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A Comparative study on the photocatalytic degradation of industrial dyes using modified commercial and synthesized TiO_2 photocatalysts

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Abstract:

Commercial and Synthesized titanium di oxide (TiO_2) prepared by conventional sol-gel method, are modified to degrade industrial dyes. Modification is done on bare TiO_2 and TiO_2 doped with various doping agents (activated charcoal/silicon dioxide/zinc oxide), followed by thermal treatments. The role of thermal treatments and doping effects on the efficiency of TiO_2 photocatalysts are highlighted and evaluated by decoloration of Methylene Blue in aqueous solution under UV and Visible light irradiation for both systems. The results revealed that increase in calcination temperature up to optimum level enhances the photocatalytic activities of the samples and doping narrows the band gap and makes the samples visible light responsive. This study also showed that activated charcoal (AC) doped TiO_2 photocatalyst is a promising one under Visible light and is thus used to degrade other dyes such as Crystal Violet and Rhodamine B. The obtained experimental data are used to study four different kinetic models: Zero order, Pseudo first order, Parabolic diffusion and Modified Freundlich model. The best fit of the experimental data are obtained by Pseudo first order and Modified Freundlich models.

Key words: Titanium di oxide, Sol-gel method, Industrial dyes, Calcination temperature, Doping agents, Activated charcoal, Kinetic model.

1. INTRODUCTION

Extensive disposal of dyes from textiles, paper, plastics, leather, food, cosmetics & many others industries to water bodies poses a great threat to environment. About 1-20% of the total world production of the dye is lost during the dyeing process & is released in the textile effluents [1-4].These industrial dyes are liable for most of the non-aesthetic pollution and eutrophication and can originate dangerous byproducts through oxidation, hydrolysis, or other chemical reactions taking place in the wastewater phase. It is, therefore, of utmost emergency to develop eco-friendly processes involving water treatment in order to prevent human and other living organisms from being affected and to provide safe drinking water in future. Considerable work has been carried out on the removal of dye from wastewater by adsorption, coagulation, flocculation, oxidation, precipitation, filtration, electrochemical processes, etc. are the common techniques reported for the removal of dyes from effluents [5]. But all these processes have many drawbacks involving high operating costs, incapability to degrade dyes completely. Now-a-days, photocatalysis is supposed to be one of the best methods for removing the dyes from wastewater because of the ability of this method to completely mineralize the target pollutants [6]. Currently, many semiconductors have been applied in heterogeneous photocatalysis such as CdS, SnO_2, WO_3, TiO_2, $ZrTiO_4$, and ZnO [7]. Among them, Titanium dioxide (TiO_2) has received the greatest interest. This is mainly due to TiO_2 nanomaterials possessing numerous important physicochemical properties and inherent advantages. These advantages include high efficiency, strong oxidation power, low cost, environmental benignity, and excellent chemical and photo-chemical stability. Consequently, tremendous efforts by the science and engineering community have been devoted to the synthesis of novel TiO_2 nanomaterials [8].

Various methods are available for the preparation of TiO_2-based photocatalysts, such as electrochemical, continuous reaction, multi-gelation, supercritical carbon dioxide, thin films and spin coating and thin film by vacuum arc plasma evaporator, combining inverse micelle and plasma treatment, dip coating and SILAR, two-step wet chemical, precipitation, thermal (ethanol thermal, hydrothermal and solvothermal), chemical solvent and chemical vapor decomposition (CSD & CVD) and sol–gel process. Sol–gel is one of the most exploited methods; it is used mainly to produce thin film and powder catalysts [1].

However, in its basic form, it functions only under UV irradiation [9].Thus only a small UV fraction of around 2–3% solar light that reaches the earth can be utilized. Sensitization of the TiO_2 to react to a much larger visible region is, therefore, of great importance [10]. To overcome some of the difficulties encountered, different dopants are being investigated with the aim of enhancing the morphology of TiO_2 in the photocatalysis. Doping is a mixing process in which an impure substance is mixed with pure semiconductor to improve the reactivity of the semiconductor. Dopants modify the electronic structure of nano-TiO_2 to broaden its effective range of light sensitivity for photocatalysis from the ultra-violet (UV) region to the visible light region [11]. In order to utilize wider range of solar

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energy, lots of efforts have been made to narrow band gap by doping with metal, transition metal or non-metals. Metal doping improves nano-doped TiO_2 performance under visible light irradiation by shifting the absorption spectra to a lower energy region. But metal doping showed several drawbacks: thermal instability of doped TiO_2, electron trapping by the metal centers, and requirement of more expensive ion-implantation facilities [12]. Non metal doping increases the percentage of the anatase phase in TiO_2, restrains the growth of crystallite size of TiO_2, and increases the specific surface area of TiO_2 [13].

In this study, TiO_2 is synthesized from Titanium (IV) Isopropoxide (TIP) by Sol gel method. The aims of the study are:

I) To determine the optimum dosage of photocatalyst

II) To compare the effect of calcination temperature on photocatalytic efficiency

III) To compare the photocatalytic degradation efficiency of Methylene Blue (MB) using synthesized (syn.) and commercial (com.) TiO_2 under UV light

IV) To compare the photocatalytic degradation efficiency of MB and other industrial dyes using doped syn. and com. TiO_2 under UV and visible light.

2. MATERIALS AND METHODS

2.1 Materials

Titanium (IV) Oxide purchased from Sigma-Aldrich, Germany was used as commercial TiO_2. Synthesized TiO_2 was prepared by sol-gel method from Titanium (IV) Isopropoxide (TIP) (Sigma-Aldrich, UK), Iso-Propanol and Distilled water (prepared in our laboratory). Silicon dioxide (SiO_2) (Sigma-Aldrich, USA), Zinc Oxide (ZnO) (Loba Chemie, India) and Activated Charcoal (AC) (Sigma-Aldrich, Germany) were combined with TiO_2 individually as doping agents. Methylene Blue (MB) (MERCK, Germany), Crystal Violet (CV) (LOBA CHEMIE) and Rhodamine B (RB) (Techno Pharm Chem, Bahadurgarh, India) were used to prepare dye solution.

2.2 Methods

2.2.1 Synthesis of TiO_2

Nanostructured TiO_2 was synthesized by sol-gel process [1]. The synthesis reactor consists of three necked round bottom flask equipped with a vertical condenser fitted to middle neck. This flask was placed over a magnetic stirrer with a tiny magnet dropped inside the flask. Typically, 42.16 ml iso-propanol was mixed with 9.82 ml distilled water under vigorous stirring at 8 rpm in the reactor. After adding 20 ml TIP drop wise to the mixture, both the necks were sealed. One neck was closed using a thermometer attached rubber stopper and another with rubber stopper. The mixture was stirred for 24h at 30˚C and TiO_2 paste was formed. This paste was then dried at room temperature to get the nanostructured TiO_2 [14].

2.2.2 Doping process

Individual doping agents (SiO_2 or ZnO or AC) were added with both com. and syn. TiO_2 separately in a crucible in a mass ratio of TiO_2 & dopants as 0.5**:**0.1 [15] and then small amount of distilled water was added for uniform mixing.

2.2.3 Calcination Process

Bare and doped TiO_2 were subjected to calcination. In a typical calcination process, the sample in a crucible was placed inside the Electric muffle furnace (JSMF-30T, Korea) for 2 h at 450˚C, 550˚C and 650˚C and then cooled to room temperature.

2.2.4 Preparation of standard curve

At first 100 ppm mother solution of dyes (MB, CV and RB) was prepared by mixing 0.1 g dye with distilled water. Then 2, 4, 6, 8 and 10 ppm dye solution were prepared from mother solution (100 ppm) for making a standard curve of absorbance vs. concentration. The wavelength in UV- spectrophotometer (UV-1650, SHIMADJU, Japan) was taken in the range of 300 – 800 nm. The highest peaks were achieved at 664.5, 588 and 544 nm wavelength for MB, CV and RB respectively and these peaks were used during entire experimental procedure. Corresponding standard curve was used to measure the unknown concentration of MB, CV and RB solutions.

2.2.5 Operation process

The photocatalytic process was conducted in a reactor (length 18 cm, width 8 cm & height 8 cm). The concentration of as-prepared 20 ppm dye solution was measured by using UV-spectrophotometer followed by dilution. Before measuring the concentration of the solution, base line correction was obviously done. Concentration of the main solution was calculated from this measured concentration by using the dilution ratio. 200 ml of dye solution & 0.16 g of the photocatalyst sample were mixed & placed in the photocatalytic reactor under light source (UV light (230V, 50Hz, BDH) / visible light (100 watt bulb)) for 1.5 hrs in the batch mode. To study the reaction kinetics, sample was collected in 15 minutes time interval and its concentration was measured by UV-Spectrophotometer. From this initial & final concentration (c_o to c), the percentage of dye degradation was calculated by using the following equation:

$$\% \text{ degradation} = \frac{C_0 - C}{C_0} \times 100\% \quad [16].$$

3. RESULTS AND DISCUSSIONS

3.1 Dosage Effect

To obtain the optimum catalyst loading, the amount of commercial TiO_2 is varied from 0.04 to 0.20 g in 200 ml of 20 ppm MB solution. Each sample solution is placed for 1.5 hr under UV light in a photocatalytic reactor and final concentration of MB is measured by UV spectrophotometer.

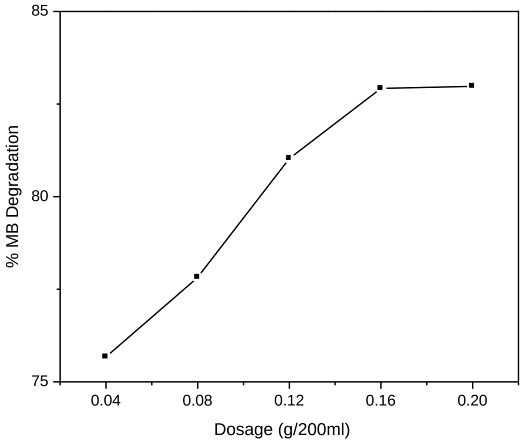

Fig. 1: % Degradation of MB vs. Dosage of commercial TiO_2.

It can be seen in Fig.1 that the dye removal efficiency increases with the increase in catalyst dosage up to 0.16g. The removal of MB is almost same for 0.16g to 0.2g catalyst loading. The reason behind this behavior is supposed that the increase in the amount of catalyst increase the number of active sites on the TiO_2 surface, which in turn, increase the number of hydroxyl and superoxide radicals. When the concentration of catalyst increased above the limiting value i.e. 0.16 g, the degradation rate decreased due to the interception of the light by the suspension [17, 18]. Moreover the increase of catalyst concentration beyond the optimum level may result in the agglomeration of catalyst particles, hence the part of the catalyst surface become unavailable for photon absorption, and thus degradation rate decreases [19]. Thus 0.16g is chosen as the optimum dosage to perform the rest of the experiments.

3.2 Thermal Effect

The photocatalytic degradation performance of com. and syn. TiO_2 calcined a different temperatures, are shown in Fig.2. From this, it is observed that the degradation of dye increases with increasing the calcination temperature. Remarkable increase in the dye removal efficiency is seen in case of TiO_2 calcined upto 550°C and then decreased. This is because, a crystallised anatase phase predominates at this temperature. However, for calcination at 650°C, there is decrease in dye removal efficiency. The calcination temperature above 550°C promote transformation of anatase to rutile phase of TiO_2 which can lower the photocatalytic activity [20, 21].

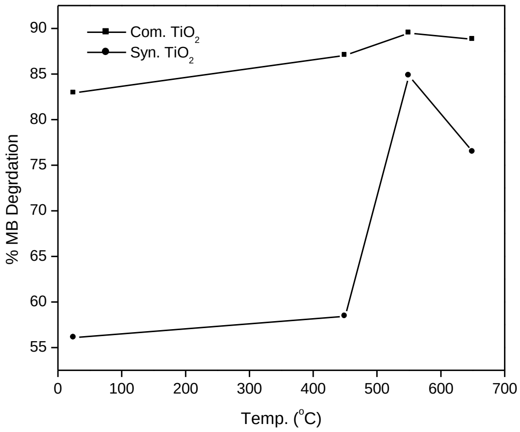

Fig. 2: % Degradation of MB vs. calcination temperature.

3.3 Doping Effect

Both com. and syn. TiO_2 are doped with SiO_2 or ZnO or AC separately and calcined at 450°C in order to investigate the doping effects of dyes degradation under UV and visible light.

Doped photocatalyst showed higher degradation effiency than that of undoped one on MB degradation under UV light (fig.3). This happens due to the fact that that non metal (AC or SiO_2) doping increases the percentage of the anatase phase in TiO_2 on thermal treatment. TiO_2 exists in four mineral forms [22] viz: anatase, rutile, brookite and titanium di oxide (B) or TiO_2 (B). Among them anatase shows maximum photo reactivity because of its slightly higher Fermi level, lower capacity to absorb oxygen and higher degree of hydroxylation. Non metal doping also restrains the growth of crystallite size of TiO_2 which prevents the transformation of anatase to rutile phase. Rutile phase is the most stable phase once it is formed and it grows much faster than anatase. Thus it is essential to prevent this transformation in order to achieve better degradation of dyes. Furthermore, Non metal doping increases the specific surface area of TiO_2. High surface area allows much dye molecules to attach to the active sites of TiO_2, leading to enhance degradation of dyes [12, 23].

Metal doping also enhances the photocatalytic activity of TiO_2 because doped metal atoms suppress the recombination of photo-induced electron-hole pairs, where the excited electron migrates from the inside of the photo catalyst to the surface of the metal so as to increase the photo quantum efficiency by trapping the electron from recombination [23].

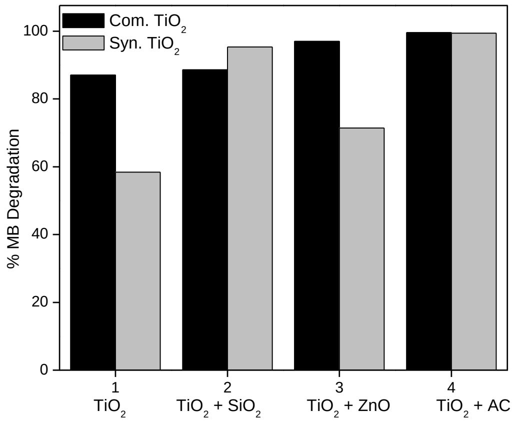

Fig. 3: % Degradation of MB under UV light using doped and undoped TiO_2 treated at 450°C.

In the Fig. 3, it is seen that the efficiency of com. TiO_2 is high compared to that of syn. TiO_2. The percentage degradation of MB varies from 87.04% to 99.59% incase of com. TiO_2 , however, incase of syn. TiO_2, it varies from 58.41% to 99.37%. Activated charcoal (AC) doped TiO_2 shows similar results for both cases. Inorder to harness the abundant and safe potential of solar energy, doping is actually done. As nonmetal doping decreases the band gap, and shifts the response to the visible part of the solar spectrum by incorporating nonmetal atoms into the lattice structure of TiO_2 so TiO_2 doped with nonmetals such carbon, silicon show better degradation of dyes [23].

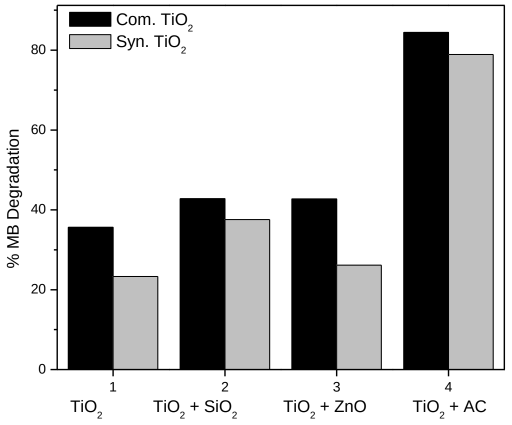

Fig. 4: % Degradation of MB under visible light using doped and undoped TiO_2 treated at 450°C.

The above figure (fig.4) shows that, under visible light photocatalytic degradation of methylene blue solution using AC doped TiO_2 is extremely high compared to others. AC doped TiO_2 causes formation of Ti^{3+}, which allows oxygen vacancy state to be present between the valence and the conduction bands. Doping with AC can narrow the band gap or form intra gap localized levels; moreover, thin carbon layer formed on TiO_2 may act as a photo sensitizer and could be excited to produce electrons by the visible light with subsequent injection of electrons into the conduction band of TiO_2 [24].

Undoped and AC doped com. and syn. TiO_2 are also used to degrade other dyes such as Crystal Violet (CV) and Rhodamine B (RB) (fig.5). The obtained results reveal that the degradation of dyes using AC doped TiO_2 is high in compared to that obtained using undoped TiO_2. The percentage degradation of AC doped TiO_2 varies within 51.72 to 71.90%. AC doped syn. TiO_2 works well under visible light compared to AC doped com. TiO_2. The percentage degradation in case of former is around 70% while the latter has around 60%.

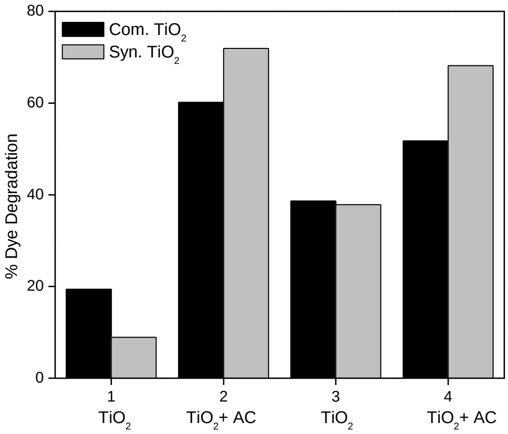

Fig. 5: % Degradation of CV (**1, 2**) and RB (**3, 4**) under visible light using AC-doped and undoped TiO_2.

3.4 Kinetics Study

To study the kinetics phenomena, the whole procedure done in batch mode is repeated in continuous mode. Then all obtained experimental data are fitted into four different kinetic models, such as Zero order, Pseudo first order, Parabolic diffusion and Modified Freundlich models. Among these, Pseudo first order and Modified Freundlich models show best fittings. The obtained result is demonstrated in the following figures (Fig. 6 - 11).

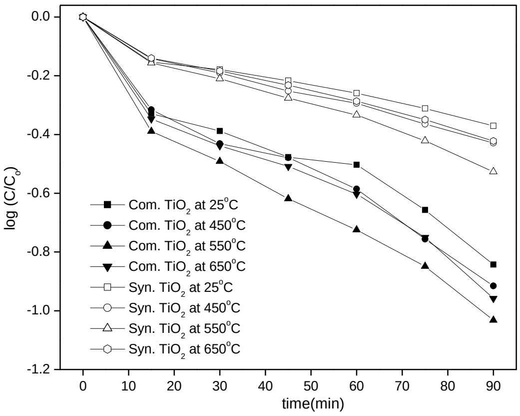

Fig. 6: Pseudo First order model under UV light.

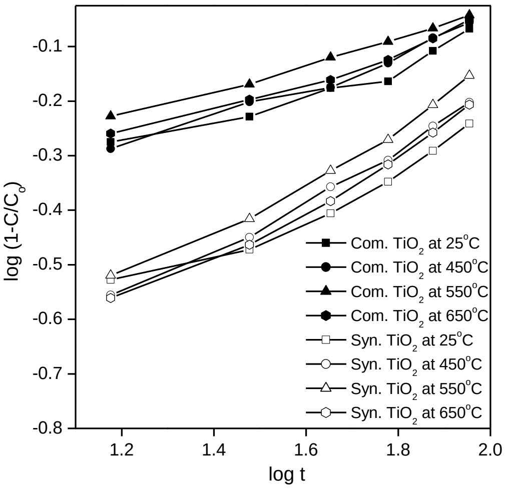

Fig. 7: Modified Freundlich model under UV light.

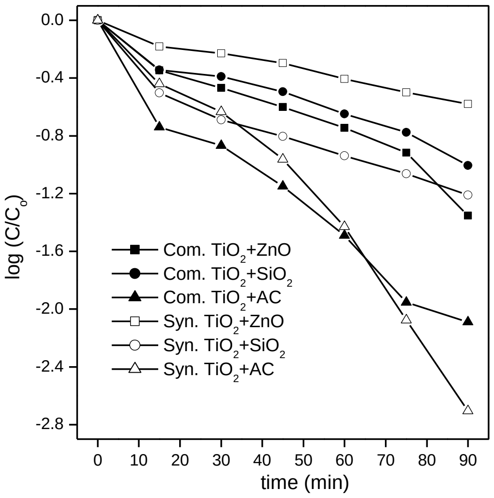

Fig.8: Pseudo First order model under UV light for doped TiO_2 calcined at 450˚C

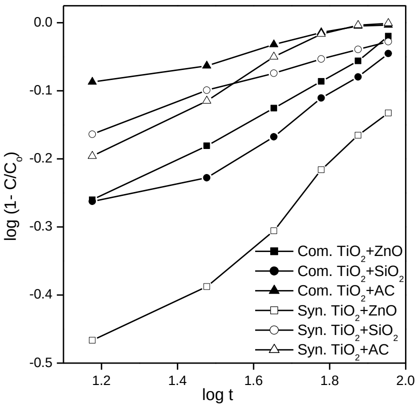

Fig. 9: Modified Freundlich model under UV light for doped TiO_2 calcined at 450˚C.

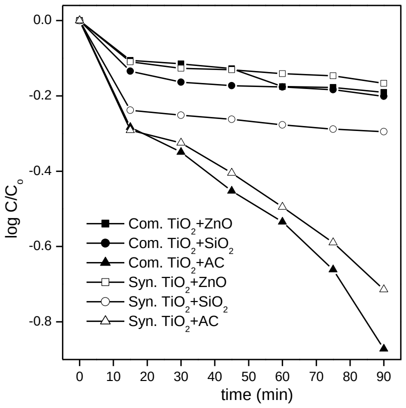

Fig.10: Pseudo First order model under visible light for doped TiO_2 calcined at 450˚C.

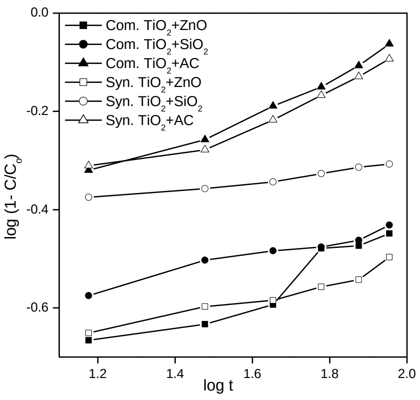

Fig. 11: Modified Freundlich model under visible light for doped TiO_2 calcined at 450˚C.

It is evident from Table.1 that Modified Freundlich model shows the best fitness for com. and syn. TiO_2, treated at different calcination temperature with R^2 values ranging from 0.936 to 0.995. Some of the samples partially fit the Pseudo First order model.

In the Table.2, it is seen that the Pseudo First Order and Modified Freundlich models provide better fitting for almost all the doped TiO_2 (commercial and synthesized) except SiO_2 doped syn. TiO_2 which fitted only in Modified Freundlich model.

Table.1: Linear correlation coefficient (R^2) & rate constant (k) for the photocatalytic degradation of MB using commercial & synthesized TiO_2 (treated at different temperatures) under UV light:

Commercial TiO_2								
Kinetic models	25˚C		450˚C		550˚C		650˚C	
	R^2	k	R^2	k	R^2	k	R^2	k
Zero order	0.473	-0.236	0.523	-0.237	0.388	-0.255	0.469	-0.228
Pseudo First order	0.868	-0.009	0.921	-0.010	0.894	-0.012	0.904	-0.010
Parabolic diffusion	0.860	-0.004	0.887	-0.004	0.886	-0.004	0.874	-0.004
Modified Freundlich	0.936	-0.592	0.977	-0.633	0.995	-0.514	0.972	-0.577
Synthesized TiO_2								
Zero order	0.709	-0.148	0.796	-0.163	0.821	-0.175	0.810	-0.157
Pseudo First order	0.872	-0.004	0.940	-0.005	0.963	-0.005	0.944	-0.004
Parabolic diffusion	0.836	-0.002	0.885	-0.002	0.869	-0.002	0.864	-0.001
Modified Freundlich	0.945	-0.988	0.989	-1.105	0.983	-1.087	0.980	-1.116

Table.2: Linear correlation coefficient (R^2) & rate constant (k) for the photocatalytic degradation of MB using doped commercial & synthesized TiO_2 calcined at 450˚C, under UV light:

Kinetic models	**Com. TiO_2 - ZnO**		**Com. TiO_2 – SiO_2**		**Com. TiO_2 - AC**	
	R^2	k	R^2	k	R^2	k
Zero order	0.543	-0.254	0.544	-0.250	0.030	-0.307
Pseudo First order	0.950	-0.013	0.940	-0.011	0.943	-0.025
Parabolic diffusion	0.892	-0.004	0.846	-0.004	0.875	-0.007
Modified Freundlich	0.994	-0.624	0.944	-0.625	0.975	-0.228
	Syn. TiO_2 - ZnO		**Syn. TiO_2 – SiO_2**		**Syn. TiO_2 - AC**	
Zero order	0.799	-0.183	0.182	-0.283	0.401	-0.299
Pseudo First order	0.966	-0.006	0.819	-0.015	0.961	-0.027
Parabolic diffusion	0.846	-0.002	0.900	-0.006	0.916	-0.005
Modified Freundlich	0.968	-1.019	0.991	-0.361	0.975	-0.503

Table.3: Linear correlation coefficient (R^2) & rate constant (k) for the photocatalytic degradation of MB using doped commercial & synthesized TiO_2 calcined at 450˚C, under Visible light:

Kinetic models	**Com. TiO_2 - ZnO**		**Com. TiO_2 – SiO_2**		**Com. TiO_2 - AC**	
	R^2	k	R^2	k	R^2	k
Zero order	0.570	-0.093	0.166	-0.100	0.615	-0.223
Pseudo First order	0.675	-0.002	0.265	-0.002	0.939	-0.009
Parabolic diffusion	0.832	-0.001	0.903	-0.002	0.866	-0.003
Modified Freundlich	0.887	-1.053	0.955	-0.762	0.973	-0.722
	Syn. TiO_2 - ZnO		**Syn. TiO_2 – SiO_2**		**Syn. TiO_2 - AC**	
Zero order	0.243	-0.086	-0.04	-0.151	0.546	-0.217
Pseudo First order	0.334	-0.002	0.070	-0.004	0.885	-0.008
Parabolic diffusion	0.877	-0.001	0.867	-0.003	0.843	-0.003
Modified Freundlich	0.937	-0.864	0.968	-0.484	0.938	-0.672

It is evident from Table.3 that Modified Freundlich model shows the best fitness for almost all the doped TiO_2 (commercial and synthesized) except ZnO doped com. TiO_2. All four models don't fit the kinetic data well for ZnO doped commercial TiO_2 calcined at 450˚C temperature.

Since most of the results followed Pseudo first order and Modified Freundlich models, the fitness of these models suggests that the whole photocatalytic degradation process consists of monolinear modeling. Pseudo First order model describe that photocatalytic degradation depends only on the concentration of dye, where amount of dye is much less than the amount of water which mean that only dye concentration changes during photo-degradation. The Modified Freundlich model describes heterogeneous diffusion from the flat surfaces to the solvent using a composition gradient. This result suggests that i) the system is adsorption-desorption controlled and ii) the photocatalytic degradation of the dye molecules are occurring on the TiO_2 surface before leaving (desorption) the surface patches [25-27].

4. CONCLUSIONS

The optimum photocatalyst dosage is found to be 0.8g/L for 20 ppm dye solution. TiO_2 is synthesized by sol-gel method and its photo catalytic performance is compared with that of commercial one.The optimum calcination temperature is evaluated as 550°C for both commercial and synthesized TiO_2. Both the samples are doped with AC or SiO_2 or ZnO separately and calcined at 450°C, this temperature is chosen because AC burns away at temperature >450°C. It is found that doping increases the efficiency of degradation under UV and visible light. Among them, AC doped TiO_2 shows the most promising result. It removes almost 80 to 85% MB under visible light. Not only that it is also able to degrade other dyes (CV, RB) effectively. This study suggests that AC doped TiO_2 has a high potential to be used as photo catalyst for industrial dye removal and it is also cost effective as it works well when exposed to visible light, which is nearly 50% in solar spectrum. Moreover it is found that most of the samples followed Pseudo First order model and Modified Freundlich model with the values of R^2 within 0.887 – 0.995.

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