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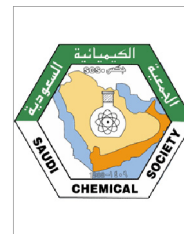
ORIGINAL ARTICLE

Synchronous role of coupled adsorption and photocatalytic degradation on CAC–TiO$_2$ composite generating excellent mineralization of alizarin cyanine green dye in aqueous solution

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Abstract   The synchronous role of coupled adsorption and photocatalytic degradation of alizarin cyanine green dye (ACG) in aqueous solution on porous Commercial Activated Carbon (CAC)–titanium dioxide (TiO$_2$) mixture have been studied under UV irradiation. The CAC–TiO$_2$ composite was prepared by simple chemical route and the as prepared composite was characterized using Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD) analysis. The photodegradation rate constant (k) for ACG dye on CAC–TiO$_2$ is (0.0666 min^{-1}), which is very much higher than that of pure TiO$_2$ 0.00368 min^{-1}. The photodegradation efficiency of the CAC–TiO$_2$ composite was eighteen order magnitudes higher than that of pure TiO$_2$ for ACG dye degradation. The total mineralization of ACG, through the combination of adsorption and degradation was achieved in a reasonable time, and can therefore be suggested as an efficient, cost-effective and environment friendly water treatment methodology.

1. Introduction

Pigments and dyes are widely used in various industries (Robinson et al., 2001), and a considerable percentage of these go into the effluent during the dyeing process. The toxicity and potentially carcinogenic nature of these represent an increasing danger for aquatic life. Therefore, many physicochemical methods such as adsorption, coagulation, precipitation, filtration and oxidation have been attempted for dye removal. The adsorption process has been found to be the most effective. Numerous adsorbents such as activated carbon

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(Demirbas et al., 2008; Al-Degs et al., 2008), alumina (Salem and El-Maazawi, 2000), and zeolite (Karadag et al., 2007) are widely used. However, they only simply transfer the dye from one medium to another and still leave the pollutants in the environment.

Photocatalytic oxidation represents an attractive solution due to the ability to completely oxidize organic contaminants to carbon dioxide, water and mineral acids hence it degraded the pollutants rather than transferring them (Lodha et al., 2011; Velmurugan et al., 2012; Barka et al., 2010). TiO_2, a well-known photocatalyst, has been extensively investigated for the degradation of organic pollutants under ultraviolet irradiation in wastewater and in air because of its photostability, nontoxicity, high activity and relatively low cost (Ding et al., 1999; Li et al., 2002, 2007). However, problems with the use of TiO_2 powder is also well recognized; specifically, (1) the difficulty in separating the TiO_2 powder from the solution after reaction is complete, (2) aggregation of particles in suspension, especially at high loadings and (3) difficulty in application to continuous flow systems (Leary and Westwood, 2011).

The incorporation of photocatalysts with adsorbents offers a new design of a photocatalytic system. Some nanocomposites which have a high adsorbing capacity as well as a high efficiency for the photocatalytic degradation have been prepared such as TiO_2/zeolite, TiO_2/activated carbon, TiO_2/Al_2O_3 and TiO_2/SiO_2. Because of the adsorbents adsorbing the substances selectively, exploring new adsorbents for the application in more industrial purposes is expected (Chen et al., 2010; Fernandez et al., 1995; Velasco et al., 2010; Tryba et al., 2003). However, reports on both physical-absorbing properties and photocatalytic properties of the CAC–TiO_2 mixtures are scanty. The present study designates the photodecolorization of ACG dye on TiO_2 in the presence of CAC. The influence of various process parameters on the photodecolorization was also studied.

2. Experimental procedure

2.1. Materials

AnalaR grade Alizarin Cyanine Green (ACG) dye purchased from E. Merck, India was used in the present study. Figure 1 shows the structure (Fig. 1a), UV–vis absorption spectrum (Fig. 1b) and wavelength for maximum absorption (λ_{max}) of ACG dye. The catalyst used in the present work is TiO_2 supplied by May & Baker Ltd., Dagenham, England. CAC was supplied by BDH, India. All the other chemicals and reagents were of AnalaR grade supplied by BDH, India, Ranboxy and SD fine chemicals. Deionized water was used for the preparation of all the solutions and reagents.

2.2. Preparation of CAC–TiO_2 composite

The CAC–TiO_2 composite was prepared by infiltration of a suspension in ethanol of commercial TiO_2 particles on the CAC in a rotary evaporator under vacuum for 45 min. After the rotation, ethanol was evaporated out and dried. Before each photocatalysis experimental studies, the CAC–TiO_2 mixture is activated and dried at 110 °C overnight. Mere TiO_2 was also used as a standard for comparison purposes.

2.3. Photodegradation studies

The photocatalytic activities of the photocatalysts were evaluated by photodegradation of ACG dye in aqueous solution at room temperature. Stock solution of ACG dye was suitably diluted to the required initial concentration with DD water. 100 ml of the dye solution of known initial concentration (C_i) was taken in a photo reactor vessel. The required amount of catalyst (TiO_2 or CAC–TiO_2 composite) was exactly weighted and then transferred into the photo reactor vessel. The photo reactor vessel was placed in the safety wood. Before illumination, it was turned on. The suspension was stirred with a magnetic stirrer. After a definite period of time, the solution was taken from the photo reactor vessel and centrifuged immediately for separation of the suspended solids. The solution was analyzed by a spectrophoto colorimetric technique by measuring the absorbance using spectrophoto colorimeter. Preliminary dark experiments without irradiation were also performed to establish the period of time needed to achieve the adsorption–desorption equilibrium of all the prepared materials and to determine $t = 0$ for the photocatalytic reactions (instant to turn on the irradiation). Although ACG dye may absorb light itself, such a self-degradation is negligible when compared with degradation catalyzed by photocatalysts.
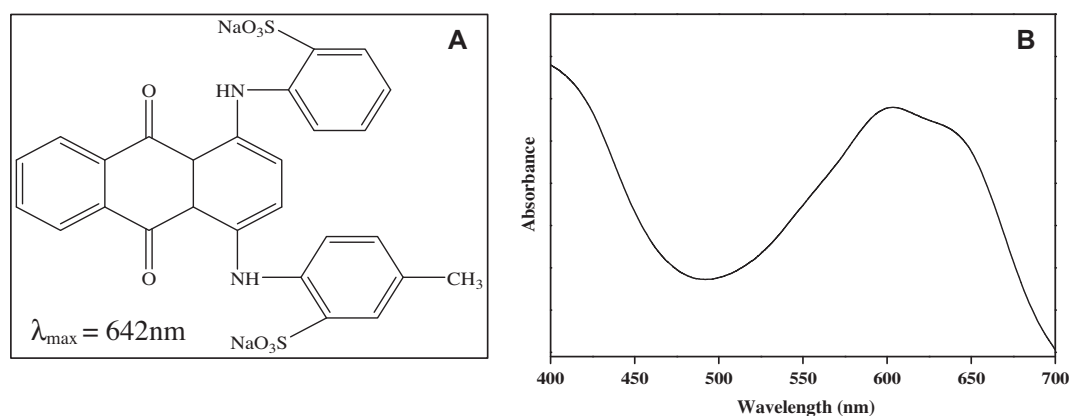

Figure 1 Structure (a) and UV–vis spectra of ACG dye.

2.4. Equipments

High irradiation was performed with a UV – high pressure ("HEBER" photoreactor, model HIPR compact-MP-8/125/400) mercury lamp (λ_{max} = 365 nm: 400 W). The X-ray diffraction pattern of the PoPD film was taken with an analytical (Model PW 3040/60) X-ray diffractometer using Cu Kα radiation. UV–visible spectra were recorded using "TECHCOMP" UV–visible spectrometer model 8500 with a matched pair of Teflon stoppard quartz cuvettes. Scanning Electron Microscopy (SEM) image was obtained using LEO 440 I model. The X-ray diffraction pattern of the PoPD film was taken with an analytical (Model PW 3040/60) X-ray diffractometer using Cu Kα radiation. Concentration of dye was determined with Spectrophotocolorimeter (Systronics-115). The pH of the dye solution was measured by using digital pen pH meter (Hanna instrument, Portugal).

3. Results and discussion

3.1. Scanning electron microscope analysis

SEM studies provide useful information regarding the surface morphology of the materials. Fig. 2 shows SEM images of the surface morphology of the mere TiO$_2$, Mere CAC and CAC–TiO$_2$ composites. The surfaces of the TiO$_2$ particles appeared spherical in shape and the particles are agglomerated (Fig. 2A). SEM photograph exhibits mere CAC to be porous in nature with uniform morphology (Fig. 2B). The surface structure of the CAC–TiO$_2$ composite clearly reveals the surface texture and porosity nature (Fig. 2C). The immobilization of TiO$_2$ in the carbon matrix partially blocked the porosity of the carbon surface, although the composite still displays a porous character with a relatively large pore volume and surface area. These results suggested that TiO$_2$ did not enter the inner pores of the carbon during the immobilization, remaining on the outer surface and most accessible pores. Consequently, the pores of smaller sizes remained unblocked. Besides, due to the synthetic route followed in the preparation of the AC–TiO$_2$ composite no chemical bonding is expected between TiO$_2$ and the carbon support, it seems that there exists a weak interaction.

3.2. XRD measurement

In order to confirm the crystalline nature of TiO$_2$ on CAC–TiO$_2$ composite, XRD pattern has been carried out for pristine CAC and 1:4 ratio of CAC:TiO$_2$ mixture (Fig. 3). The XRD pattern of the pure CAC shows two broad diffraction peaks at 25.9° and 41.2°, which can be indexed to (0 0 2) and (1 0 0) diffraction for typical graphite carbons. For CAC–TiO$_2$ composite catalysts, all the sharp peaks observed in the XRD patterns belong to the anatase phase of TiO$_2$ [JCPDS No. 21 = 1272]. The peaks at 2θ = 25.3°, 37.8°, 48.0°, 53.9°, and 55.1° can be assigned to the diffractions of (1 0 1), (0 0 4), (2 0 0), (1 0 5) and (2 1 1) crystal planes of the anatase phase. It is noteworthy that the characteristic peaks of CAC can hardly been identified from all the patterns of the composite catalysts. The reason may be that the main peak of CAC at 24.9° is overlapped with the main
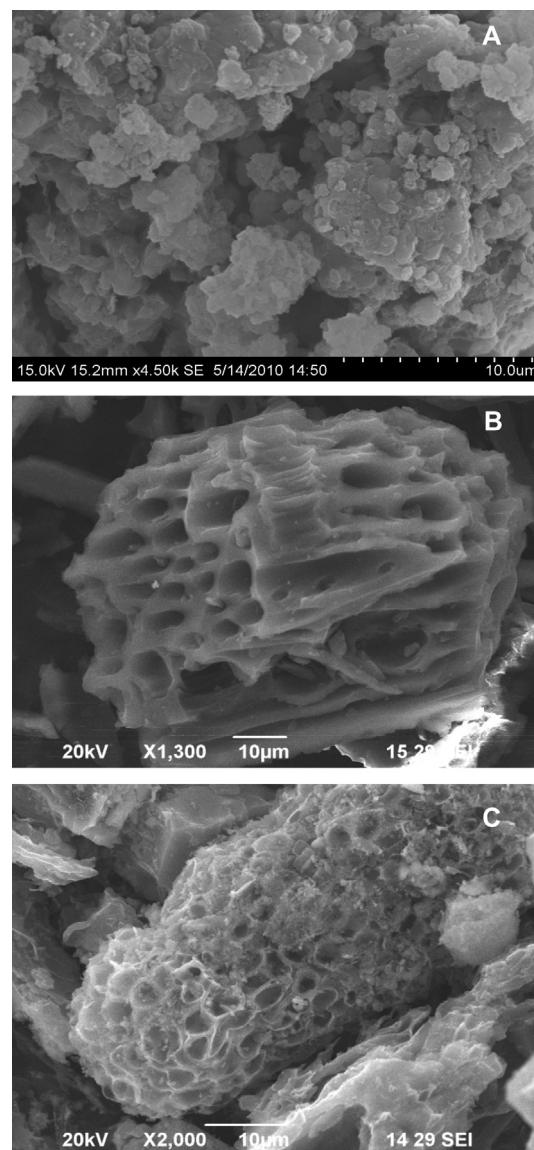

Figure 2 Surface morphology of the (A) pure TiO$_2$; (B) pure CAC and (C) CAC–TiO$_2$ mixture.
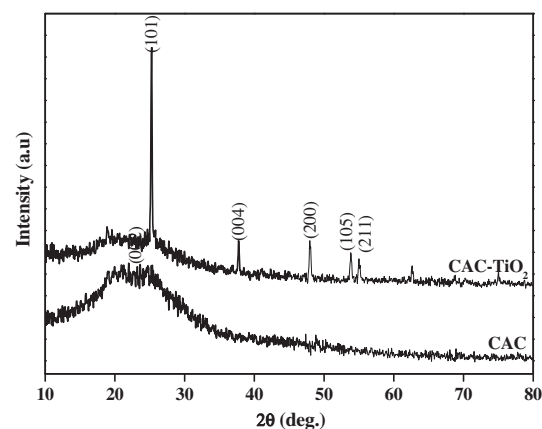

Figure 3 XRD pattern of Mere CAC and CAC–TiO$_2$ composites.

peak of anatase TiO$_2$ at 25.3° (Liu et al., 2007; Velasco et al., 2010; Muthirulan et al., 2012a).

3.3. Effect of initial concentration on photodegradation of ACG

The effect of dye concentration on the degradation rate was studied by keeping the mass of composite and irradiation time constant while the concentration of the dye varies in the range 10–40 ppm. Similarly, the photocatalytic degradation of ACG dye was also carried out under same experimental conditions in the presence of CAC.

The extent of removal of the dye, in terms of the values of percentage removal of dye has been calculated using the following relationship:

$$\text{Percentage removal} = 100(C_i - C_f)/C_i \qquad (1)$$

where, C_i = initial concentration of dye (ppm); C_f = finial concentration of dye (ppm) at given time.

It was observed from Fig. 4, that the percentage removal (%R) of ACG dye decreases exponentially with the increase in the initial concentration. An important step in the photocatalytic process of the present system is the adsorption of reacting substances onto the surface of the catalyst. AC has a well-developed pore structure, very large surface area with strong adsorption capacity and is widely used as an adsorbent and catalyst support. AC in the CAC–TiO$_2$ catalysts can act as an active center where dye molecules can be absorbed before transferring to the decomposition center, illuminated by TiO$_2$, which is located on the AC surface, because of the concentration difference. Meanwhile anatase nanocrystals generate •OH radicals by UV irradiation, which simultaneously attack the pre-enriched ACG dye from many different directions. As a result, the ACG dye is in no time cleaved into small molecules. Subsequently, the resultants diffuse out of the pores into the solution. In this process, the •OH radicals are highly efficiently utilized because of the synchronous role of adsorption and photocatalytic oxidation, generating the excellent activity (Muthirulan et al., 2012a,b).

On the other hand, using activated carbon as a catalyst support will help increase the photodegradation rate by progressively allowing an increased quantity of substrate to come in contact with TiO$_2$ through means of adsorption. This is important because researchers have established that the oxidizing species (•OH) generated by the photocatalyst, does not migrate very far from the active centers of TiO$_2$ and therefore degradation takes place virtually on the catalyst surface. In this respect, activated carbon will prove to be an invaluable support in promoting the photocatalytic process in providing a synergistic effect by creating a common interface between both the activated carbon phase and the TiO$_2$ particle phase. The synergistic effect can be explained as an enhanced adsorption of the target pollutant onto the activated carbon phase followed closely by a transfer through an interphase to the TiO$_2$ phase, giving a complete photodegradation process.

3.4. Effect of irradiation time on photodegradation of ACG

In order to study the effect of irradiation time (range 15–120 min) on the extent of removal of ACG dye, the photodegradation experiments were carried out at constant dose of the catalysts (200 mg) and constant dose of the CAC (40 mg) and optimum initial concentration of dye (30 ppm). Fig. 5 represents that as the irradiation time increases the %R also increases. UV–vis absorption spectrum of ACG with different reaction times under UV irradiation in the presence CAC–TiO$_2$ composites is illustrated in Fig. 6a. UV irradiation leads to a continuous decrease in the absorbance of ACG in the presence of photocatalyst and the decrease of the absorption band intensities of the dye indicated that dye has been degraded. As can be seen in this figure, the disappearance of the characteristic band of ACG dye at 642 nm after 90 min under UV light irradiation indicates that ACG has been degraded completely.

The following pseudo-first order kinetic equation was used to study the kinetics of photodegradation of ACG dye.

$$\ln(C_0/C_f) = Kt \qquad (2)$$

where, C_0 = initial concentration of dye solution (in ppm), C_f = final concentration of dye solution at time t (in ppm), k = pseudo-first order rate constant for degradation of dye (in min.$^{-1}$).
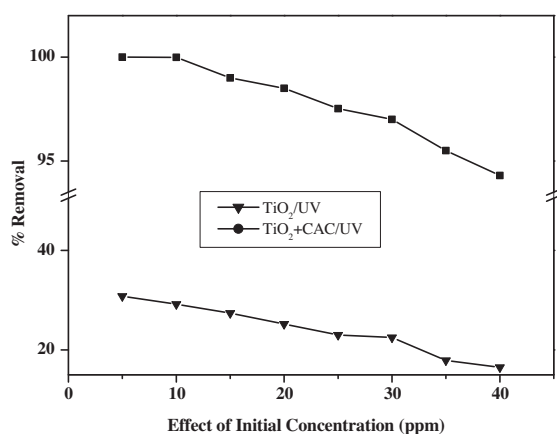

Figure 4 Effect of initial concentration of ACG dye in the presence and absence of CAC [Contact time: 90 min; Dose of the catalyst: TiO$_2$-200 mg and CAC-40 mg].
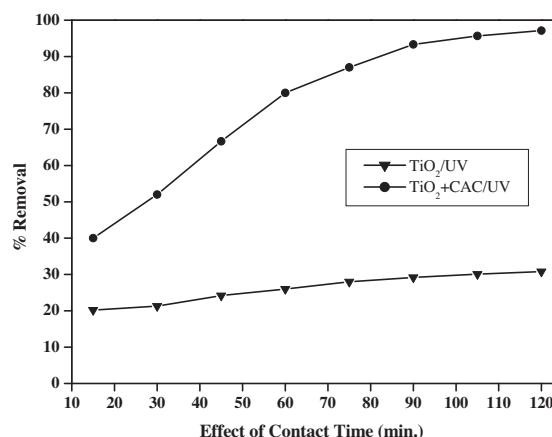

Figure 5 Effect of Irradiation time of ACG dye in the presence and absence of CAC [Initial concentration of ACG: 30 ppm; Dose of the catalyst: TiO$_2$-200 mg and CAC-40 mg].
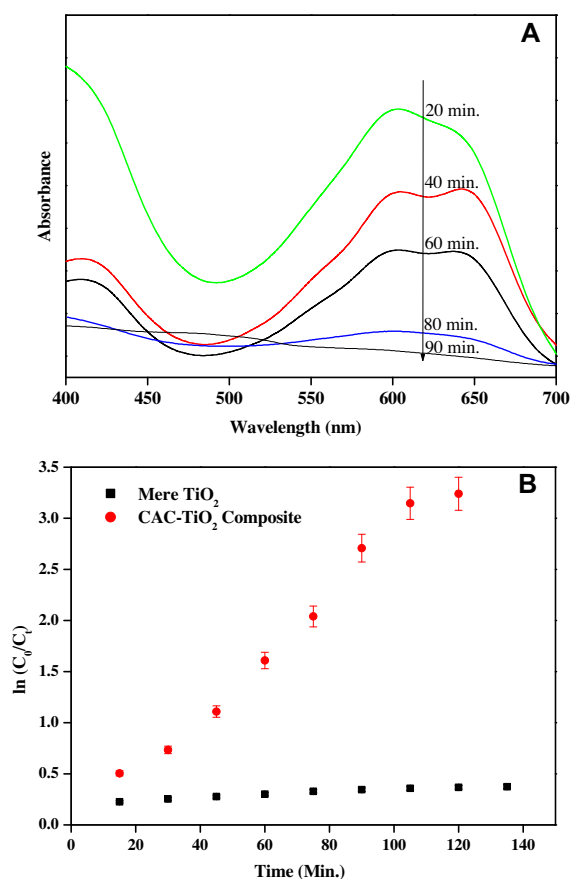
Figure 6 UV–vis absorption spectra (A) and Kinetics (B) of ACG dye degradation in the presence and absence of CAC.

Figure 7 Effect of dose of ACG dye in the presence and absence of CAC [Initial concentration of ACG: 30 ppm; Contact time: 90 min].

The degradation experiments by UV irradiation of ACG dye containing TiO_2 in the presence and absence of CAC follow pseudo-first-order kinetics with respect to the irradiation time (t) (Fig. 6b). The value of $\ln(C_0/C_f)$ is plotted against time (in min.,) and the plots were found to be linear. From the slope, the rate constants were calculated for the degradation of ACG dye in the presence and absence of CAC. The pseudo first order rate constant (k in min^{-1}) for TiO_2 in the absence of CAC is 0.00368 and for CAC–TiO_2 is 0.0666. The degradation efficiency of the ACG dye on CAC–TiO_2 composite is eighteen times higher than that of mere TiO_2. These results indicate the synchronous role of CAC on the photocatalytic degradation of ACG in the presence of TiO_2. The enormous enhancement in the photodegradation efficiency for CAC–TiO_2 is due to porous frameworks which link mutually and coexist to form unique composite-walls, providing unprecedented spaces for "the synchronous role of coupled adsorption and photocatalytic oxidation". CAC is an excellent adsorbent, providing better adsorption centers and enriching dye pollutant molecules; while TiO_2 behaves as photocatalytic active sites to oxidize the dye molecules pre-enriched by the surrounding CAC. Moreover, the high accessible surface areas can provide more adsorptive and photocatalytically active sites; and the pore channels allow the reactive molecules to diffuse more easily both into and out of the inner surfaces before and after photocatalytic reactions (Muthirulan et al., 2012a,b).
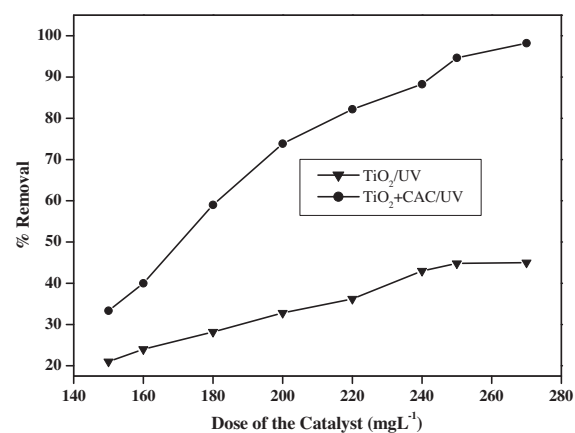
3.5. Effect of dose of the catalyst on photodegradation of ACG

The effect of ACG dye decolorization using both the catalyst (CAC and TiO_2) separately (alone) by varying their amount in the AC–TiO_2 mixture. Fig. 7 shows the optimized condition of the effect of dose of the catalyst. The plot of percentage removal versus dose of the catalyst is found to be exponential for both the ACG–TiO_2 and ACG–TiO_2–CAC systems. Increasing the dose of CAC and keeping the dose of TiO_2 as constant in the CAC–TiO_2 mixture leads adsorption of ACG dye and this process is favor and limited only certain level of concentrations (at low concentrations) and tends to became saturated (at higher concentrations). This may be due to reduction in immediate solute adsorption, owing to the lack of available active sites on the adsorbents' surface compared to the relatively large number of active sites required for high concentrations of dye.

Moreover, it should be pointed out that, the catalyst loading affects number of active sites on the photocatalyst and the penetration of radiation through the suspension. As the catalyst loading increases the % removal of ACG dye decreases due to the enhancement of light reflectance by CAC. The number of active sites increases but the penetration of radiation decreases due to shielding effect. Photocatalytic degradation rate, which is influenced by both the number of active sites and the penetration of irradiation light, must therefore pass through a maximum at optimum amount of catalyst. Also, the decrease in adsorption density with an increase in adsorbent amount is due to the high number of unsaturated adsorption sites. However, strong adsorption of pollutant molecules may inhibit subsequent photocatalytic reactions. But, increasing the dose of TiO_2 and keeping the dose of CAC in the CAC–TiO_2 mixture as constant, the photodegradation favors predominantly not only at lower concentrations but also at higher concentrations up to optimum level (1:5 ratio of CAC and TiO_2). This observation is understandable because too high loading of TiO_2 commonly results in the formation of agglomerated particles that have small active surfaces for catalytic performance (Muthirulan et al., 2012a,b).
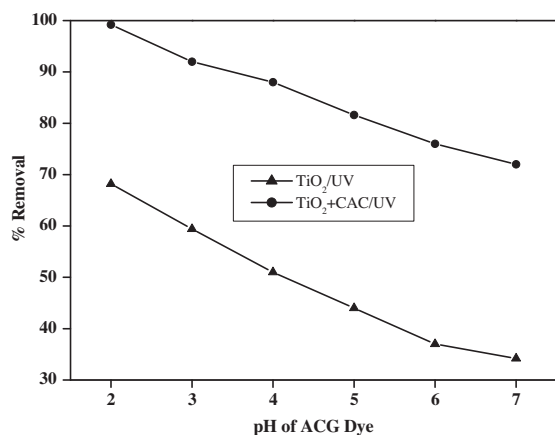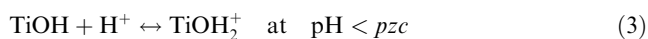
Figure 8 Effect of pH of ACG dye in the presence and absence of CAC [C_i: 30 ppm; Dose of the catalyst: TiO_2-200 mg and CAC-40 mg; Contact time: 90 min.].

3.6. Influence of solution pH on photodegradation of ACG

Wastewaters from textile industries usually have a wide range of pH values. Usually, pH plays an important role in the characteristics of dye wastewaters and is one of the most important parameters that influence the photo-oxidation processes. The effect of the initial solution pH on the photocatalytic decolorization is presented in Fig. 8. The ACG dye decolorization percentages increase with a decrease in the initial pH of the dye solution at optimum concentration of dye, dose of the catalyst and time of irradiation under UV irradiation. The effect of pH on the dye photocatalytic decolorization is difficult to explain since it had multiple roles. First, it was related to the surface-charge properties of the photocatalysts, and could be explained based on the point of zero charge (pzc).

The point of zero charge (pzc) of TiO_2 is 6.2. In acidic media (pH < 6.2) the surface of TiO_2 is positively charged, whereas, it is negatively charged under alkaline conditions (pH > 6.2) according to Eqs. (3) and (4),

$$TiOH + H^+ \leftrightarrow TiOH_2^+ \quad at \quad pH < pzc \quad (3)$$

$$TiOH + OH^- \leftrightarrow TiO^- + H_2O \quad at \quad pH > pzc \quad (4)$$

ACG is negatively charged due to the sulfonated groups which are ionized in water; their electrostatic attraction to the composite surface is favorable in acidic solution and forbidden in alkaline media due to the columbic repulsion between the negatively charged surface of TiO_2 and the negatively charged dye molecules. Thus, the reaction rate reached a maximum value at very low pH. Moreover, the generation of OH^- radicals by the effect of UV-light on TiO_2 of the composite may also be the factor responsible for increasing reaction rate in an acidic environment. In strong alkaline medium (pH < 7) such radical species are rapidly scavenged and therefore the reaction rate decreases. Hence, the degradation is very efficient at low pH on both TiO_2/UV and TiO_2 + CAC/UV systems (Muthirulan et al., 2012a,b).

3.7. Decolorization mechanism

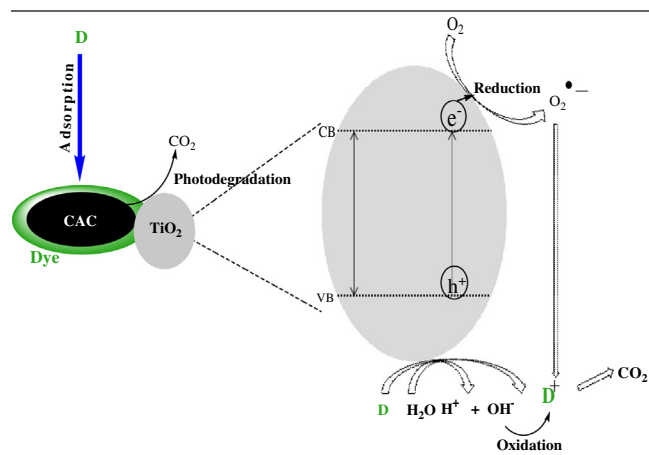The ACG removal by photodegradation in the presence of CAC is higher than that obtained by the sum of the contribu-

Figure 9 Photodegradation mechanism of ACG degradation on CAC–TiO_2.

tion of photodegradation and subsequent adsorption indicating, a synergistic effect. The mechanism of photodegradation on TiO_2 in the presence of CAC is shown in Fig. 9. In heterogeneous photocatalysis, the liquid phase organic compounds are degraded to its corresponding intermediates and further mineralized to carbon dioxide and water, if the irradiation time is extended.

The overall photocatalysis reaction as portrayed as follows

a. Mass transfer of the organic contaminant(s) in the liquid phase to the TiO_2 surface.
b. Adsorption of the organic contaminant(s) onto the photon activated TiO_2 surface photocatalysis reaction for the adsorbed phase on the TiO_2 surface.
c. Desorption of the intermediate(s) from the TiO_2 surface.
d. Mass transfer of the intermediate(s) from the interface region to the bulk fluid.

$$AGC\ Dye \xrightarrow[hv]{CAC\text{-}TiO_2} Intermediates \rightarrow CO_2 + H_2O \quad (5)$$
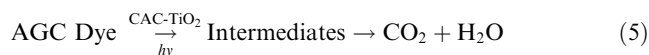
The proposed mechanism of synergistic enhancement in AC–TiO_2 composites is shown in Fig. 9 and the explanations are as follows: (i) Adsorption onto the AC provides a high concentration of reactants near TiO_2, which may then be photocatalyzed, possibly passing through intermediate stages; (ii) In the absence of adsorbent AC, reactants must collide with TiO_2 by chance, and remain in contact for the photocatalysis to proceed. When this is not achieved, the reactants or intermediate products will pass back into solution and can only react further when they collide with TiO_2 again. In other words, CAC and TiO_2, which link mutually and coexist to form unique mixtures, owning coupled performances of "adsorption-photocatalysis oxidation" and providing unprecedented spaces for the "synchronous role" (Muthirulan et al., 2012a,b), Leary and Westwood, 2011; Velasco et al., 2010; Tryba et al., 2003).

3.8. Desorption studies

After 90 min of photodegradation experiment, the residue of CAC–TiO_2 composite was separated and immersed in 4 mL of ethanol under ultrasonication for 20 min. Then the filtrate

was collected and analyzed by UV–vis spectrophotometer. The UV–vis spectrum (figure not shown) of filtrate in ethanol solution does not show any significant peak corresponding to ACG dye (disappearance absorption peak), which confirms that the removal of color is due to photodegradation and not by adsorption. This result clearly illustrates that molecules of ACG that have been adsorbed and accumulated on CAC during the initial photocatalytic degradation are able to be transferred to TiO$_2$ where they are decomposed under irradiation. Continuous migration and subsequent photocatalytic oxidation on the surface of TiO$_2$ accelerated ACG removal efficiency greatly. This transfer occurs through the CAC–TiO$_2$ interface with the concentration gradient as the driving force.

From the above studies we conclude that the decolorization of ACG dye is due to the photodegradation process and not by pure adsorption and the enhancement of photodegradation efficiency is due to synergistic or cooperative effect.

4. Conclusions

In conclusion, our results showed that the synergetic roles of coupled adsorption and photocatalytic oxidation remarkably enhance the activities, but the synchronous role generates excellent degradation activity of ACG, which is much lower than that of commercial TiO$_2$ photocatalyst. The results depict that the pores frameworks consist of CAC and TiO$_2$, which link mutually and coexist to form unique mixtures, possessing coupled performances of "adsorption-photocatalysis oxidation" and providing unprecedented spaces for the "synchronous role". The results of the present study imply the rational viability of using CAC–TiO$_2$ in the presence of UV light for ecofriendly mineralization of ACG dye in textile waste water treatment.

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