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Tailoring the photocatalytic efficiency of activated carbon doped commercial TiO_2 photocatalyst on Methylene Blue, Rhodamine-B & Crystal Violet dyes under visible light source

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- TiO_2;
- Activated carbon;
- Photo catalyst;
- MethyleneBlue dye;
- Rhodamine-B dye;
- Crystal Violet dye;
- Kinetic models.

Abstract: Dyes are very important chemicals in modern industrial world, especially in the textile industry. But it is considered to be highly responsible for water pollution. A large group of industrial and textile wastes is organic dyes used in various processes. Semiconductor photo-catalysis plays a helping hand in this case. As an Advanced Oxidation Process (AOP), semiconductor photo-catalysis has profound efficiency in the photo degradation of various hazardous chemicals. This study highlights the photo degradation efficiency of activated carbon (AC) doped TiO_2 photo catalysts on Methylene Blue (MB), Rhodamine-B (RB) and Crystal Violet (CV) dyes under visible light source. The effects of dopant, catalyst dosage, and calcination temperature on the efficiency of this photo catalyst are also studied. To do the work, different dosages of AC doped TiO_2 photo catalyst were added to 200ml 20ppm solution of the aforementioned dyes. The catalyst calcined at 300 ˚C was found to be the efficient one in this experiment. The optimum catalyst dosage was found to be 0.20g to degrade 20 ppm 200 ml solution of industrial dyes. To evaluate the kinetics of this work, the resultant experimental data were plotted into four kinetic models: Zero order, Pseudo first order, Parabolic diffusion and Modified Freundlich model.

1. Introduction:

Demand of meeting of clean energy, tackling environmental pollution & treatment of industrial water all aforementioned processes can be done by the utilization of photocatalytic processes. Since photocatalytic reaction proceeds in air saturated & H_2O rich environment, the employed catalysts should remain stable under these conditions. Global warming poses one of the most serious threats to the environment ever faced in human history. The environment pollutions will cause an unprecedented onslaught of deadly & costly weather disasters such as severe storms, droughts, heat waves & rising seas & floods all over the world [1–3]. One of the major water pollutions is the residual dyes from different sources (e.g. textile industries, paper & pulp industries, dye & dye intermediates industries, pharmaceutical industries, tannery & craft bleaching industries etc.) which are considered a wide variety of persistent organic pollutants introduced into the natural water resources or wastewater treatment systems [4]. Water purification is the process of removing undesirable chemicals, biological contaminants, suspended solids &

gases from contaminated water. Most water is disinfected for human consumption & meeting the requirements of medical, pharmacological, chemical, industrial applications. Currently available water treatment technologies merely concentrates the pollutants present by transferring them to other phases without destroying them & most of these involve high operating costs & waste disposal problem along with a generation of toxic secondary pollutants into the ecosystem[5]. Due to these drawbacks of conventional processes, the semiconductor photocatalyst has appeared to be a promising technology. Among the metal oxide semi-conductors, TiO_2 have been investigated extensively due to their chemical stability & efficient photocatalytic properties [6].

The aim of this research is to study the efficiency of TiO_2 photocatalyst under visible light source for different dyes, the effect of calcination temperature and effect of activated carbon (AC) doping.

2. Experimental:

2.1 Materials:

- Titanium (IV) Oxide (TiO_2) (Product of SIGMA-ALDRICH, Germany)
- Activated Charcoal (AC) (Product of LOBA CHEMIE, India)
- Methylene Blue (LOBA CHEMIE, India)
- Crystal Violet (LOBA CHEMIE, India)
- Rhodamine-B (TECHNO PHARMACHEM, India)
- Absolute Ethanol (MERCK, India)
- Acetone (MERCK, India).

2.2 catalyst preparation:

2.2.1 Calcination process:

Commercial TiO_2 samples were subjected to calcination process. Prepared & grinded powdered form were put into the 50 ml crucible disc, followed by calcination at 100˚C, 200˚C, 300˚C, 400˚C, 500˚C, 600˚C respectively in the electric muffle furnace for 2 hour.

2.2.2 Doping process:

Calcinated TiO_2 (100˚C, 200˚C, 300˚C, 400˚C, 500˚C, 600˚C) were used along with commercial activated carbon (AC) in 5:1 ratio followed by dry impregnation method [7]. Firstly, TiO_2 photocatalyst & AC were weighted appropriately by maintaining the ratio of 5:1. Measured quantity were taken in 3 neck conical flask. Secondly, 30ml of absolute ethanol was added to this sample & mixed properly using magnetic stirrer. Stirring was done for 15 minutes without heating. Then, heating along with stirring was done for approximately 45 minutes maintaining temperature at 65˚C. Then when the mixture became more viscous then the stirring was stopped. At last, dry mixture was obtained which was grinded after cooling to room temperature.

2.3 Operational procedure:

The operational process contains several steps below:

- Preparation of solution of dyes maintain initial concentration each time
- Mixing of catalyst with dyes
- Experimental run in batch reactor
- Separation of catalyst from dyes
- Measurement of dyes concentration.

3. Results & Discussion:

3.1 Effect of calcination temperature & catalyst loading:

Catalyst loading & calcination temperature have a profound effect on the photocatalytic activity of TiO_2. In order to decrease catalyst loss it is essential to determine the optimum catalyst dosage. Increasing catalyst dosage increases degradation rate till an optimum dosage. Further increase in dosage causes deposition of catalyst which decreases the degradation rate. Calcination temperature has prominent influence on the catalyst size, structure, activity, phase etc. With an increase in calcination temperature TiO_2 transfers from anatase to rutile phase, decreasing the surface area & photocatalytic activity as well. An optimum calcination temperature gives the best result. It was found that TiO_2 treated at 300˚C & 0.20g dosage showed the best result (Figure 1).

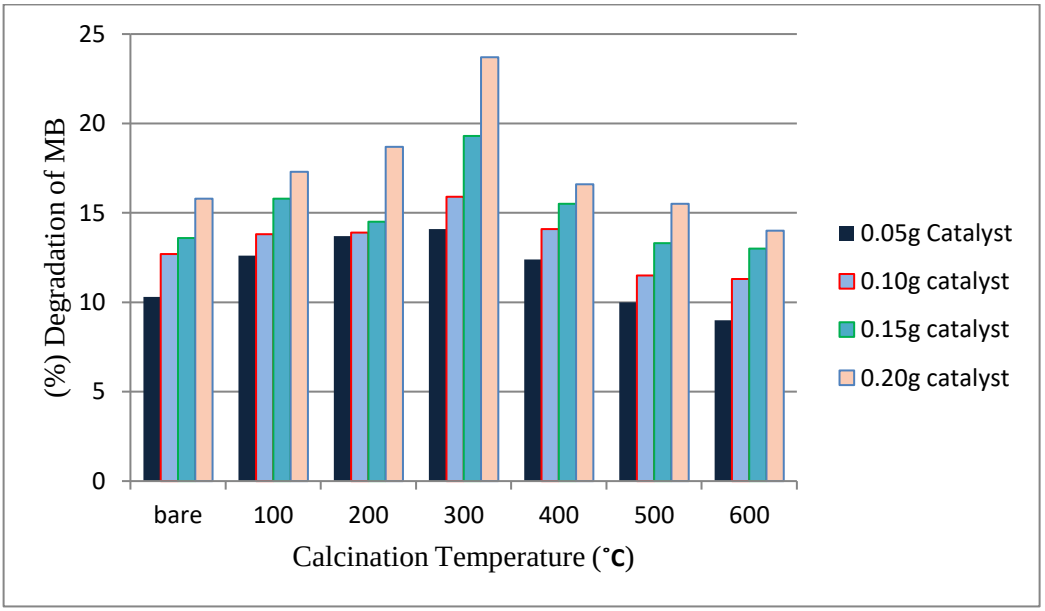

Figure 1: Effect of calcination temperature & loading of TiO_2 catalyst on MB degradation under visible light.

3.2 Effect of dopant ratio:

To determine the effect of dopant (AC) ratio, various amount of AC with TiO_2 were doped into thermally treated 300^0C TiO_2 e.g. 5:1, 5:2 & 10:1, all as TiO_2:AC. 0.20g of the above mentioned doped TiO_2 was taken into 200ml 20ppm solution of MB & kept under visible light for 1.30 hr. The result found was plotted into the graph. From the figure 2 it was found that 5:1 ratio of TiO_2 and AC shows the best result. This is because nonmetal doping increases the surface area of the catalyst, enhancing its activity. Excess dopant particles on TiO_2 surface lessens the specific area, leading to adsorption of reactant and simultaneously decreasing degradation rate.

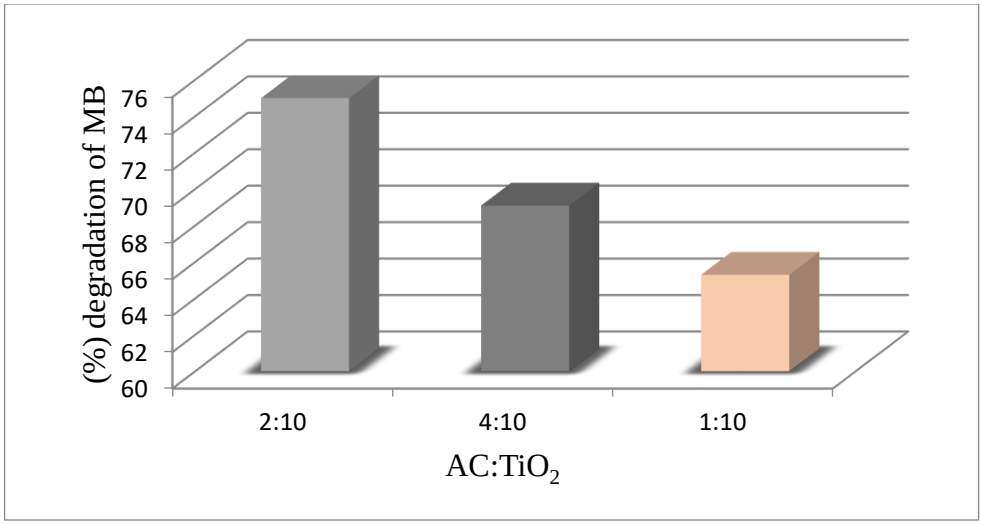

Figure 2: Effect of dopant ratio

3.3 Effect of AC doping:

Treated and untreated TiO_2 was doped with AC at 5:1 ratio. Different dosage of the AC doped TiO_2 was taken into 200ml 20ppm solution of MB and kept under visible light. The result was plotted into the graph (Figure 3). It was found that AC doped TiO_2 shows better result than the undoped one. The catalyst treated at 300˚C and doped with AC shows the highest degradation.

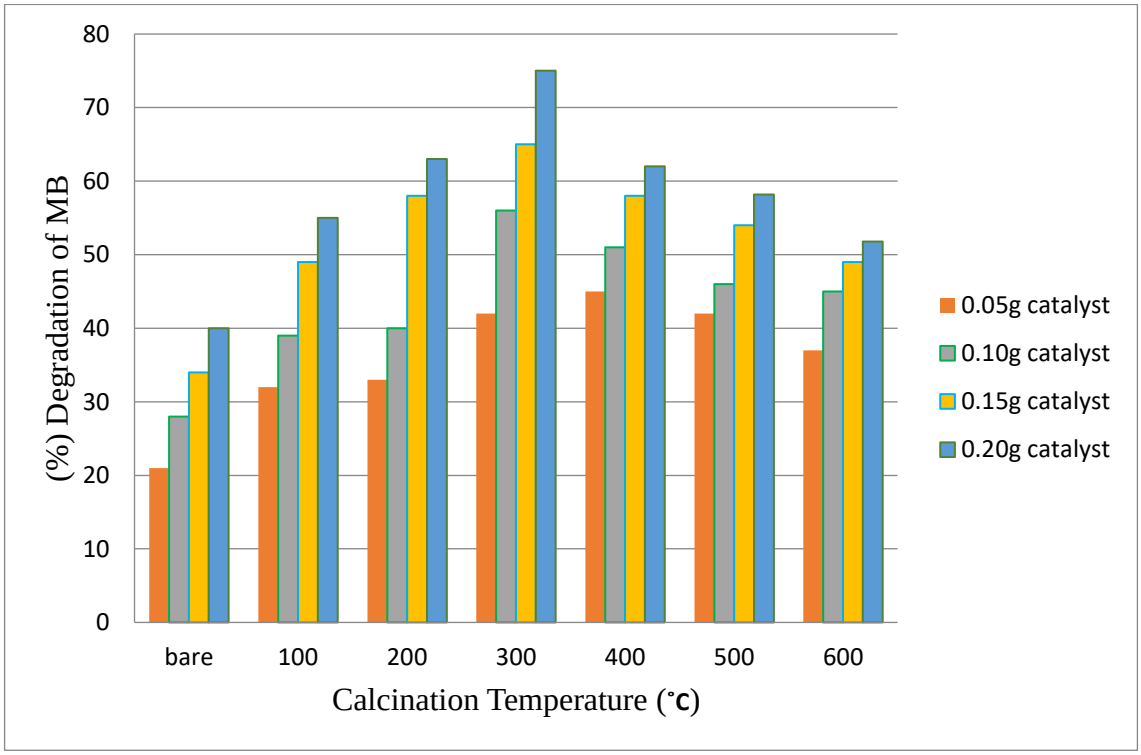

Figure 3: Effect of calcination temperature & loading of AC doped TiO_2 catalyst on MB degradation under visible light.

Mastab, Asheka, Biplob* and Rakib; (bikashsen.chem.tech@gmail.com)

3.4 Degradation efficiency of doped and undoped catalyst on different dyes:

To obtain the comparative result of doped and undoped TiO_2, 0.20g of TiO_2 (treated at 300˚C)& 0.20g of TiO_2 (treated at 300˚C) doped with AC were added to 20ppm 200ml solution of MB, CV & RB dyes. It was found that TiO_2 doped with AC shows better result than undoped TiO_2. AC doped TiO_2 shows 51.3%, 38% & 35.05% higher efficiency for MB, RB & CV dyes respectively.

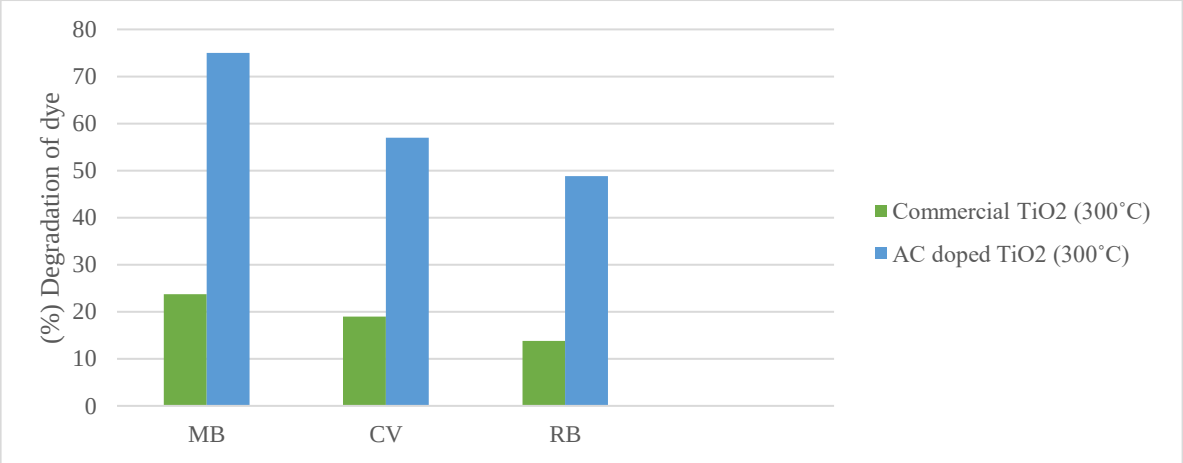

Figure 4: degradation efficiency of doped and undoped TiO_2 catalyst

3.5 Kinetic study:

In order to study the kinetics, the reaction was run into continuous mode. The obtained results were plotted into four kinetic models such as Zero order, First order, Parabolic diffusion & Modified Freundlich models. Rate constant (K) & correlation coefficient (R^2) of the kinetic models for MB & RB dyes are listed in the following table. From the table it is evident that Zero order models fits well except for RB dye with AC doped TiO_2. Further experiments should be done to study the kinetics well.

Table: Linear correlation coefficient (R^2) & rate constant (K) of kinetic models for photocatalytic degradation of MB & RB dyes under visible light source.

Degradation of MB & RB under visible light				
	(300°C TiO_2)		(AC doped TiO_2)	
Kinetic models	R^2	K	R^2	K
Zero order (MB)	0.9973	0.167	0.913	0.038
First order (MB)	0.8604	-0.00088	0.9306	-0.0058
Parabolic diffusion (MB)	0.9533	0.00426	0.1576	0.0094
Modified Freundlich (MB)	0.9533	0.0043	0.1575	0.0094
Zero order (RB)	0.972	0.143	0.761	0.037
First order (RB)	0.3511	-0.00088	0.9666	-0.0043
Parabolic diffusion (RB)	0.9428	0.00544	0.05435	0.00654
Modified Freundlich (RB)	0.9528	0.00540	0.05435	0.06650

4. Conclusion:

Water is constantly being polluted by industrial dyes. Photocatalysis can serve as an important process in the degradation of industrial dyes. Our work is focused on the photocatalytic efficiency of calcined TiO_2 & activated carbon (AC) doped TiO_2 photocatalyst under visible light source for different dyes. Implementation of photocatalysis for waste water treatment can bring about a great result. Further research can be done using different photocatalysts & dopants to determine the most feasible one that can degrade significant amount of dyes under visible light source.

5. References:

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