Photocatalytic Degradation of Amaranth Dye over Immobilized Nano-crystals of TiO$_2$

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Abstract: The present work is focused on the heterogeneous photocatalytic degradation of Amaranth dye over immobilized nano-crystals of TiO$_2$. Immobilization has been an acceptable approach to overcome the drawbacks encountered with powder suspensions. Immobilization is performed using polyvinyl alcohol-formaldehyde binder. This method of immobilization does not require thermal heating at high temperature. Combination of adsorption and photodegradation processes is also studied. Adding high adsorption capacity activated carbon to photoactive Titanium dioxide induces strong beneficial effects in the removal of Amaranth dye.

Key-Words: Photodegradation, Nano sized TiO$_2$ powder, Adsorption, Activated carbon.

1 Introduction
Dye and dye intermediates with high degree aromaticity and low-biodegradability are introduced into the aquatic system which results in the increase of the environmental risk. Conventional methods such as biological, physical and chemical processes are having several drawbacks and they are not effective for complete degradation of organic compounds. The development of alternative methods able to degrade toxic organic compounds is necessary. In this regard advanced oxidation processes (AOP) have attracted a great attention. Heterogeneous photocatalysis mediated by TiO$_2$ is of considerable interest for the effluent treatment. Many semiconductors like TiO$_2$, ZnO, CdS, etc., have been employed as photocatalysts. As generally observed TiO$_2$ is an efficient photocatalyst with high quantum yields. Photocatalysis by TiO$_2$ ($E_g = 3.2$ eV) involves under UV light excitation the generation of e$^-$ and h$^+$ in conduction band and in the valence band, respectively. These species undergo charge transfer reactions across the interface with the oxygen, water or organic pollutants adsorbed on TiO2 surface. The reaction of h$^+$ with OH$^-$ or H$_2$O leads to the generation of reactive •OH radicals which are powerful oxidants attacking the recalcitrant organic compounds of interest.

Most of the studies related to photodegradation have been carried out using the suspension of powder TiO$_2$ in aqueous solutions. However, the use of aqueous suspension is limited for practical application by filtration problems due to the small size of TiO$_2$ particles. Alternatively, the catalyst may be immobilized on to a suitable solid inert support, which eliminates the need of filtration of the catalyst. Unfortunately, when the catalyst is immobilized there is a decrease in the available surface area for the reaction since the catalyst must adhere to the solid support and the reactor design is limited by the optical absorption constraints.

Many techniques were proposed for the immobilization of TiO$_2$ on solid supports like glass, quartz, silica, activated carbon, fiberglass cloth, zeolites and stainless steel. However, supporting TiO$_2$ is commonly reported to be less photoactive. Generally, the process of immobilization involves the
use of expensive precursors of TiO\textsubscript{2} in the form of sol–gel and a thermal treatment of the film between 400 and 500 °C.

In present study, commercially available TiO\textsubscript{2} powder (Degussa P25) is immobilized in the form of a film using polyvinyl alcohol-formaldehyde binder by simply brushing on fiberglass sheet (25mm × 75mm).

A combination of adsorption & photodegradation processes has been proposed by many researchers after realizing the noble potentials in both processes. It has been observed that activated carbon (AC) adsorption works well with photodegradation using TiO\textsubscript{2} in removing various pollutants. The dual effect is capable of increasing the efficiency or performance of the whole removal system. Therefore, in this study, the removal efficiency of Amaranth dye by using immobilized TiO\textsubscript{2} and TiO\textsubscript{2}/AC (mixture of TiO\textsubscript{2} and activated carbon) is compared.

2 Problem Formulation
The TiO\textsubscript{2} and TiO\textsubscript{2}/AC was immobilized on fiberglass slides (25mm × 75mm) using polyvinyl alcohol-formaldehyde binder. Photocatalytic degradation was carried out in a photocatalytic chamber.

2.1 Materials and Methods
Titanium dioxide powder (nano-crystals) Degussa P25 (size of crystallites =30 nm, surface area = 55±15 m\textsuperscript{2}/g) was used. Polyvinyl alcohol LR, Formaldehyde LR and Amaranth dye powder were obtained from s d Fine-Chem Ltd, Mumbai India. Activated carbon was obtained from Merck (India) Ltd Mumbai India.

TiO\textsubscript{2} powder was mixed with activated carbon in a ratio of 50:50 before adding 10ml of double distilled water. The mixture was stirred for 1hour for homogeneity to prepare TiO\textsubscript{2}/AC suspension.

A 6.25% w/v polyvinyl alcohol-formaldehyde binder was prepared under constant stirring at 70°C. The binder was used to attach TiO\textsubscript{2}/AC to the substrate (Fiberglass slides with dimensions 25mm × 75mm). The slide was first applied with a thin layer of binder. The TiO\textsubscript{2}/AC suspension was then brushed onto the layer of binder to immobilize it. The same procedure was carried out to immobilize TiO\textsubscript{2} on fiberglass sheet.

Amaranth dye stock solution with concentration of 100ppm was prepared by dissolving the dye powder in double distilled water. Dye solution with a concentration of 10ppm was prepared by diluting the stock solution and used for photocatalytic degradation.

Photocatalytic degradation experiments were carried out in a photocatalytic chamber containing two 15W lamps as source of UV light. A magnetic stirrer was used to provide mixing. A dye solution of 50ml with concentration of 10ppm was used for degradation in each run. Fiberglass sheet with immobilized materials was dipped in the dye solution and illuminated with UV light to achieve degradation of the dye.

3 Results and Discussion
The photocatalytic degradation of the dye was measured over a period of 5.0 hour and 2.5 hour in case of immobilized TiO\textsubscript{2} and TiO\textsubscript{2}/AC respectively. Fig. 1 shows that the concentration of Amaranth decreases from 10ppm to 5.25ppm in 2.0 hours in case of immobilized TiO\textsubscript{2}. Fig. 2 shows that the concentration of Amaranth drops from 10ppm to 3.04ppm in 2.0 hours in case of immobilized TiO\textsubscript{2}/AC. It is clear that degradation rate is much higher in case of immobilized TiO\textsubscript{2}/AC than immobilized TiO\textsubscript{2} due to combined effect of adsorption and photocatalysis.

3.1 Kinetic Modeling
The photodegradation of Amaranth follows Langmuir – Hinshelwood (L-H) kinetic of heterogeneous photocatalytic reactions.
According to L-H model, when initial concentration $C_o$ is very small the following pseudo-first order rate equation is followed.

$$\ln \left( \frac{C}{C_0} \right) = -kt$$

where $k$ is pseudo-first order rate constant and $t$ is time. A plot of $\ln(C/C_o)$ versus time represents a straight line, the slope of which upon linear regression equals the pseudo-first order rate constant $k$. Fig.3 and Fig.4 shows $\ln(C/C_0)$ versus time plot for immobilized TiO$_2$ and immobilized TiO$_2$/AC. It is obvious from the plots that degradation follows pseudo first order kinetic. Table 1 shows the values of Half-life time ($t_{1/2}$) and rate constant for both immobilized TiO$_2$ and TiO$_2$/AC. It is clear from Table 1 that the immobilized TiO$_2$/AC removes Amaranth dye much faster than immobilized TiO$_2$ with rate constant 0.588 hour$^{-1}$ and Half-life time 1.2 hour.
**Fig. 3** In \((C/Co)\) versus time plot for immobilized TiO\(_2\).  

**Fig. 4** In \((C/Co)\) versus time plot for immobilized TiO\(_2\)/AC

**Table 1** Half life time \((t_{1/2})\) and pseudo-first order rate constant.

<table>
<thead>
<tr>
<th>Type of immobilization</th>
<th>(t_{1/2}) (hour)</th>
<th>Rate constant (k) (hour(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO(_2)</td>
<td>2.1</td>
<td>0.337</td>
</tr>
<tr>
<td>TiO(_2)/AC</td>
<td>1.2</td>
<td>0.588</td>
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</tbody>
</table>
4 Conclusion

This study evaluates the ability and effectiveness of the immobilized system containing TiO$_2$ and TiO$_2$/AC. Combination of adsorption and photodegradation process has much better capability to degrade Amaranth dye. Pseudo-first order rate constant is higher and Half-life time is quite less in case of immobilized TiO$_2$/AC as compared to immobilized TiO$_2$. Immobilized TiO$_2$/AC showed a great potential in degrading Amaranth dye.

References: