Solar light assisted photocatalytic mineralization of an azo dye, sunset yellow by using CAC/TiO$_2$ composite catalyst

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Received 25 June 2014; revised and accepted 13 April 2015

CAC/TiO$_2$ composite photocatalysts have been prepared by sol gel method and photocatalytic activity investigated for the degradation of sunset yellow in aqueous solution using solar light. CAC/TiO$_2$ is found to be more efficient than TiO$_2$ and TiO$_2$-P25 at pH 7 for the mineralization of the dye. Effects of operational parameters such as the amount of photocatalyst, dye concentration and initial pH on photomineralization of SY have been analyzed. The degradation is strongly enhanced in the presence of electron acceptors such as oxone, KIO$_4$ and KBrO$_3$. Mineralization of the dye has been confirmed by COD measurements. The proposed mechanism of degradation by CAC/TiO$_2$ shows a pseudo-first order. The catalyst is found to be reusable up to the fourth cycle.

Keywords: Photocatalysis, Sol gel method, Degradation, Dye degradation, Solar light, Titania

The treatment of toxic and persistent organic pollutants, particularly non-biodegradable dyes, contaminating the aquatic environment is one of the most important challenges facing environmental scientists. In recent times, heterogeneous photocatalysis is one of the most efficient methods for eliminating organic pollutants and dyes from aqueous media. In this process, electron-hole pairs are generated under irradiation of a semiconductor material and play a major role in the degradation or decolorization of pollutants. Heterogeneous photocatalysis is a branch of advanced oxidation processes (AOPs) which has the capability of generating active radical oxidants such as hydroxyl or superoxide radicals in solution. Among the advantages of AOPs is the strong potential for biorecalcitrant wastewater treatment (even at low concentrations) without the formation of hazardous byproducts. On the other hand, relatively high operating costs of these processes compared to those of a biological treatment are the main disadvantage. An important parameter which plays a crucial role in the enhancement of the activity of the catalyst is the irradiation source. Important criteria for a new energy source are low cost, ample supply, safety, and being pollution free. UV radiation sources commonly used are expensive and are themselves pollutants. Therefore AOPs which can be driven by solar radiation are of special interest, making the development of suitable technologies for practical applications very attractive. As the majority of the solar radiation intensity reaching the earth surface is in the visible range (400–600 nm), visible light active systems are of high priority for developing future generation of photocatalytic materials. In order to use sunlight energy effectively, the design and development of photocatalytic systems capable of operating under visible or solar light irradiation are desirable for application of photocatalytic systems to address environmental concerns.

Among the semiconductors, TiO$_2$ as a photocatalyst is one of the most popular and effective materials because of its chemical and physical stability, strong oxidation and reduction abilities, and nontoxicity. The photocatalytic activity of TiO$_2$ varies depending on its crystal phase, crystallite size and crystallinity. It is known that anatase-form of TiO$_2$ crystallite with small crystallite size and high crystallinity exhibits better photocatalytic activity. Activated carbon (AC) has proved to be an effective adsorbent and is widely used for the removal of a variety of organic pollutants. Velmurugan and co-workers investigated photocatalytic activity of TiO$_2$/CNP through degradation of Reactive Red 120 dye. They found that the photocatalytic activity of CNP-TiO$_2$ for degradation of Reactive Red 120 using solar light was higher than for TiO$_2$-P25 and TiO$_2$. On the other hand, it was reported that wood charcoal or
activated carbon is effective for removal of harmful substances in the environment by their excellent adsorption ability. Therefore, some researches on the preparation of TiO₂-carbon composites that were composed of carbon as an adsorbent and the anatase-form of TiO₂ crystallite as a photocatalyst have been reported. Doi et al. developed the carbonized TiO₂-woody composites by thermal treatment where anatase-form of TiO₂ crystallites was deposited in the wood lumen, cell wall and the surface of the carbonized wood particles, separately, which have the synergetic effect of adsorption and photocatalytic activity for formaldehyde.

Although there are several reports on photodegradation of dyes, in the present work, we focus on the preparation and characterization of TiO₂ and CAC/TiO₂ composite catalysts, prepared using sol-gel method, modified by an activated carbon additive. The commercial activated carbon is a cheap and easily available material. The surface and porous advantage of activated carbon was utilized to optimize the surface and morphological properties of CAC/TiO₂ composite catalysts. The purpose of this study is to examine the photodegradation efficiency of coupled CAC/TiO₂ using sunset yellow (SY) as a test substrate under direct sun light. Utilization of solar energy is an economically favourable process and hence, this method can be effectively used for dye wastewater treatment.

**Material and Methods**

The commercial azo dye SY (λ_{max} = 313 nm) obtained from Aldrich was used as such. AnalAR grade titanium isopropoxide (99%), (Himedia), 2-propanol (99.5% spectrochem), and commercial activated carbon (SD fine) were used as received. A gift sample of TiO₂-P25 (80:20 mixture of anatase and rutile) was obtained from Degussa (Germany). It had a particle size of 30 nm and BET specific area of 50±5 m² g⁻¹. Doubly distilled water was used to prepare experimental solutions. UV spectral measurements were made on a Hitachi-U-2001 spectrometer. The pH of the solution was measured by using Elico (LI-10T model) digital pH meter.

For solar experiments, all photocatalytic degradations were carried out under similar conditions on sunny days between 11 AM to 2 PM. An open borosilicate glass tube of 50 mL capacity, 40 cm height, and 20 mm diameter was used as the reaction vessel. Fifty SY (3×10⁻⁴ M, 50 mL) with the appropriate amount of catalyst was stirred for 30 min in the dark prior to illumination in order to achieve maximum adsorption of dye onto the semiconductor surface. Irradiation was carried out in the open air average temperature 30 °C with continuous aeration by a pump to provide oxygen and for complete mixing of the reaction solution. During the illumination time no volatility of the solvent was observed, the solvent being water. In all cases, 50 mL of reaction mixture was irradiated. At specific time intervals, 2–3 mL of the sample was withdrawn and centrifuged to separate the catalyst. One milliliter of the sample was suitably diluted, and the dye concentration was determined from the absorbance at the analytical wavelength (λ_{max}=313 nm for SY).

Solar light intensity was measured at every 15 min and the average light intensity over the duration of each experiment was calculated. The sensor was always set at the position of maximum intensity. The intensity of solar light was measured using LT Lutron LX-10/A digital Lux meter and was found to be nearly constant during the experiments.

**Preparation of CAC/TiO₂ photocatalysts**

CAC/TiO₂ composite was prepared by sol-gel method. Commercial activated carbon (~0.540 g) was added to a mixture of 12.5 mL of titanium isopropoxide and 80 mL of 2-propanol with 3 mL of water under magnetic stirring. The resulting colloidal suspension was stirred for 4 h. The gel obtained was filtered, washed and dried in an air oven at 100 °C for 12 h. The sample was calcinated at 450 °C in a muffle furnace for 5 h. The obtained CAC/TiO₂ (containing 20 wt% CAC loaded TiO₂) was blackish white powder. Catalysts with 5, 10, 15, 25 and 30 wt% commercial activated carbon were prepared with the same procedure. Pure titania (TiO₂) was prepared by a similar procedure without the addition of commercial activated carbon.

For determining the COD, the sample was refluxed with HgSO₄ and known volumes of standard K₂Cr₂O₇, Ag₂SO₄ and H₂SO₄ over two hours and titrated with standard ferrous ammonium sulfate (FAS) using ferroin indicator. A blank titration was carried out with distilled water instead of dye sample. COD was determined using the following equation:

\[
\text{COD} = \frac{(\text{Blank titre} - \text{dye titre}) \times N_{\text{FAS}} \times 8 \times 1000}{\text{Vol. of sample}}
\]
Results and Discussion

Preparation and characterization of 20 wt% CAC/TiO₂ and its photocatalytic activity for the degradation of SY by UV light have been reported earlier.³¹ XRD analysis of CAC/TiO₂ shows one new peak with 2θ value of 25.3° corresponding to CAC.³², ³³ The SEM images reveal very small tiny agglomerated spherical structures in the CAC/TiO₂ composite, which are uniformly distributed over a smooth homogenous background. The EDS of CAC/TiO₂ reveals the presence of Ti, O, and C, while the UV-DRS spectra show that CAC/TiO₂ has higher absorption than bare TiO₂ in the entire visible region. The loading of CAC with TiO₂ does not shift the emission of TiO₂, although the intensity of PL emission decreases when compared to that of bare TiO₂. This is because of suppression of recombination of electron-hole pairs by TiO₂. BET surface area and pore volume of CAC/TiO₂ (189.72 m² g⁻¹ and 0.3600 cm³ g⁻¹) is higher than that of the bare TiO₂ (89.20 m² g⁻¹ and 0.2402 cm³ g⁻¹). High surface area increases the photocatalytic activity.

Photodegradability of SY

Figure 1 shows the percentage of SY on irradiation of an aqueous solution of SY (3×10⁻⁴ M) in the presence of different photocatalysts under solar light. In the presence of CAC/TiO₂, 95.5% degradation of SY takes place at 80 min under solar light. This is in contrast to 44.0% decrease in dye concentration the same experiment performed with CAC/TiO₂ in the absence of solar light. This may be due to adsorption of the dye on the surface of the catalyst. Negligible degradation (0.7%) occurred in the presence of solar light without any catalyst. These observations reveal that solar light and photocatalyst are needed for effective destruction of SY dye. When prepared TiO₂ and TiO₂-P25 were used under same conditions, only 57.9% and 73.5% of degradation occurred, respectively. With CAC alone, under the same conditions, 22.1% decrease in dye concentration occurred due to adsorption of the dye on CAC. This shows that solar/CAC loaded TiO₂ process is more efficient in SY degradation than other processes.

Effect of operational parameters

The solution pH plays an important role in the photocatalytic degradation process of various pollutants.³⁴, ³⁵ Furthermore, the solution pH also determines the surface charge properties of TiO₂, the size of aggregates formed, the charge of dye molecules, adsorption of dyes onto CAC/TiO₂ surface and the concentration of hydroxyl radicals. The effect of pH on the photodegradation of SY was studied in the pH range 3–11. The pH of the solution was adjusted before irradiation and was not controlled during the course of the reaction. A study of SY degradation as a function of initial pH shows, the photocatalytic degradation efficiency of CAC/TiO₂ to be highest at neutral pH 7. To study this further, dark adsorption of SY dye were carried out at different pH. The percentages of adsorption at pH 3, 5, 7, 9 and 11 were found to be 26.2, 37.2, 44.0, 35.4 and 22.8 after the attainment of adsorption equilibrium (30 min). Maximum adsorption was observed at pH 7. Hence, the higher degradation efficiency is due to the strong adsorption of SY on the catalyst surface.

To avoid the use of excess catalyst, it is necessary to find out the optimum loading for efficient removal of dye molecule. Several authors have investigated the reaction rate as a function of catalyst loading in photocatalytic degradation process.³⁶-³⁹ The effect of the catalyst amount on the photocatalytic degradation SY was carried out in the range 50–300 mg of the catalyst for 50 mL of solution. It was observed that the amount of the catalyst was increased from 50 mg to 200 mg, the degradation increased from 42.2% to 83.7% at 60 min of irradiation time. This is due to increase in the number of CAC/TiO₂ particles, which increases the absorption of photons and adsorption of dye molecule. Further increase of CAC/TiO₂ loading decreased the removal rate. Increase of the catalyst loading beyond 200 mg/50 mL, i.e., 4 g L⁻¹, may cause screening effect and reduce the specific activity.

Fig. 1—Photodegradability of sunset yellow: [SY] = 3×10⁻⁴ M; catalyst suspended = 4 g L⁻¹; pH = 7±0.1; airflow rate = 8.1 mL s⁻¹; I_{solar} = (1250×100)±100 Lux. [1, Dye+Solar; 2, CAC; 3, CAC/TiO₂+dark; 4, Prepared TiO₂; 5, TiO₂-P25; 6, CAC/TiO₂].
of the catalyst\textsuperscript{36}. At high loadings of catalyst, particle aggregation may also reduce the catalytic activity. The optimum amount of catalyst for efficient degradation was found to be 200 mg/50 mL of SY.

The effect of various initial dye concentrations on the degradation of SY on CAC/TiO\textsubscript{2} surface was investigated (Fig. 2). It was found that increase of dye concentration from 3 to 9×10\textsuperscript{-4} M decreases the degradation from 95.5% to 48.5% at 80 min. The rate of degradation relates to the \( \cdot \)OH radical formation on catalyst surface and probability of \( \cdot \)OH radical reacting with dye molecule. For all initial dye concentrations, the catalyst amount and light intensity were same. Since the generation of hydroxyl radical remains constant, the probability of dye molecule to react with hydroxyl radical decreases. At high initial dye concentrations, the path length of photon entering into the solution also decreases, and the photocatalytic degradation efficiency decreases. However, at low concentration the reverse effect was observed, thereby increasing photon absorption by the catalyst\textsuperscript{40}. The large amount of adsorbed dye may also have a competing effect on the adsorption of oxygen and OH\textsuperscript{-} onto the surface of catalyst.

**Kinetic analysis**

The heterogeneous photocatalytic degradation of sunset yellow containing CAC/TiO\textsubscript{2} obeys apparently pseudo-first order kinetics at low initial substrate (sunset yellow) concentration, according to the rate expression, \( \frac{d[C]}{dt} = k' [C] \), where \( k' \) is pseudo-first order rate constant and equilibrium concentration of dye is taken as its initial concentration. Integration of this equation with the limit of \( C = C_0 \) at \( t = 0 \) with \( C_0 \) being the equilibrium concentration of the bulk solution gives \( \ln[C_0/C] = k't \), where, \( C_0 \) is equilibrium concentration of sunset yellow and \( C \) is the concentration of time '\( t \). For initial dye concentration of the dye in the range of (3-9)×10\textsuperscript{-4} mol/L, \( k' \) was in the range of 0.0302–0.0045 min\textsuperscript{-1}.

A linear relation between sunset yellow concentration and irradiation time has been observed for solar light degradation as shown in the plots of \( \ln[C_0/C] \) versus time (Fig. 3). Many authors\textsuperscript{41-43} have used the Langmuir-Hinshelwood (L-H) kinetic expression to analyze the heterogeneous photocatalytic reaction successfully. The experimental data has been rationalized in terms of the modified form of L-H kinetic model to describe the solid-liquid reaction\textsuperscript{44}.

The rate of oxidation of sunset yellow at surface reaction is proportional to the surface coverage of sunset yellow on the CAC-TiO\textsubscript{2} assuming that sunset yellow is strongly adsorbed on the catalytic surface than the intermediate products\textsuperscript{35}. The effect of sunset yellow concentration on the rate of degradation is given as\textsuperscript{46}.

\[
r = K_1 K_2 C/1 + K_1 C
\]

and

\[
1/r = 1/K_1 K_2 C + 1/K_2
\]

where ‘\( C \)’ is the concentration of the sunset yellow at time \( t \), \( K_1 \) is the constant related to adsorption and \( K_2 \) to the reaction properties of the substrate (sunset yellow).

\[\text{Fig. 2—Effect of initial dye concentration on SY degradation.} \quad [\text{pH} = 7 \pm 0.1; \ 20 \text{ wt\% CAC/TiO}_2 \text{ suspended} = 4 \text{ g L}^{-1}; \ \text{airflow rate} = 8.1 \text{ mL s}^{-1}; \ \text{I}_\text{solar} = (1250 \pm 100) \text{ Lux.} \ [1, \ 9 \times 10^{-4} M; 2, \ 7 \times 10^{-4} M; 3, \ 5 \times 10^{-4} M; 4, \ 3 \times 10^{-4} M].\]

\[\text{Fig. 3—Kinetics of SY degradation for different initial concentrations by solar/CAC loaded TiO}_2. \quad [\text{pH} = 7 \pm 0.1; \ 20.0 \text{ wt\% catalyst suspended} = 4 \text{ g L}^{-1}. \ [1, \ 9 \times 10^{-4} M; 2, \ 7 \times 10^{-4} M; 3, \ 5 \times 10^{-4} M; 4, \ 3 \times 10^{-4} M].\]
yellow). The applicability of L-H equation for the degradation has been confirmed by the linear plot obtained by plotting the reciprocal of initial rate (1/r) against reciprocal of initial concentration of the sunset yellow (1/C). From the slope and intercept of the linear plot $K_1$ and $K_2$ for solar light photocatalytic degradation are found to be $4.34 \times 10^4$ M$^{-1}$ and $1.17 \times 10^{5}$ M min$^{-1}$, respectively.

Effect of oxidants
The effect of oxidants such as KIO$_4$, H$_2$K$_3$O$_8$S$_4$ (oxone) and KBrO$_3$ in addition to molecular oxygen on the photocatalytic oxidation of the SY was investigated. In the absence of any oxidant, almost complete mineralisation (95.5%) was achieved at 80 min irradiation. However, at 60 min of irradiation, only 83.7% degradation was achieved in the absence of oxidants. It was found that at 60 min irradiation, addition of oxidants enhanced the photodegradation of SY. The order of degradation (%) activity under optimum conditions and at 60 min of irradiation is: only CAC/TiO$_2$ (83.7) < oxone (90.2) < KBrO$_3$ (92.5) < KIO$_4$ (96.7). Peroxymonosulfate (HOOSO$_5^-$) (oxone), more commonly noted as HSO$_5^-$, has been used in a restricted way as an oxidant in light induced processes. The higher degree of degradation in the process with the oxidants is due to the formation of highly reactive radical intermediates (IO$_3^-$, O$_2^-$, OH$^-$) and the electron capture by these oxidants (Eqs 1–5). These radicals are used for the degradation. Here IO$_3^-$ can produce highly reactive radicals such as IO$_3^-$, O$_2^-$, OH$^-$.

Hence, KIO$_4$ shows the highest enhancement of degradation as compared to the other oxidants.

\[
\begin{align*}
IO_3^- + h\nu & \rightarrow IO_3^- + O_2^- & \ldots(1) \\
O^2^- + H^+ & \rightarrow \cdot OH & \ldots(2) \\
HSO_5^- & \rightarrow SO_4^{2-} + \cdot OH & \ldots(3) \\
SO_4^{2-} + H_2O & \rightarrow \cdot OH + SO_4^{2-} + H^+ & \ldots(4) \\
BrO_3^- + 6e_{cb}^- + 6H^+ & \rightarrow Br^- + 3H_2O & \ldots(5)
\end{align*}
\]

Reusability of the catalyst makes the process economical and hence it is an important factor. After the reaction, the catalyst was centrifuged, washed with water and air-dried at 100 °C for 4 h and reused for next run. Nearly 99% of the catalyst was recovered after each run. No leaching of CAC was observed from TiO$_2$. The catalyst exhibited 94.0% activity after four successive cycles under the solar irradiation. These results indicate that CAC/TiO$_2$ catalyst remains effective and reusable under solar light.

To confirm the mineralization of SY, the degradation was also analyzed by COD values. After 20 min irradiation, 53.4% COD reduction was observed, which after 80 min irradiation increased to 96.2% COD reduction. This indicates the mineralization of dye.

Mechanism of degradation
CAC/TiO$_2$ composite is found to be more efficient than prepared TiO$_2$ and Degussa-P25 for the degradation of SY dye under solar light. The degradation mechanism has been proposed based on properties of CAC and TiO$_2$ (Scheme 1). TiO$_2$ behaves as the photoactive center, i.e., generating electron-hole pair under solar irradiation, while CAC provide better adsorption sites in the vicinity of the TiO$_2$. The adsorbent (CAC) increases the concentration of SY dye near the photoactive center (TiO$_2$). There is synergism between CAC and TiO$_2$ and due to this synergistic effect, CAC/TiO$_2$ composite adsorbs more dye (44.0%) as compared to CAC alone (22.1%) and prepared TiO$_2$ (10.7%). Furthermore, photocatalytic degradation is a surface phenomenon and thus there is a need to increase interaction between organic dye (SY) and surface of the catalyst for effective degradation. It is already reported that adsorption of the dye on the surface of the catalyst is required for effective degradation. When CAC/TiO$_2$ is irradiated with solar light, an electron is excited from VB of TiO$_2$ to CB of TiO$_2$, leaving a hole in VB. Due to this charge separation, valence band holes react with water, producing more
hydroxyl radicals (‘OH), whereas CB electrons react with molecular oxygen producing superoxide radical anions (O$_2^-$). Both species (super oxide radical anions and hydroxyl radicals) are very reactive towards dye (SY) degradation. Hence, photocatalytic activity of CAC/TiO$_2$ is significantly enhanced.

**Conclusions**

CAC loaded TiO$_2$ was synthesized by sol gel method. CAC/TiO$_2$ is found to be more efficient than bare TiO$_2$ and TiO$_2$-P25 for degradation of SY under solar light. The optimum pH and catalyst loading for efficient removal of dye are found to be 7 and 4 g L$^{-1}$, respectively. Increase in initial dye concentration decreases the removal rate. All processes follow pseudo-first order kinetics. Addition of oxidants such as KIO$_4$, H$_2$K$_2$O$_8$S$_2$ (oxone) and KBrO$_3$ enhanced the degradation rate. The catalyst is found to be reusable up to four cycles without much loss of reactivity. COD measurements confirm the mineralization of SY molecule. Mechanism of dye degradation by CAC/TiO$_2$ is proposed on the basis of band energy levels of CAC and TiO$_2$.

**Acknowledgement**

One of the authors (MS) is highly thankful to University Grants Commission, New Delhi, India, for financial support through research project F.No 41-288/2012 (SR).

**References**