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PREPARATION OF TiO_2-ACTIVATED KAOLINITE COMPOSITE FOR PHOTOCATALYTIC DEGRADATION OF RHODAMINE B DYE

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ABSTRACT. Rhodamine B (RhB) is one of the prominent dyes discovered to be carcinogenic and mutagenic substance present in the ecosystem. Alteration of the characteristics of TiO_2 through modification with clay influences the behavior of some organic molecules at its surface, and thus its photocatalytic properties. This study investigates the photocatalytic degradation of RhB using TiO_2-activated kaolinite composite (TiO_2-AKC). TiO_2-AKC was prepared in absolute ethanol and characterized using SEM, EDX, TEM, BET and FTIR. The photodegradation of RhB using TiO_2-AKC at room temperature under visible-light was studied at various time intervals and the concentration of RhB was monitored using Ultraviolet-Visible spectrophotometer. Characterisation of TiO_2-AKC revealed an adequate distribution of TiO_2 over the AKC surface, with an enhanced surface area (TiO_2-AKC 808 m^2g^{-1}, TiO_2 50.0 m^2g^{-1}, AKC 20.6 m^2g^{-1}) necessary for effective degradation. The degradation was efficient in TiO_2-AKC than in sole TiO_2 resulting in 99.51% and 88.35%, respectively. The experimental data was analysed using zeroth and first order kinetics, parabolic diffusion, and modified Freundlich model. The degradation kinetics conforms to first order kinetics in TiO_2-AKC and sole TiO_2. The mechanism of the degradation using TiO_2-AKC fit into modified Freundlich model and parabolic diffusion model while sole TiO_2 was best described by parabolic diffusion model.

KEY WORDS: Kaolin, Kinetics, Organic dyes, Photodegradation, Pollutants, Titanium(IV) oxide

INTRODUCTION

One of the many synthetic dyes is Rhodamine B which had remained a prominent, more useful industrial organic dye. It is used mainly in textile and paper industries, and also applicable in water tracing and cell membrane studies. It is however true that more than 12% of working dyes used in textiles and paper are released as effluents to the environment [1]. These colored effluents usually impact greater degree of environmental pollution, and therefore necessary to treat the effluent before discharging to the environment [2]. Though attempt have been made using several processes such as; adsorption, membrane filtration, chemical coagulation, biological treatment among others for the removal of these toxic materials. However, some of the processes either generate secondary pollutants or were not cost effective. In recent years, photodegradation using semiconductors such as titanium(IV) oxide (TiO_2), as photocatalyst had been employed [3-5].

TiO_2 and ZnO are semiconductors which are often used as catalytic agents due to their high stability, low cost and high efficiency. TiO_2 has been reported to exhibits higher catalytic activity under the ultraviolet radiation than ZnO [1]. Previously, researchers had sought for several ways of degrading dyes. Whereas, degradation of dyes using TiO_2 nanostripe has been applied to dyes degradation in wastewater [6]. Titanium(IV) oxide-activated carbon composite (TiO_2-AC) has also been prepared for degrading Rhodamine B (RhB) dye with high RhB removal efficiency [7].

Kaolinite, a class of layered silicate mineral with one tetrahedral sheet and one octahedral sheet has various uses as a result of its properties such as natural whiteness, fine particle, non-abrasive, and chemical stability [8]. It has been considered a good effluent removal in

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wastewaters, especially due to its high porous structure, which accounts for its high adsorptive property [9]. Titanium(IV) oxide-kaolinitic clay composite has been considered as a more potent photocatalyst for degradation, due to its high photo stability, cost effectiveness and high degrading efficiency. To the best of our knowledge, there is an unfilled vacuum in research findings into the use of titanium(IV) oxide-activated kolinitic clay composite for photocatalytic degaradation of dyes. Therefore, it is very important to dig-in for alternative routes aiming at more cost effective and environment friendly methods of the previously established degrading types. This research targets investigations into the effectiveness of photocatalytic degradation of Rhodamine B dye from aqueous solution using TiO_2-AKC composite.

EXPERIMENTAL

Reagents

Analytical grade reagents and chemicals used in this work are as follows: TiO_2 powders (80% anatase, 20% rutile; BET surface area 50 m^2/g), Rhodamine B dye (RhB), nitric acid (purity 98%, 1.51g/cm^3), and absolute ethanol (BDH Analar, 95% UN No. 1097).

Preparation of sample

The kaolin clay sample was ground, washed with deionised water, dried and sieved into particle size of <90 µm. It was impregnated into 1 M HCl for 4 h to remove impurities, washed with deionised water and then dried in the oven at 105 °C for 2 h [10, 11]. A 100 g of the pre-treated sample was activated with 400 mL of 1 M $HNO_3$and stirred at 500 rpm for 2½ h at 90 °C. The sample was then filtered, washed to neutral pH with deionized water and oven dried at 105 °C to prepare activated kaolinitic clay (AKC) samples [11].

Composite preparation

A 10 g of AKC was disperse in 1000 mL of deionised water and stirred for 2 h. 7 g of the TiO_2 was mixed with the dispersion to obtain 0.7: 1 TiO_2-AKC slurry which was then stirred for 24 h. The resulting slurry was centrifuged at 4,000 rpm for 10 min. The solid layer was washed with deionised water and centrifuged. A 1:1 water-ethanolic mixture was then added to the resulting TiO_2-AKC composite, prior to hydrothermal treatment in an autoclave at 120 °C for 2 h. The composite was re-centrifuged at 4000 rpm for 15 min and oven dried at 110 °C for 1 h. It was then ground to fine particles and stored for further use [12, 13].

Characterization of the prepared composite

Transmission electron microscope (TEM) and scanning electron microscope (SEM) Model JSM-7600F was used for morphological studies. Energy dispersive X-ray spectroscope (EDS), Oxford Instrument was used for chemical composition. Fourier transform infrared spectroscope (FTIR), Model spectrum 100, Perkin-Elmer was employed to determine the functional properties. The surface area and pore dimensions were assessed using Brunauer-Emmett-Teller (BET) instrument.

Photocatalytic experiment

A 0.5 g of TiO_2-AKC composite was taken into 250 mL conical flask and 100 mL of 50 mg/L Rhodamine B was added. Prior to irradiation, the suspension was stirred in the dark for 30 min on a magnetic stirrer for adsorption/desorption equilibria to be established on the surface of the prepared TiO_2-AKC particles. Thereafter, the suspension was placed under solar light irradiated at $75 \pm 3x10^3$ I_x and 15 mL of the component mixture were taken at time intervals of 5, 10, 30, 60, 90, 120 min, centrifuged immediately after taken and then filtered through a millipore filter paper (0.22 mm). The residual concentrations of the dye in the solution were analysed using UV-Visible spectrophotometer at 554 nm to determine the extent of degradation of RhB [12, 14]. The percentage of Rhodamine B dye degradation efficiency was calculated using equation 1:

$$D_e(\%) = \frac{Co - Ce}{Co} \times 100 \tag{1}$$

where D_e is the degradation efficiency in percent (%), C_o is the initial concentration of RhB dye prepared, and C_e is the equilibrium concentration of RhB.

Degradation kinetic model

Photodegradation kinetics using TiO_2-AKC composite, under different reaction conditions was examined using zero and first order kinetics. The mechanism of degradation process was monitored using parabolic diffusion and modified Freundlich model [15-16].

Zero order kinetics describes the degradation process and expressed using equation 2,

$$C_e - C_o = -\mathrm{kt} \tag{2}$$

First order kinetics describes the systems where the rate of degradation of dyes depends on the amount of dye molecules and expressed with equation 3,

$$\log\left(\frac{C_e}{C_o}\right) = -\mathrm{kt} \tag{3}$$

Parabolic diffusion model explains the degradation process as diffusion controlled process. The expression is given in equation 4,

$$\frac{1-(\frac{C_e}{C_o})}{t} = -\mathrm{kt}^{-1/2} + \mathrm{a} \tag{4}$$

The modified Freundlich model explains experimental data in terms of ion exchange and diffusion-controlled process. A good fit into the Freundlich model indicates a heterogeneous surface binding. The expression is given in equation 5

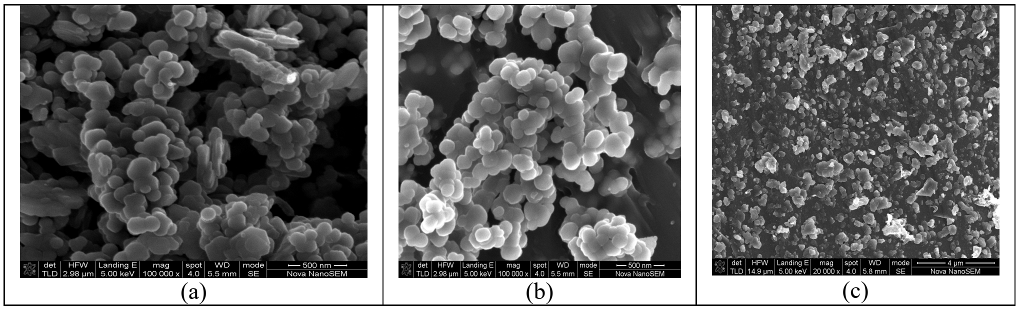
$$\log(1 - \mathrm{C_e/C_o}) = \log\mathrm{k} + \mathrm{b}\log\mathrm{t} \tag{5}$$

where, C_e - equilibrium concentration (mg/L), C_o - initial concentration of the dye(mg/L), k - rate constant, t - time, while a and b are non-specific constant obtained from the graphical data.

RESULTS AND DISCUSSION

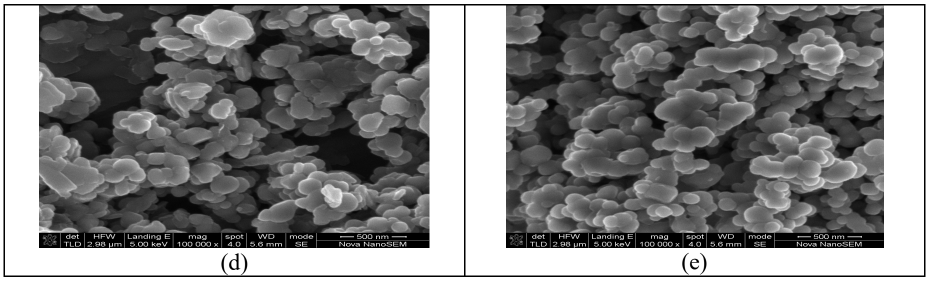
Scanning electron microscopy (SEM)

Figure 1a shows the SEM micrograph of TiO_2-AKC, pure TiO_2 and AKC. The SEM micrograph of TiO_2-AKC indicates changes in surface morphology with the emergence of spongy discrete particles that differ from pure TiO_2 and AKC. The SEM micrograph of TiO_2-AKC and TiO_2 (Figure 1b) after degradation revealed that the dye molecules were not retained on the pore surfaces, and had been degraded in both TiO_2-AKC and TiO_2 surfaces, respectively [17].



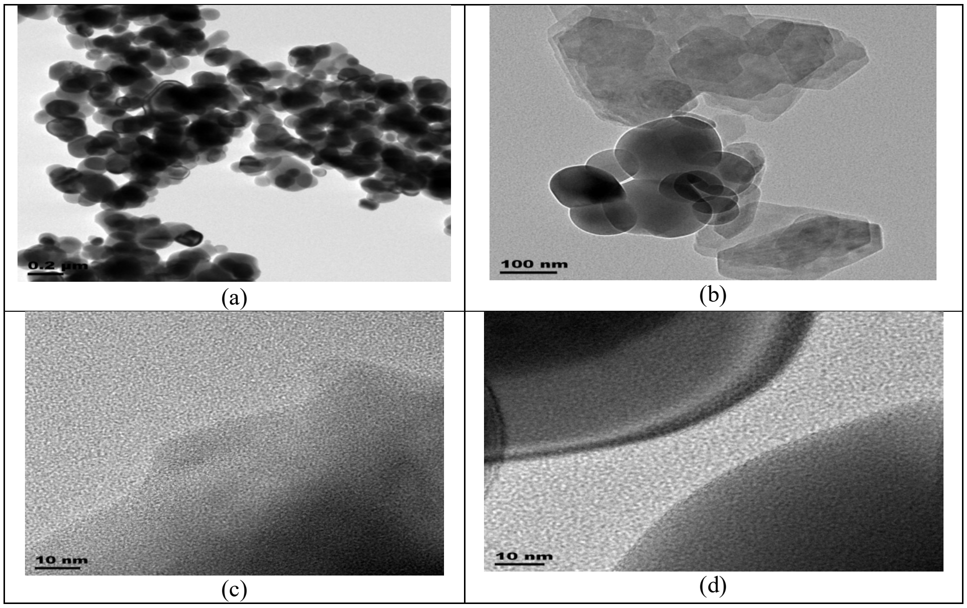
(a) (b) (c)

Figure 1a. SEM imaging of (a) TiO_2-AKC, (b) TiO_2 and (c) AKC.



(d) (e)

Figure 1b. SEM images after degradation of (d) TiO_2-AKC and (e) TiO_2.



(a) (b) (c) (d)

Figure 2. TEM images of (a) TiO_2-AKC, (b) TiO_2, (c) after TiO_2-AKC and (d) after TiO_2.

Transmission electron microscopy

The TEM micrographs of TiO_2-AKCand TiO_2 before and after photodegradation show that there is internal distribution of TiO_2, over the AKC surface as shown in Figure 2. TiO_2 is uniformly distributed on AKC and the photocatalytic activity of the TiO_2 composite depends on their surface morphology.

Energy dispersed X-ray spectroscopy (EDX) analysis

The EDX analysis was done to ascertain the percentage weight contents in the prepared composite. The spectra as shown in Figure 3 indicate the presence of Ti, Si, O, C and Al has major elements with composition of 15.2%, 8.61%, 48.71%, 22.34%, and 5.15%, respectively. This confirms that the composite preparation was achieved.

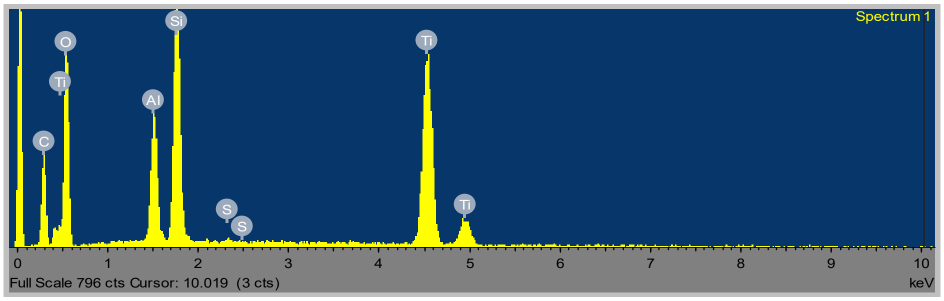


Figure 3. EDX spectrum of the TiO_2-AKC composite.

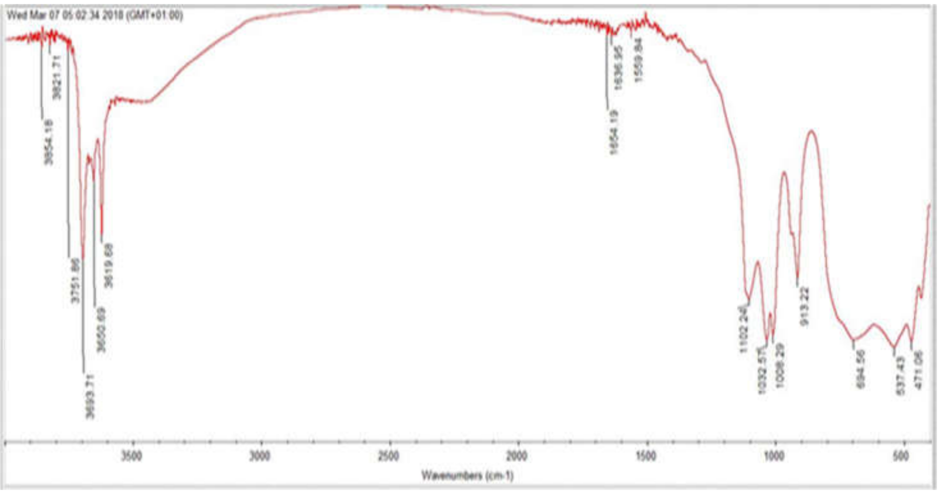


Figure 4a. FTIR spectra TiO2-AKC.

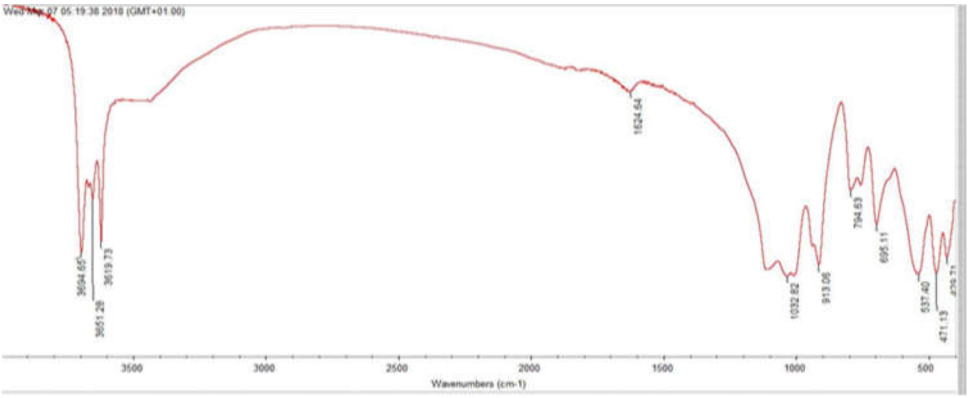


Figure 4b. FTIR spectra of AKC.

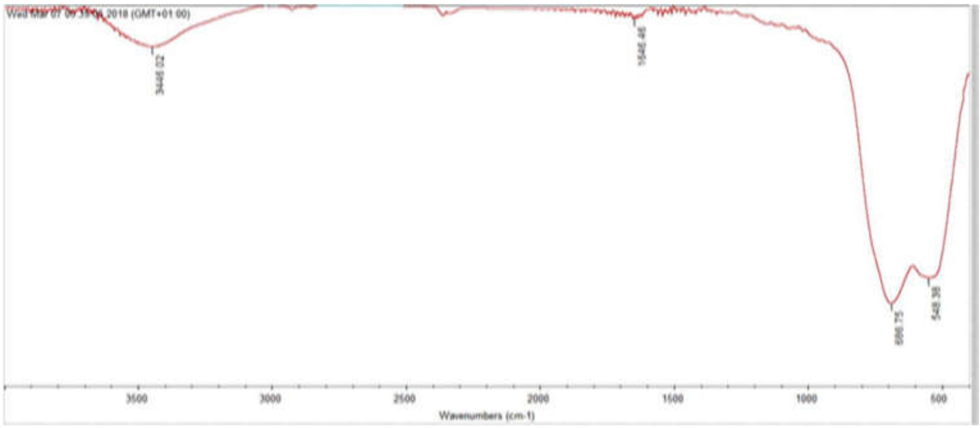


Figure 4c. FTIR spectra of TiO_2.

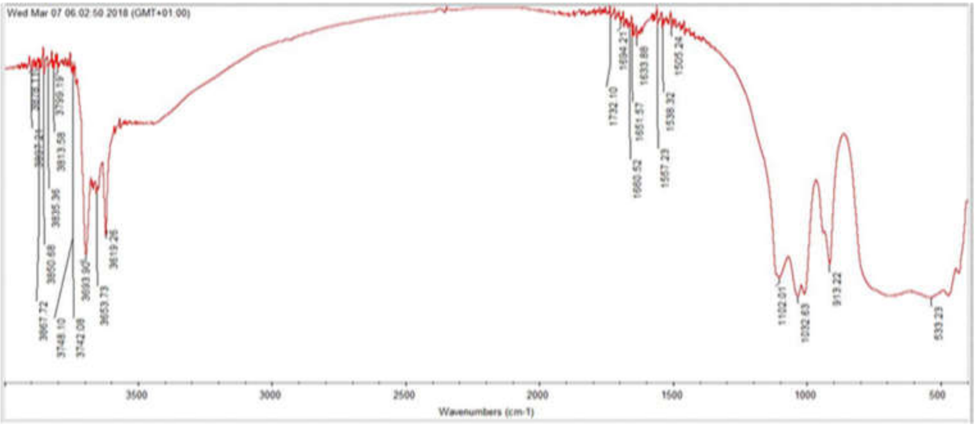


Figure 4d. FTIR spectra of TiO_2-AKC after degradation.

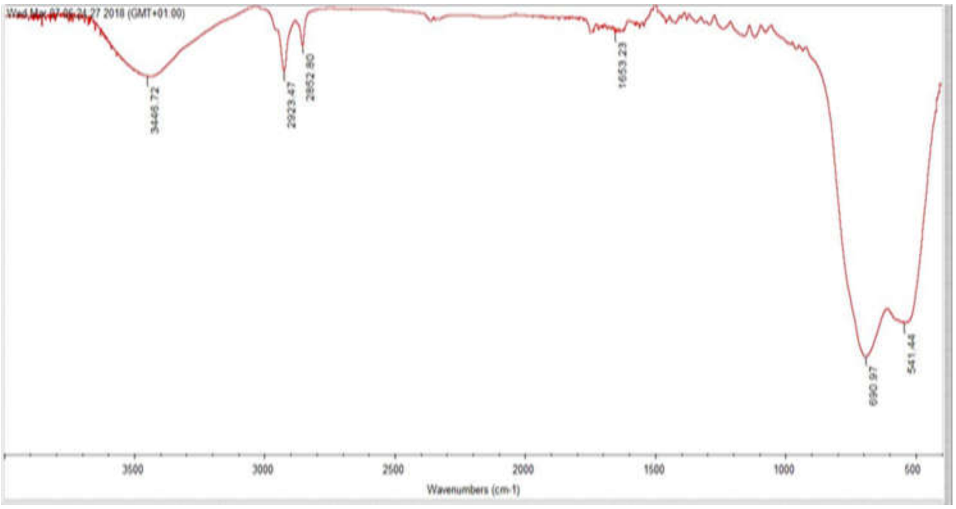


Figure 4e. FTIR spectra of TiO_2 after degradation.

Fourier transformed infra-red spectroscopy (FTIR) analysis

The FTIR spectra of TiO_2-AKC composite and pure TiO_2 analysis before and after degradation of RhB are presented in Figure 4a-4e. The characteristics absorption signals in AKC spectra at 3694, 3651 and 3619 cm^{-1} is attributed to OH stretching vibrations; 1032 and 471 cm^{-1} vibrations are attributed to Si-O [18]. The observed stretching vibration at 3448 and 1648 cm^{-1} on TiO_2 spectra is assigned to OH stretch and Ti-OH vibration signals respectively [19]. Distinct vibrational signals at 3821 and 3751 cm^{-1} that appears on TiO_2-AKC composite's spectra could result from the incorporation of TiO_2 onto AKC. Formation TiO_2-AKC composite could also account for the disappearance of distinct OH stretching vibration of TiO_2 at 3446 cm^{-1} in TiO_2-AKC spectra. Similar characteristics signals were observed on TiO_2-AKC and pure TiO_2 spectra before and after degradation. For instance, the spectra of TiO_2-AKC before and after degradation show slight shift in absorption bands from 3751 cm^{-1} (before) to 3748 cm^{-1} (after); 3650 cm^{-1} (before) to 3653 cm^{-1} (after). This is an indication that RhB was not retained on the TiO_2-AKC composite and pure TiO_2, and hence a suggestion that photodegradation had taken place at both TiO_2-AKC and pure TiO_2, respectively [20].

Table 1. Brunauer Emmett and Teller (BET) analysis.

Sample	Specific surface area (m^2g^{-1})	Average pore volume (cm^3g^{-1})	Average pore diameter (nm)
TiO_2-AKC	808	0.274	1.947
Pure TiO_2	50.0	0.087	9.894
AKC	20.6	0.018	3.48

BET analysis on TiO_2-AKC composite and TiO_2.

Brunauer Emmett and Teller (BET) analysis

Table 1 summarizes BET analysis of the composite. The results reveal that AKC and pure TiO_2 are mesoporous materials. However, the specific surface area and average pore volume of the composite TiO_2-AKC was found to be microporous. This could be as a result of the processing method employed for the preparation of the composite. International Union of Pure and Applied Chemistry classified pores as micropore (< 2 nm), mesopores (2-50 nm) and macropores (> 50 nm) [21].

Photocatalytic degradation experiment

Photocatalytic activity experiment of the pure TiO_2 as well as TiO_2-AKC composites was studied by evaluating the degradation rate of RhB in aqueous solution in the presence of UV light irradiation. As shown in Figure 5a and 5b, the result revealed that the removal of RhB increases gradually with the increasing illumination time. Initially, about 51% and 33% of RhB was adsorbed on TiO_2-AKC and TiO_2, respectively, until adsorption equilibrium was attained at the end of 30 min in the dark. The concentration of RhB decreases with increase in degradation time under light irradiation.

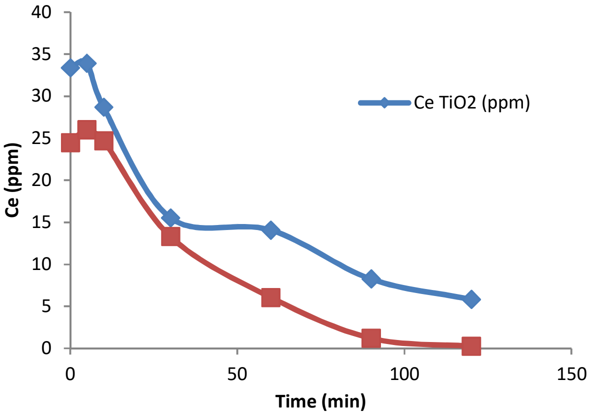


Figure 5a. Degradation of RhB by TiO_2 and TiO_2-AKC composite (C_o= 50 mg/L, w = 0.5 g, t = 0-120 min, T = 28 ± 2 °C, n = 3, SD = 0.03).

TiO_2-AKC composite shows better performance for degradation of RhB than the pure TiO_2. This could result from the enhancement of photocatalytic degradation activity of pure TiO_2 by AKC, which had been initially lowered during calcination as reported by Tayade *et al.* [22].

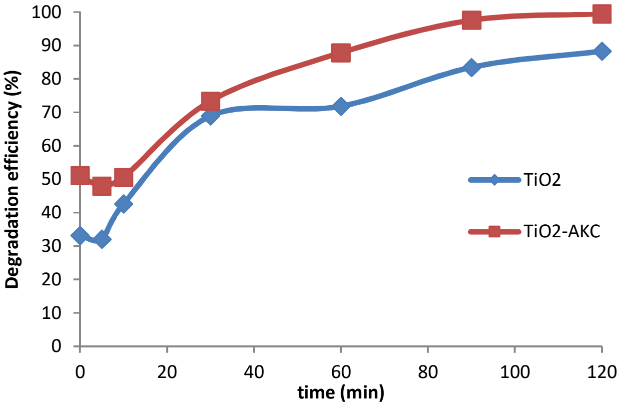


Figure 5b. Degradation efficiency of RhB by TiO_2 and TiO_2-AKC composite. (C_o= 50 mg/L, w = 0.5 g, t = 0-120 min, T = 28 ± 2 °C, n = 3, SD = 0.03).

Degradation kinetic studies

The rate and mechanism of successive adsorption and degradation processes were analysed using zero-order, first-order, parabolic-diffusion and modified Freundlich model. The correlation coefficient (R^2) and rate constants (k) are shown in Table 2.

Table 2. Correlation coefficient (R^2) and the rate constant (k) of the zero-order, first order, parabolic diffusion and the modified Freundlich kinetic model for both TiO$_2$ and TiO$_2$-AKC.

Kinetic models	TiO$_2$		TiO$_2$-AKC	
	R^2	*k*	R^2	*k*
Zero order (mgL^{-1}min^{-1})	0.023	-0.650	-1.45	0.668
First order (min^{-1})	0.979	-0.015	0.936	-0.017
Parabolic diffusion (mgkg^{-1}min$^{-1/2}$)	0.999	0.155	0.977	4.025
Modified Freundlich (Lg^{-1}min^{-1})	0.993	9.462	0.978	0.298

Correlation coefficient (R^2) and the rate constant (*k*) of the zero-order, first order, parabolic diffusion and the modified Freundlich kinetic model for both TiO$_2$ and TiO$_2$-AKC.

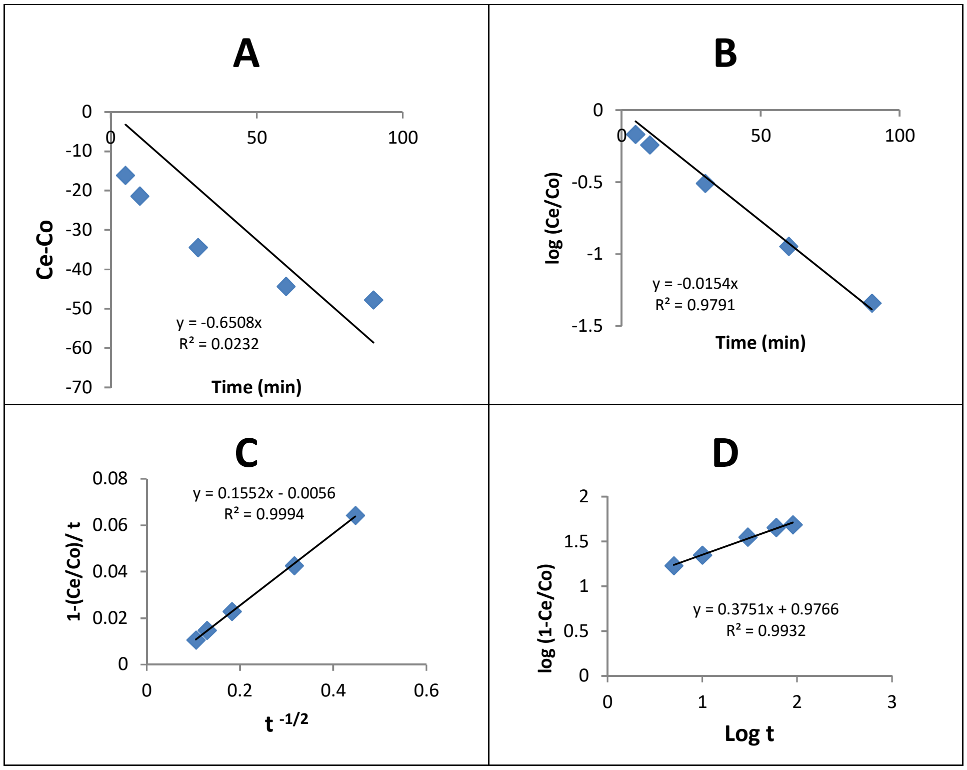


Figure 6. Photocatalytic degradation kinetics plot for (A) zeroth order, (B) first order, (C) parabolic diffusion model and (D) modified Freundlich model of TiO$_2$.

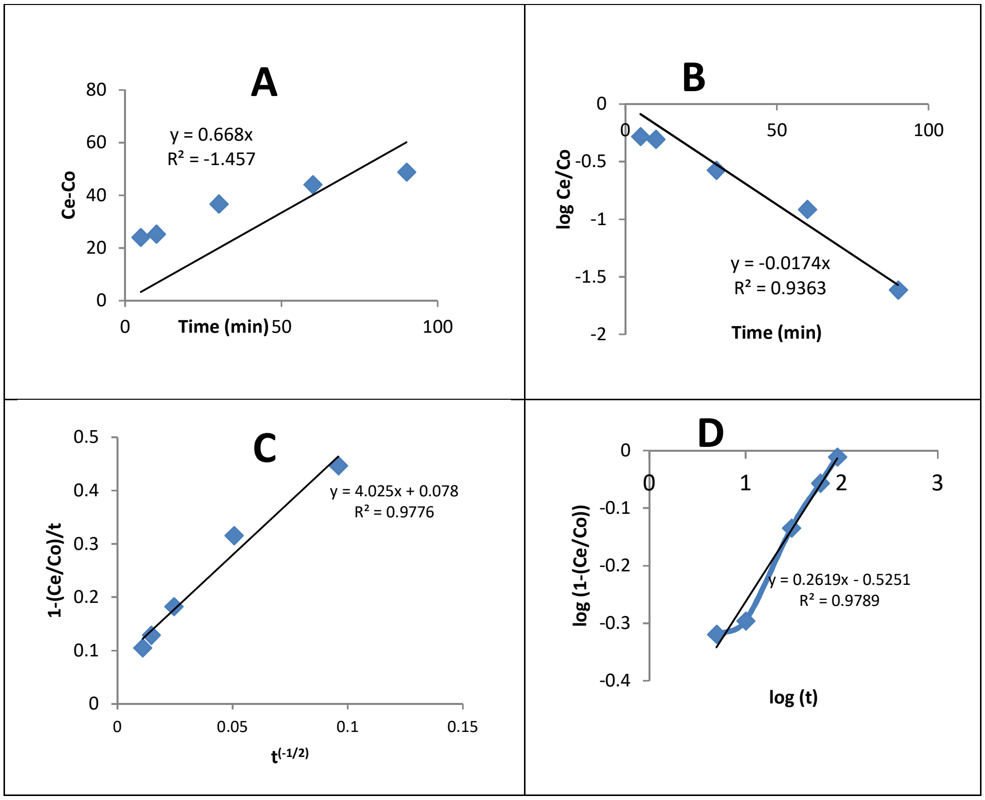


Figure 7. Photocatalytic degradation kinetics plot for (A) zeroth order, (B) first order, (C) parabolic diffusion model and (D) modified Freundlich model of TiO_2-AKC.

The degradation kinetics model of TiO_2-AKC and TiO_2 could be described using first order, parabolic diffusion and Freundlich kinetic model. Though, parabolic diffusion best describes the kinetics of RhB in TiO_2 as shown in Table 2. This suggested that the process is controlled by heterogeneous diffusion similar to the report of Mukhlish *et al.* [16]. TiO_2-AKC composite fits into the modified Freundlich and parabolic diffusion model therefore; the process involves molecular ion exchange [16].

CONCLUSION

The prepared TiO_2-AKC composite was effective for photocatalytic degradation of Rhodamine B dye in aqueous solutions. The experimental results also revealed that TiO_2-AKC composite was more effective for degradation of Rhodamine B dye than sole TiO_2 using solar light. The experimental data analysed using zeroth and first order kinetics, parabolic diffusion, and modified Freundlich model conform into first order kinetics in TiO_2-AKC and sole TiO_2. The mechanism of the degradation process of RhB using TiO_2 fit best into parabolic diffusion model while TiO_2-AKC composite fit into the modified Freundlich and parabolic diffusion model. This finding also suggests that TiO_2-activated kaolinite composite is a good photocatalyst for the degradation of dyes.

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