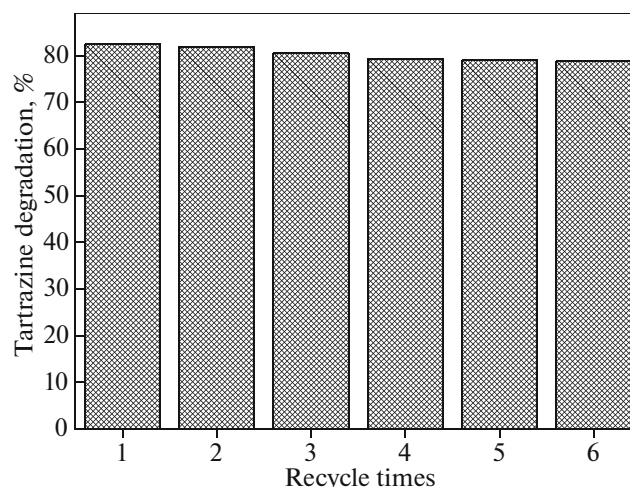


Fig. 13. Photodegradation of tartrazine over six catalytic cycles in sunlight ($C_{\text{TAR}} = 20$ mg/L, $C_{\text{catalyst}} = 0.1$ g/L, and free pH 6).

(0.1 g/L), and concentration of dye (20 mg/L). The values of COD were found to be reduced from 103 mg/L initial COD of TAR dye to 34 mg/L at the final experiments, and the percentage of mineralization is 66.99%. Similar results was also observed by Tayeb et al. [2].

CONCLUSIONS

The present work reported the development of TiO₂ immobilized on a layered double hydroxides (LDH) materials by co-precipitation method and their application for degradation of tartrazine using solar irradiation. The results show that TiO₂/ZnAl-LDH exhibited good photocatalytic activity with a degradation of 82% for tartrazine at free pH 6 has been found within 120 min under solar irradiation. It can be concluded that TiO₂/ZnAl-LDH is a stable, robust, effective, recyclable, and separable photocatalyst for dye removal. Thus, it is a promising material for environmental remediation.

ACKNOWLEDGMENTS

This work was supported by the Solar Equipment Development Unit (UDES) Algeria.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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