# Photocatalytic degradation of methylene blue dye from aqueous solution using $TiO_2$ doped Activated carbon

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***Abstract***

*The effluent coming out from the textile, paper and food industries containing dye is strongly coloured and reveals very harmful effects on living beings. In order to reduce wastewater pollution, the degradation of dye into non-toxic form is desirable. The photo catalytic degradation of methylene blue is reported in the present study. The irradiation of aqueous solution of methylene blue dye in presence of photo catalyst and UV light was carried out in the batch photo reactor. Titanium dioxide $TiO_2$ /CFAC was used as photo catalyst for the study.*

*The rate of decolorisation was estimated from residual concentration spectrophotometrically. Effects of various operating parameters such as the irradiation time, initial pH and the amounts of catalyst on the degradation of the dyes were investigated. Results show that the degradation kinetics fitted well to pseudo second order rate law. The maximum decolorizing efficiency occurred in less than 50min with 50mg of $TiO_2$ /CFAC catalyst dose.*

**Keywords:** Photocatalyst, methylene blue**,** spectophotometrically, decolorisation.

## Introduction

Photocatalysis method based on the utilized the semiconductors from disinfection and purification of water and air has been reported[26]. Nowadays, metal oxide semiconductors have been of recent attention for a variety of practical applications[11]. Among several semiconductors, $TiO_2$ has become a highly promising technology for the removal of the pollutant from wastewater[4,15,23,32,33]. Titanium dioxide ($TiO_2$) is found to be more efficient catalyst for photo catalytic degradation of pollutants due to faster electron transfer to molecular oxygen, due to its non selectivity for environmental engineering application; it is nontoxic, insoluble, reusable and photo stable. $TiO_2$ is most widely used catalyst in photo catalytic degradation of pollutants due to its suitable band gap energy.

However, widespread use of $TiO_2$ for large scale water treatment is uneconomical. Titanic is a vital useful photo catalyst because it possesses considerable properties such as: high activity[8], chemical and biological internees[31], commercial availability[9] etc. $TiO_2$ is a very applicable in many areas, for example solar cell[5], biosensors, semiconductors electrode, UV radiation inhibitor[25] etc. Photocatalytic activity is a significant function of titania[7]. Anatase, brookite and rutile are different structures of titanium dioxide[16]. The photocatalytic activity of $TiO_2$ started under UV light irradiation. The first step of this reaction is to initiate establishing the electron – hole pairs under appropriate illumination[24].

Among the various structure of $TiO_2$, anatase appears to be most active from another structure in photocatalytic process. The band gap for anatase is 3.2 ev and for rutile is 3.1 ev. The efficiency of photocatalytic activity of $TiO_2$ depends on the crystalline structure and that this originated from synthesize process of $TiO_2$[27].

Recently doping $TiO_2$ with metal or non–metal elements decreases this recombination. Resulting deposition element into titanic matrix increase whole concentration, down bond gap energy to visible light and cause the suitable photoactive system[29]. Titanium dioxide is commonly benefited in two forms: powder (suspension) and immobilize (film). Using of suspension has several problems. Filtration and retrieval stage are time consuming and costly for the suspension forms.

## Material and Methods

**Photo reactor:** A specially designed photocatalytic reactor system made of wooden chamber was used for photodegradation experiments. A UV lamp (Philips TUV-08) of 15 W having wavelength 365 nm was kept inside the wooden chamber.

**Methylene blue:** Methylene blue (MB), a cationic dye, is most commonly used as colouring agent for silk, wool, cotton and so on. It is also used as a staining agent to make certain body fluids and tissues easier to view during surgery and diagnostic examinations. In spite of many applications, this dye has a number of negative impacts on human beings and animals such as irritation of mouth, throat and stomach with symptoms of nausea, abdominal discomfort, vomiting and diarrhoea. The molecular formula of MB is $C_{16}H_{18}N_3SCl$. Its IUPAC name is 3,7-bis(Dimethylamino)-phenothiazin-5-ium chloride. The structural formula is shown in fig. 1. The present study investigates the degradation of methylene blue using $TiO_2$ / CFAC in presence of UV light. Subsequent experiments were conducted to investigate the effects of various amounts of catalyst dosing on the process performance.

**Preparation of dye solutions:** The methylene blue dye used in the present work was purchased from textile company of Tirupur. A stock solution of methylene blue dye

was prepared by dissolving 1g of methylene blue dye in1000mL double distilled water to give a concentration of 1000 ppm. The working solutions were prepared by diluting the stock solution with double distilled water to get 40 and 50ppm used for photocatalytic degradation studies.

**Preparation of Activated carbon (CFAC):** The copper pod fruit wastes were collected from various places such as PSG CAS, houses and road sides of Coimbatore. They were first peeled off to obtain the outer skin of the fruit and then the inner fleshy layer was removed. The peel was washed with ordinary tap water to remove any dirt or sand. The washed materials were dried under sunlight until the moisture was evaporated and then dried in a hot air oven to remove the residual moisture present in it. The dried materials were carbonized with 1:1(w/w) sulphuric acid for 24 h at room temperature.

After that, the charred material was filtered and washed with excess of water to remove the residual acid from the pores of the carbon particles. The filtered material was kept in a Muffle furnace at 600 °C for 30 min. The carbonized material was washed with distilled water until the pH of the washing solution reached to 7. Then the material was ground to fine powder and sieved with a particle size of 53 µm. The sieved copper pod fruit activated carbon (CFAC) was dried at 100 °C in an air oven and kept in an airtight container for further adsorption studies.

**Synthesis of $TiO_2$/CFAC for photocatalytic degradation:** In this process, titanium (IV) isopropoxide, isopropanol and acetone were analytically graded and purchased from Merk Specialties Private Limited. $TiO_2$/CFAC nanocomposite was synthesized by sol gel method using titanium (IV) isopropoxide as a binder. 96% of titanium (IV) isopropoxide was dissolved in 98% of anhydrous isopropanol. The mixture was subjected to constant stirring for 5 minutes followed by the addition of known amount of CFAC and the constant stirring was continued for 1 h. After a while, 5mL of water was added dropwise into the mixture until the solution turns homogeneous gel. Then the resulting solution obtained was filtered and washed with deionized water for several times and oven dried for 24 h at 100$^o$C. The final solid material was then ground and calcined at 400$^o$C for 3 h.

**Photocatalytic activity of nanocomposites of activated carbon:** The photocatalytic efficiency of nanocomposites $TiO_2$/CFAC was investigated in the presence of visible light for the degradation of dye methylene blue from aqueous solution in slurry batch visible light photo reactor. All the experiments were carried out in a cylindrical photo chemical reactor of 30 cm x 2 cm with a water circulation arrangement to maintain the temperature in the range of 30$^o$C. An anodized aluminium reflector consisting of 300 W Tungsten Xenon lamp was used as the visible light source and placed 6 cm away from the reactor tube. The prepared $TiO_2$/CFAC nanocomposites were taken in a glass tube with the addition of 40, 50 ppm of 100 mL of methylene blue dye solution and then oxygen was bubbled into the solution. The solution was continuously stirred for 30 min and then irradiated with visible light of wavelength above 400 nm.

For the specific time intervals of 30 min, 5 mL of the solution were withdrawn and centrifuged to remove the nanocomposite particles. The experiments were conducted by varying pH, photocatalyst concentration and irradiation time. The filtrate was analyzed by using UV-Visible spectrophotometer at the required wavelength of methylene blue dye to evaluate the efficiency of nanocomposites. The decolorization efficiency was analysed by the following equation:

$$\text{Photocatalytic efficiency } (\%) = \frac{(C_0 - C_e)}{C_0} \text{ X } 100 \qquad (1)$$

## Results and Discussion

**SEM Analysis:** Scanning electron microscopy (SEM) gives valuable information regarding the shape and distribution of the $TiO_2$/CFAC. $TiO_2$ particles with a non-uniformly distribution have crystallized like spherical agglomerates on the adsorbent.

The SEM images are used to investigate the morphology of the $TiO_2$/CFAC. The SEM images of $TiO_2$ / CFAC are shown in fig. 2. The surface modifier could not only affect the dispersibility of the $TiO_2$ particles, but also change their size and morphology of the particles. It is clearly found that the rough and heterogeneous porous surface of CFAC are available to entrap $TiO_2$.

It also shows the presence of clusters of $TiO_2$ nanoparticles on the surface of CFAC. Thus the SEM images reveal that the spherical shaped $TiO_2$ are well dispersed and intertwined on the surface of CFAC.

The size of the nanoparticle creates a larger surface area onto which the dyes can adsorb. It can be observed that the prepared composite mainly consists of shaped particles and has a high tendency to accumulate. However, it was indicated that the activated carbon has much pore structure and $TiO_2$ particles are blocked into the pore of activated carbon or coated on the activated carbon[6].

**X-Ray diffraction:** X- ray diffraction technique is used to investigate the crystalline structure and size of $TiO_2$ and $TiO_2$/CFAC. Fig. 3 and fig. 4 show the diffraction patterns of $TiO_2$/CFAC. The diffraction peaks were observed at 2θ = 25°, 37°, 38°, 39°, 48°, 54°, 55°, 63°, 69°, 70.5°, 75.5° and 76.2°. The 2θ peaks at 25° confirm the $TiO_2$ anatase structure. Strong diffraction peaks at 25° and 48° indicate $TiO_2$ in the anatase phase. The intensity of XRD peaks of the sample reflects that the formed nanoparticles are crystalline and broad diffraction peaks indicate very small size[17].

The average crystalline size was determined using Debye-Scherrer's equation:

$$D = \frac{0.9\lambda}{\beta\cos\theta} \quad (2)$$

where λ –X ray wave length, θ –Bragg diffraction angle and β –peak width of half maximum. This X – ray diffraction analysis results the crystalline size of $TiO_2$/CFAC about 53 nm.

**BET Surface Area and Pore Size Distribution:** The textural parameters such as surface area pore diameter and pore volume explained by BET analysis are listed in table 1. Based on BET analysis, the specific surface of CFAC was found to be 886$m^2$/g. It was decreased for $TiO_2$/CFAC due to the more amount of weight contribution from $TiO_2$ on the surface of CFAC after doping. The pore volume was decreased by impregnation of $TiO_2$ into the pores of CFAC. However, the pores responsible to hold the dye molecules during degradation are bigger after the deposition of $TiO_2$.

**FTIR Spectra:** The functional groups present in the modified $TiO_2$ can be studied using FTIR spectroscopy. Fig. 5 shows the FTIR spectra of the adsorbent samples. The peak at 3387 $cm^{-1}$ is related to stretching vibration of (O-H) hydroxyl group. The peak at 2376.30 $cm^{-1}$ is characteristic to $CH_2$. The peak at 1573.91 $cm^{-1}$ is related to CO stretching mode conjugated to NH deformation mode. The peak at 1473.62 is attributed to olefinic C-H bending vibration[10].

**Effect of pH:** The effect of pH at a range of 2.0-12.0 on the adsorption and photocatalytic degradation of methylene blue is shown in fig. 6. As shown in fig. 6, the removal capacity increased with increasing pH value from 2.0 to 7.0 and then decreased with the more increase of the pH from 7.0 to 12.0. Therefore, the optimum pH value for the adsorption and photocatalytic degradation of MB was 7.0. Consequently, at pH higher than 7.0, the $TiO_2$ surface would remain negatively charged. However, the dye removal capacity decreased at pH higher than 7. Hence, the optimum pH for this study is pH 7.

Similar types of results were reported for the photocatalytic efficiency of $TiO_2$ for decolorization of azo dyes[3]. The interpretation of pH effects on the efficiency of the photocatalytic degradation process is a very difficult task because of its multiple roles. First, it is related to the acid base property of the metal oxide surface and can be explained on the basis of zero point charge. The adsorption of water molecules at surficial metal sites is followed by the dissociation of $OH^-$ charge groups leading to coverage with chemically equivalent metal hydroxyl groups (M-OH).

**Effect of the Photocatalyst dosage:** The effect of Photocatalyst dosage on the colour removal of methylene blue dye molecules was carried out by varying the amount of $TiO_2$/CFAC from 0.05 g to 1 g in 40 and 50 ppm of 50 mL of each dye solution and the obtained results are shown in fig. 7. The photocatalytic degradation depends on the availability of active sites on the catalyst surface and the penetration of visible light into the solution. So the rate of decolorization increases with the increasing amount of photocatalyst.

As shown in fig. 7, the dye removal efficiency increased with the addition of $TiO_2$/CFAC from 0.05 g to 0.04 g in the adsorption process, by fixing other factors as constant because the adsorption surface and accessibility of adsorption sites increased. However, further increase of the $TiO_2$/CFAC did not provide more increment in the percentage of the dye removed. This can be attributed to the fact that after a certain dosage of $TiO_2$/CFAC, the maximum removal is achieved and the amount of dyes adsorbed and the amount of free dyes remain constant even with further addition of the $TiO_2$/CFAC. Therefore, 0.04 g as an optimal dosage of $TiO_2$/CFAC for the degradation of methylene blue was used in all the studies.

At higher dosage, the vacant sites are consumed by the intermediate products obtained during the reactions which retard further degradation of the substrate. Hence the percent degradation decreased or retained without a noticeable change. Moreover, the particle-particle interaction becomes significant as the amount of particles in solution increases which reduces the active site density for the surface excited holes and electrons. The higher activity is also attributed to the highly ordered nature of the catalyst and its method of preparation[3, 20].

**Effect of Irradiation time:** The effect of irradiation time on photocatalytic decolorisation of dye was performed by measuring the percentage of dye removal at different periods under visible light irradiation time above 410 nm. The decolorization was performed by taking 100 mg of $TiO_2$/CFAC in 50 mL of 40 ppm and 50 ppm of dye solution by fixing other variable at optimum conditions.

The percentage of each dye removal increased with an increase in irradiation time and is shown in fig. 8. The adsorption percentage of each dye on $TiO_2$/CFAC was large upto 50 min. Beyond this limit of time (50 min), there is no noticeable change. This result indicates that when the time of irradiation increases, the percent degradation increases and reaches a maximum for 50 minutes irradiation.

**Table 1**
**Textural parameters obtained from $N_2$ adsorption – desorption isotherms.**

| Samples | BET Surface area ($m^2$/g) | Pore volume(cc/g) | Pore diameter (nm) |
|---|---|---|---|
| CFAC | 886 | 0.756 | 1.701 |
| $TiO_2$/CFAC | 151.25 | 0.328 | 3.950 |

**Table 2**
**Pseudo-first order and Pseudo-second order kinetic constants for methylene blue dye**

| Conc. (mg/L) | $q_{e(exp)}$ | Pseudo - first order kinetic constants | | | Pseudo-second order kinetic constants | | |
|---|---|---|---|---|---|---|---|
| | | $k_1$ | $q_{e(cal)}$ | $R_2$ | $K_2$ | $q_{e(cal)}$ | $R_2$ |
| 40 | 39.44 | 0.0207 | 6.77 | 0.875 | 0.0064 | 40.66 | 0.998 |
| 50 | 49.39 | 0.0230 | 6.72 | 0.677 | 0.0062 | 50.63 | 0.999 |

With increase of time, more and more light energy falls on the catalyst surfaces which increased the formation of photo excited species and enhanced the photocatalytic activity[1,22].

**Adsorption Kinetic Study:** Adsorption kinetics influenced physical and chemical characteristics of the adsorbent material $TiO_2$/CFAC that also stimulates the adsorption mechanism[30]. The validity of the order of adsorption process was based on the two criteria, regression coefficient and calculated $q_e$ values. In the literature, several models have been applied to know the order of the adsorbent-adsorbate interactions and the rate of adsorption of the dyes. In this present study, the following four kinetic models are applied for the experimental data.

- **Pseudo first order:** The linearized form of pseudo first order Lagergren equation is given as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (3)$$

- **Pseudo second order:** The linear form of the second-order model is presented as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where $q_t$ and $q_e$ are the adsorption capacities at time t and at equilibrium respectively (mg/g), $k_1$ and $k_2$ are the rate constants of pseudo-first and second order adsorption (1/min) respectively and t is the contact time (min).

**Pseudo first order kinetics:** The lower correlation coefficients and qe values are not relevant, it suggest that the adsorption of methylene blue on prepared photocatalyst does not follow the pseudo-first order kinetics[28]. It does not comply with the kinetic data which can be attributed to the control of boundary layer over mehtylene blue dye adsorption at the entire range of initial concentrations studied.

**Pseudo second order kinetics:** It is observed that the correlation coefficient values are higher than the values of pseudo-first-order model. Also the rate constant $k_2$ decreases with the increase in initial dye concentration[2]. Hence adsorption of methylene blue dyes onto $TiO_2$/CFAC fits well to the pseudo-second-order kinetic model.

## Conclusion

Various weight % of $TiO_2$ doped activated carbon nanocrystals were prepared by using simple precipitation method. All the prepared samples were characterized by using various techniques like X-ray diffraction, Scanning electron microscope and UV-Vis spectroscopy. The photocatalytic decolourization was analysed for $TiO_2$ /CFAC by using methylene blue as model dye. The optimum parameters are identified for maximum degradation.

A detailed feasibility study has been carried out on photo catalytic degradation of methylene blue using $TiO_2$ /CFAC as a photo catalyst under UV radiation. It was observed that irradiation time, initial pH and catalyst dosages all significantly affect the photo catalytic degradation of methylene blue. The maximum decolorisation occurred in ≤ 50 min. It follows the pseudo second order kinetics.

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