



Study of Photocatalysts for the Treatment of Dye-Contaminated Wastewater

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Abstract

Anatase phase TiO_2 was prepared by sol-gel method followed by heat treatment at 500°C . Preliminary study showed that the photocatalytic activity of the synthesized photocatalyst for the degradation of methylene blue (MB) was higher than that of commercial TiO_2 under UV irradiation. The photocatalytic degradation of MB by the synthesized TiO_2 was investigated at different operational parameters such as initial concentration and pH of methylene blue solution. The degradation of MB increased with increasing pH and decreasing concentration. This higher activity was quantitatively confirmed by kinetic study using first order kinetic model. In order to investigate the industrial applicability of the synthesized photocatalysts, recyclability of the catalyst was also performed. The catalyst was found to be recyclable. Attempts were also taken to prepare p-n junction heterostructure CuO-TiO_2 (0.1-0.25 wt% CuO) photocatalyst to enhance the photocatalytic efficiency of the catalyst.

Keywords : Photocatalytic degradation, Dye removal, Methylene blue, TiO_2 , Sol-gel method

1. Introduction

One of the main sources with severe pollution problems is dye-containing wastewaters, where the dyes create breakdown products that are toxic, carcinogenic or mutagenic to life forms [1,2]. Without adequate treatment these dyes can persist in the environment for a long period of time. It is obligatory to remove them from industrial effluents before being disposed into hydrological systems [3]. Broadly, wastewater treatment methods fall under three categories- Physical, Chemical and Biological. Physical method is ineffective in dye-removal and conventional chemical methods have high operating costs and produces huge hazardous sludge. Synthetic dyes are hardly biodegradable and hence biological methods are inefficient. Photocatalysis, an advanced chemical method could overcome all these problems. Different types of semiconductor materials such as TiO_2 , ZnO , Fe_2O_3 , CdS and ZnS are used as photocatalysts. Among them, TiO_2 is most widely used one. It is advantageous over the others in that it is chemically and biologically inert, photocatalytically stable, relatively easy to produce and to use, able to efficiently catalyze reactions, cheap and not risky to environment or humans [4]. Commercial

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TiO_2 is a mixture of anatase and rutile phase and traces of brookite phase. Synthesis parameters such as the crystal structure, surface morphology, and phase stability should be controlled and optimized as the chemical and physical properties exhibited by TiO_2 nanoparticles depend on both the composition and the degree of homogeneity [5]. It has been seen from various studies that due to the combination of phases, commercial TiO_2 causes recombination of electrons and holes and thus the photocatalytic efficiency is reduced. Higher crystallinity offers fewer defects acting as recombination sites between photo-generated electrons and holes and for this reason, anatase TiO_2 with higher crystallinity is used mainly as a photocatalyst under UV irradiation [6].

A lot of research works have already been conducted on the synthesis of TiO_2 of anatase phase by various routes. These studies include pyrolysis reactions or hydrolysis methods [7,8], gas-phase reaction method (e.g. CVD) [9], co-precipitation, flame hydrolysis and impregnation methods [10,11]. So far, sol-gel route has proved to be highly perspective for controlling the bulk and surface properties of the oxides [12-14] and for preparing pure anatase phase TiO_2 . TiO_2 nanoparticles synthesized by sol-gel method using Titanium (IV) isopropoxide as precursor

can effectively remove MB (98%) and congo red (CR) (98%) under UV light [15]. In another study, the degradation of MB and CR has been achieved with TiO₂ that is synthesized by one step sol-gel method using Titanium isobutoxide and characterized by SEM, XRD and EDS [16]. Although intensive efforts have been devoted to the synthesis of anatase TiO₂, its preparation in pure form still remains largely unexplored. Moreover, nanostructuring CuO with TiO₂ can be expected to improve the photocatalytic activity of TiO₂ due to the formation of an inner electric field which would promote charge separation and minimize or inhibit charge-carrier recombination. Doping with a very small amount of CuO (0.1 wt%) by deposition precipitation method also significantly enhances the photocatalytic activity of TiO₂ [17].

In this work, anatase phase TiO₂ was prepared using titanium butoxide as precursor by sol-gel method and its photocatalytic efficiency was evaluated based on the degradation of MB. Freshly synthesized TiO₂ showed better efficiency than the commercial TiO₂. The effect of operating parameters (concentration, pH, recyclability) on the activity of TiO₂ nanoparticles were investigated. The degradation process is found to follow first order reaction kinetics. In addition, CuO-TiO₂ heterostructures were synthesized by sol-gel method and their photocatalytic activity were compared with that of bare TiO₂.

2. Materials and Method

2.1 Materials

All chemicals used in this experiment were of analytical grade and used without further purification. The chemicals used were: titanium (IV) oxide (TiO₂) (product of SIGMA-ALDRICH, Germany), copper sulfate pentahydrate (CuSO₄.5H₂O) (MERCK, Mumbai), titanium butoxide (Merck Specialities Private Limited, Mumbai), n-butanol (BDH Laboratory Supplies, England), acetic acid (Merck kGaA, Germany) and methylene blue (MB) (Loba Chemie Pvt. Ltd., Mumbai). All solutions were prepared with distilled water.

2.2 Preparation of TiO₂ and CuO-TiO₂ heterostructures

Bare TiO₂ and heterostructures were prepared by room temperature sol-gel route. For bare TiO₂, 4 mL of titanium butoxide was added into a mixture of 4.3 mL n-butanol and 2.6 mL acetic acid. Subsequently,

a colloidal solution of TiO₂ was obtained by adding dropwise 4 mL of deionized water to the above solution and stirred vigorously overnight. The colloidal solution thus obtained was then dried at 150°C for 2 h and the resulting powder was annealed in air at 500°C for 2 h. For 0.1wt% CuO-TiO₂, all the conditions were same like that for pure TiO₂ except that 0.0029g CuSO₄.5H₂O was added to the colloid of TiO₂ after stirring for 8 h and then stirred vigorously overnight. For 0.12wt% and 0.25wt% CuO-TiO₂, the amount of CuSO₄.5H₂O was 0.0037g and 0.0072g respectively and the rest of the procedure is the same as before.

2.3 Photocatalytic experiments

The photocatalytic activities were evaluated by the degradation of MB dye. The degradation experiment was performed in a beaker used as reactor. An UV lamp (Model:SB-6/T5) of 6 watt was held by a clamp at the central position of the beaker with its bottom around 1 inch away from the bottom surface of the beaker and was kept in a fume-cupboard covered with black carbon paper to protect the environment from irradiation. In each experiment, 0.15 g of the catalyst was dispersed in 500 mL of MB solution of different initial concentrations. Prior to irradiation, the solution was kept in dark under stirring for 40 min to obtain adsorption-desorption equilibria. Then the solution was irradiated with UV and 4 mL samples were collected at regular intervals. The solution was then centrifuged (4000 rpm, 10 min) to separate the photocatalyst particles. The degradation process was monitored by an UV-vis spectrophotometer (Shimadzu, UV-1650 pc), measuring the absorbance at 664 nm. The degradation of MB, D , at time t was calculated by the following relation:

$$D\% = \frac{C_0 - C_t}{C_0} \times 100\%$$

Where C_0 is the initial concentration and that at the time t is C_t

To investigate the effect of concentration, 500 mL 10 ppm MB solutions of three initial concentrations (4.22 ppm, 9.53 ppm, 15.08 ppm) were run with 0.15g catalyst. To investigate the effect of pH, MB solutions of three different pH (2.81, 9.23 and 6.4) were run with 0.15 g catalyst. To investigate the efficiency of the recycled catalyst, 500 mL 9.53 ppm MB solution was run with 0.15 g of the used catalyst successively two more times (for initial concentrations of 8.74 ppm and 13.40 ppm). The data were analyzed with C/C_0 vs t plot.

3. Results and Discussion

3.1 Photocatalytic degradation of MB

To evidence the photocatalytic activity of as-synthesized TiO_2 , the photocatalytic decomposition of MB was performed as test reaction. The photocatalytic activity of the as-synthesized TiO_2 is compared with that of commercial TiO_2 and is shown in Fig.1. From the Fig.1, it is obvious that the degradation efficiency of as-synthesized TiO_2 is higher than that of the commercial TiO_2 . After 120 min of UV light irradiation, degradation efficiency of TiO_2 is 96.7%, whereas the degradation efficiency of commercial TiO_2 is 76.7%. The higher photocatalytic activity of anatase TiO_2 is also evident from the greater value of first order kinetic constant,

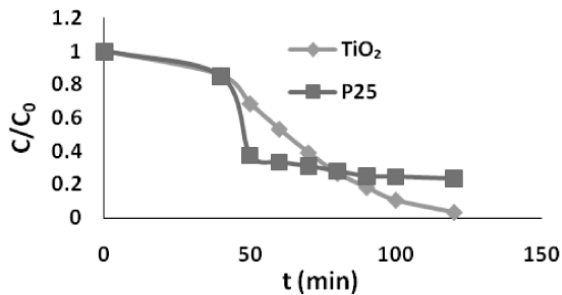


Fig. 1 : Comparison of photocatalytic activity of as-synthesized TiO_2 and commercial TiO_2

k (0.008 min^{-1}) compared to k (0.006 min^{-1}) for commercial TiO_2 . Due to the recombination of electrons and holes, the photocatalytic efficiency of the commercial TiO_2 is reduced. On the other hand, in case of anatase TiO_2 , higher crystallinity offers fewer defects acting as recombination sites. Moreover, slightly higher Fermi level, higher capacity to adsorb oxygen and higher degree of hydroxylation of the surface act as mention worthy reasons for increased photocatalytic activity of anatase TiO_2 than that of commercial TiO_2 [18].

3.2 Effect of concentration

The effect of dye concentrations on the photocatalytic decomposition is shown in Fig.2. Fig.2 shows that the photocatalytic degradation efficiency increases from 84.6% to 99.5% when the concentration is decreased from 15.1 to 4.2 mg/L. The efficiency of dye degradation decreased with an increase in concentration of dye. The reason is that when the initial concentration of dye is increased, more and more dye molecules are adsorbed on the surface of TiO_2 . Since the existence of the large amount of adsorbed dye results in the lack of any direct

contact with the holes or hydroxyl radicals, this might have an inhibitive effect on the dye degradation. Another possible reason for this result is the effect of UV screening of the dye itself. In high dye concentrations, a major amount of UV tends to be absorbed by dye molecules. This reduces the efficiency of the catalytic reaction due to the decline in $\text{OH}\cdot$ and $\text{OH}_2\cdot$ concentrations. In addition, an increase in substrate concentration can lead to the generation of intermediates, which may adsorb on the surface of the catalyst. Slow diffusion of the generated intermediates from the catalyst surface can result in the deactivation of active sites on the photocatalyst and result in a reduction in the degradation rate [19-21]. The decreasing order in the value of first-order rate constant, k from lower to higher concentration shows a better understanding of the result stated above. The k values were 0.017 min^{-1} , 0.008 min^{-1} , 0.005 min^{-1} for 4.22 ppm, 9.53 ppm and 15.08 ppm respectively.

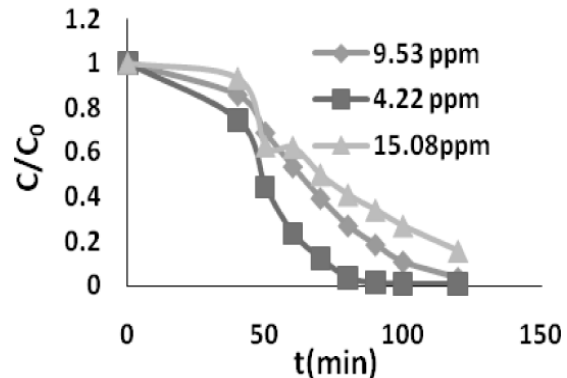


Fig. 2: Effect of concentration on photocatalytic degradation of MB with bare synthesized TiO_2

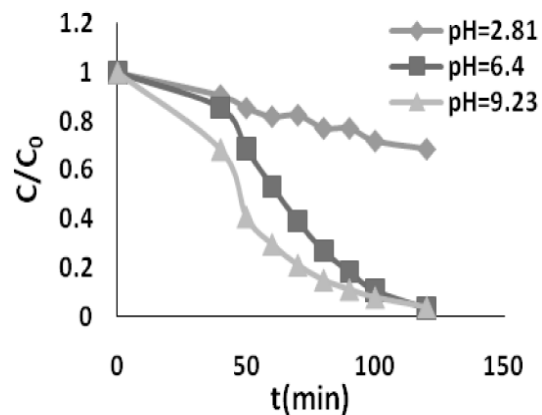


Fig. 3: Effect of initial pH on photocatalytic degradation of MB with bare synthesized TiO_2

3.3 Effect of pH

The effect of pH on the photocatalytic degradation of MB by as-synthesized photocatalyst is shown in Fig.3. It can be seen from Fig.3 that, at lower pH (pH = 2.81, efficiency = 31.5%), photocatalytic efficiency of the catalyst decreases significantly compared with medium (pH = 6.4, efficiency = 96.7%) or higher pH (pH = 9.23, efficiency = 95.7%). From the trend of the curves, it is evident that the more steeper curve was found for pH = 9.23, which means that at higher pH degradation process is quicker and there is a sharp drop in the concentration of MB within a very short time period. First, it is related to the ionization state of the surface, reactant dyes and products. Second, hydroxyl radicals can be formed by the reaction between hydroxide ions and positive holes. In alkaline solution, $\bullet\text{OH}$ radicals are easier to be generated by oxidizing more hydroxide ions available on TiO_2 surface, thus the efficiency of the process is logically enhanced [22]. Third, TiO_2 particles tend to agglomerate under acidic condition and the surface area available for dye adsorption and photon absorption would be reduced [23]. Fourth, the mechanism of the photocatalytic reaction in the presence of TiO_2 consists of a free radical reaction initiated by UV light. In some cases, the mechanism may depend significantly on the adsorption of the degraded compound on the surface of catalyst. The extent of such adsorption depends on many factors, and one of these factors is the charge of the degraded compound. It was found that in photocatalytic degradation, the adsorption level on unmodified TiO_2 is higher for dyes with a positive charge (cationic) than for those with a negative charge (anionic) [24]. As the charge depends on the pH of a given solution, it follows that both pH and the nature of a particular dye influence the photocatalytic activity. Finally, since MB is a cationic dye, at higher pH there is a Coulombic attraction between the positively charged surface of photocatalyst and the hydroxide anions. So, hydroxyl radicals can easily be generated, hence photocatalytic efficiency of the process is increased. The reverse process occurs at lower pH. The first-order rate constant, k values were 0.001 min^{-1} , 0.008 min^{-1} and 0.010 min^{-1} for pH values of 2.81, 6.4 and 9.23 respectively. The decreasing order in the values of k from higher to lower pH gives a better understanding of the result stated above.

3.4 Effect of recycling

For the purpose of practical implementation, it is essential to evaluate the stability and reuse of the catalyst. Because, a photocatalyst should be resistive

to photocorrosion, stable under different reaction conditions, and capable of promoting reactions efficiently upon repetitive use. From Fig.4 it can be seen that, there is no significant change in the catalytic efficiency for the degradation of MB dye by the photocatalysts after two successive cycles of use under UV irradiation. However, catalytic activity drops abruptly after second cycle. Further study is required to overcome this problem of stability for industrial application. First-order rate constant, k values were 0.008 min^{-1} and 0.006 min^{-1} for first and second cycle respectively giving evidence of the result stated above.

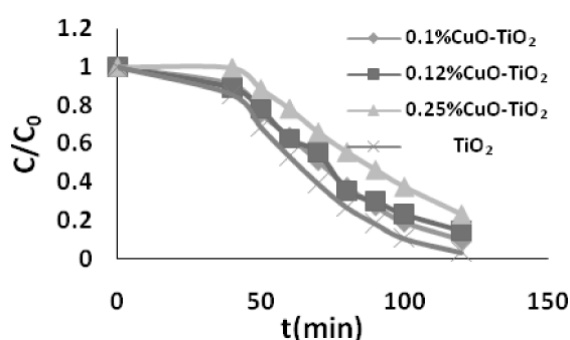


Fig. 4: Effect of adding CuO on the photocatalytic activity of anatase phase TiO_2 for the degradation of MB

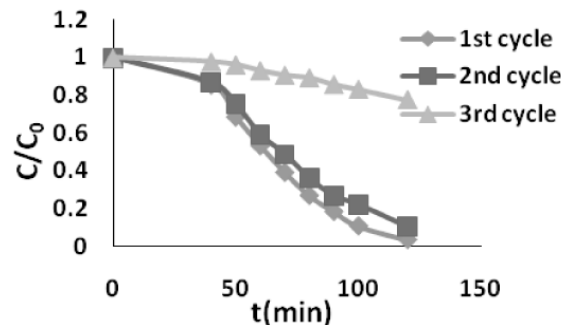


Fig. 5: Recyclability of synthesized TiO_2 for the degradation of MB

3.5 Evaluation of photocatalytic activity of CuO-TiO2 heterostructures

The photocatalytic activity of CuO-TiO_2 heterostructures is shown in Fig. 5. From Fig. 5, it can be seen that the degradation efficiencies of heterostructure CuO-TiO_2 containing 0.1wt%, 0.12 wt% and 0.25 wt% CuO are 90.2%, 85.4% and 76.7% respectively, which are lower than that of bare TiO_2 (96.7% photocatalytic efficiency) for the same irradiation time. There can be various reasons lying behind lower activity of heterostructures than that of bare TiO_2 . Firstly, a heterostructure always gives

maximum photocatalytic activity at its optimum dose. Secondly, The more "Janus" (two faces on opposite sides) the structure is, the more band bending is obtained at the interface and the more efficient the electron-hole pair separation is. Thirdly, at higher loadings, the bulk form of CuO creates charge recombination centers lowering the photocatalytic activity of the composites. Further study is required to determine the optimum dose of CuO in the heterostructures which could result higher catalytic activity for the degradation of organic dyes.

4. Conclusion

TiO₂ was prepared successfully by sol-gel method which gave better photocatalytic activity than commercial TiO₂ for the degradation of MB. The effects of various operating parameters (concentration, pH) were also found to coincide with theory. Again prepared TiO₂ showed significant degradation efficiency upon recycling. Reasons for lower photocatalytic activity of heterostructures than bare TiO₂ could be structural disorder, non-uniform dispersion or Inefficiency of p-n type heterostructures compared to n-n type heterostructures. But the most important reason is that, heterostructure always gives maximum efficiency at its optimum value, which could not be found out due to time limitation. Further study in this field is recommended for the synthesis of more efficient heterostructures.

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