Photodegradation of methylene blue dye using UV/BaTiO₃, UV/H₂O₂ and UV/H₂O₂/BaTiO₃ oxidation processes

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The photocatalytic degradation of methylene blue (MB) in aqueous solution was studied using UV source in presence of synthesized BaTiO₃ as photocatalyst and in combination with different concentrations of H₂O₂. The experiments were carried at different catalyst loading (0.05 & 0.1 wt %), pH (3, 7 & 9) and H₂O₂ dosage (0.5 – 6 mL/L). The degradation rate was found to be strongly dependent upon various experimental parameters such as catalyst loading, pH, and dosage of H₂O₂. There was no appreciable degradation seen in presence of catalyst alone. Discoloration of the dye was very nearly complete using UV/H₂O₂. Neither UV radiation nor H₂O₂ alone was able to decolourize the dye. The best degradation results were observed under optimum conditions of catalyst loading of 0.05 wt%, pH 9 for BaTiO₃/UV system. The optimum dosage of H₂O₂ for 12 ppm concentration of the dye was found to be 2 mL/L for UV/H₂O₂. The experimental kinetic data on the degradation of the dye followed the pseudo first order rate. Tests were further carried out for degradation of the dye using BaTiO₃/UV/H₂O₂ system. An enhancement in the degradation rate was observed with this system compared to UV/H₂O₂ system.

Keywords: Methylene blue, BaTiO₃, Photocatalytic, Discolouration

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A variety of hazardous pollutants are discharged into the environment from several industrial streams. Textile dyes and other commercial dyestuffs have become a focus of environmental remediation efforts in the last few years. Conventional methods for the abatement of pollution namely adsorption, absorption, incineration, and biodegradation were found to be ineffective, expensive or they are involved in the conversion of the pollutants from one phase to the other. Moreover, they pose secondary disposal problems and associated increase in cost and operation time.

Recent developments have been made in the domain of chemical water treatment techniques leading to the improvements in oxidative degradation procedures by applying photocatalytic methods for organic compounds dissolved or dispersed in aqueous media. The significance of this technique is that it is cost effective, it can degrade (detoxify) various complex organic chemicals, which was not possible to achieve by several other methods of purification. The key to success of the Advanced Oxidation Process (AOPs) is the production of highly reactive, transient hydroxyl (OH⁻) radicals, which are very powerful oxidants. A hydroxyl radical reacts much faster than the common oxidizing agents such as ozone (O₃) and hydrogen peroxide (H₂O₂). The AOPs fall under two categories namely homogeneous and heterogeneous photocatalysis. The homogeneous photocatalysis include UV/H₂O₂, UV/O₃ and Photo-Fenton processes that employ UV photolysis of H₂O₂ or O₃ in order to produce hydroxyl radicals. The heterogeneous photocatalysis utilizes semiconductor photocatalysts such as TiO₂, ZnO and CdS in conjunction with UV-irradiation. The semiconductor absorbs UV light, generates hydroxyl radicals mainly from adsorbed H₂O and hydroxide ions. Compared to the homogeneous AOPs or other conventional technologies, heterogeneous photocatalysis has many potential advantages for the degradation of organic contaminants in water. It has higher destruction rates, photocatalysts can be reused, renders high degradation quantum yield and the reaction can be carried out at room temperature and atmospheric pressure. Hetero-
geneous photo catalysis has proved to be an effective treatment method for the removal of toxic pollutants from the industrial wastewaters owing to its ability to convert them into innocuous end products such as CO₂, H₂O and mineral acids. It’s applicability for oxidation of several model pollutants has been experimentally verified⁴⁻⁷. Reactivity of doped TiO₂ seems to be complex function of the doped concentration, energy level of the dopants within the TiO₂ lattice, the distribution of dopants, electron donor concentration and the light intensity⁸⁻¹⁰.

In the present study, an attempt has been made to investigate the degradation kinetics of methylene blue in presence of UV light using synthesized BaTiO₃. The effect of addition of an oxidant like H₂O₂ was examined. Suitability of the kinetic models proposed for the degradation studies were also tested. To the best of the literature review by authors, BaTiO₃ has not been examined as photocatalyst.

Experimental Procedure

Materials and Reagents

Methylene blue (C₁₆H₁₈ClN₃SCl) was obtained from Qualigens Fine Chemicals (India). Its chemical structure as shown in Fig. 1 makes it to fall under a group of azin dyes. λ<sub>max</sub> for the dye is 664.8 nm. A medium pressure UV lamp of 25W procured from Philips was used as an irradiation source. All the chemicals used to prepare the buffer solutions were obtained from Ranbaxy Chemicals (India). High purity TiCl₄ (99.5% assay) was procured from LOBA chemicals for photocatalyst preparation. Hydrogen peroxide solution (H₂O₂) (30% stabilized for synthesis) was procured from Ranbaxy Chemicals (India). Barium Hydroxide Ba(OH)₂.8H₂O for doping of TiO₂ was obtained from Merck Ltd. Potable water (pH=7.9, DO=7.5 ppm, Total alkalinity=360 mg/L of CaCO₃, Turbidity 10 NTU) was used for the preparation of dye solutions.

Preparation of semiconductor photocatalyst (BaTiO₃)

Hydrothermal method of preparation was used to prepare BaTiO₃. This method offers lot of advantages in producing fine powders. Hydrothermal method of preparation yields high purity and single phase oxides at relatively rapid rates under elevated water vapour pressures and temperatures with minimum contamination¹¹,¹². About 20 mL of high purity TiCl₄ was carefully diluted by adding it drop wise to 1500 mL of ice cold and distilled water. The solution was acidified by adding sulphuric acid. Reactive gel of TiO₂ was then precipitated out by slow addition of NH₄OH (pH being maintained above 7). The gel was then washed with distilled water till it is chloride free. The TiO₂ gel was then suspended in 0.13 M Ba(OH)₂ solution, the slurry was then charged into an autoclave. The system was heated at 120-150°C for about two hours. The product obtained (BaTiO₃) was then separated, dried and powdered.

Product characterization

SEM Analysis

SEM figure of BaTiO₃ is as shown in Fig. 2. The analysis infers the formation of cluster. Spherical morphology is clearly seen. Particles in the nano range have been synthesized effectively. Size range is around 40 nm for the synthesized particles.

XRD Analysis

The major peaks of the XRD pattern for the synthesized BaTiO₃ as shown in Fig. 3, matched with that for pure BaTiO₃¹₃. The synthesized product is not fully crystalline which is clearly noticeable from the analysis.

Experimental procedure for degradation studies

A 100 mL substrate solution of known concentration was prepared in water. BaTiO₃ prepared with varying concentrations (0.05 and 0.1 wt %), was
added to the solution and the mixture was transferred to the reaction vessel. Reaction temperature was maintained at room temperature at 27°C (±3°C) for all the experimental trials. Optimal conditions were fixed for degradation at atmospheric conditions. The substrate solution was stirred to maintain uniform catalyst suspension. A slow stream of air was bubbled through the suspension and the mixture was exposed to UV light. The aliquots were withdrawn from the reaction mixture at regular intervals and were centrifuged before analyzing the dye concentration. The concentration of dye was measured using UV spectrophotometer (Systronics-117). The pH of the solutions was adjusted with an Inlab pH meter. Experiments were conducted under different pH conditions (3, 7 and 9). Further degradation studies were carried out for UV/H2O2 and UV/H2O2/BaTiO3 systems. A standard 12 ppm solution was used for degradation tests. The degradation experiments conducted in presence of H2O2 was carried out in absence of air.

Results and Discussions

Effect of catalyst

In order to determine optimal amount of photocatalyst to affect oxidation, experiments were carried out without and with catalyst loadings (0.05 and 0.1 wt%) under constant pH (3, 7 and 9) conditions at room temperature and atmospheric pressure conditions. No degradation was observed without catalyst loading. Figure 4 represents the percentage of unreacted MB as a function of irradiation time. It was found that after 2 h the extent of colour degradation in presence of catalyst, at a loading of 0.05 wt% gives a better performance than 0.1 wt%, when studied under constant pH conditions. The decrease in rate from 0.05 to 0.1 wt% catalyst loading is perhaps due to light scattering, caused by the suspended catalyst. Further increase in catalyst loading decreased the rate of discolouration. This phenomenon may be explained as follows: with an increase in catalyst loading the light penetration through the solution becomes difficult. Increase in catalyst concentration may decrease photo absorption, which in turn, reduces the dye adsorption thus reducing the rates14-17. Optimal wt% of the catalyst depends on geometry of the photo reactor, working condition and the incident radiation reflux18,19,15. Chemically modified TiO2 by doping to yield BaTiO3 has shown a better performance in degrading methylene blue in presence of UV light. BaTiO3 has an energy gap of 3.2eV, similar to TiO2, even after the chemical modification. Photogenerated charge carriers are able to move more freely in chemically modified TiO2 (BaTiO3) lattice and efficiently react with the adsorbed species on the surface of the photocatalyst. In presence of UV light, on the surface of BaTiO3 photodecomposition of H2O2 to hydroxide radicals occurs quite readily. The amount of OH* radicals increases as H2O2 concentration increases at the catalyst solution interface. The hydroxyl radical drives the chemical reaction by attacking oxidizable contaminants producing progressive breaking of molecules yielding CO2, H2O and dilute inorganic acids.

Effect of pH

The photocatalytic degradation was studied in the pH range of 3-9. It was observed that the degradation rate increased with increase in pH. This is indicative of the surface property of the photocatalyst, which can be explained on the basis of zero point charge of
Adsorption of H₂O molecules at the surface metal sites is followed by the dissociation of the OH groups leading to a coverage with chemically equivalent metal hydroxyl groups (M-OH). Due to the amphoteric nature of most metal hydroxides, the following equilibrium can be considered.

\[ \text{M-OH} + \text{H}^+ \rightarrow \text{M-OH}_2^+ k_1 \]

\[ \text{M-OH} \rightarrow \text{M-O}^- + \text{H}^+ k_2 \]

The zero point charge \( (p\text{H}_{zpc}) \) of the metal oxide is defined as the pH at which the concentration of the protonated and the deprotonated surface groups are equal. The isoelectric points of BaTiO₃ may vary over a range of pH depending upon the processing history, Ba/Ti ratio etc. This makes the effects of pH on the dissolution of BaTiO₃ powders in aqueous solutions still unclear. The pHzpc of BaTiO₃ is generally around 4 to 6 where there is predominance of positive charge below \( p\text{H}_{zpc} \) and negative charge above 21-27. Considering the positive charge on MB (MB⁺), the effect of pH on the photocatalytic degradation can be accounted for on the basis of the electrostatic adsorption model where these cations are more readily accommodated at the negative sites. Alkaline medium (\( p\text{H}=9 \)) gives relatively better degradation than neutral or acidic medium as observed. Degradation rates are higher at higher concentration as shown in Fig. 4. It is observed that degradation of MB stops after a particular time in acidic medium, though with basic and neutral media, proceeds at extremely low rates.

**Effect of H₂O₂**

Discolouration tests were carried out for varying H₂O₂ doses in 12 ppm MB solution prepared using water (\( p\text{H} 7 \)) and the results (% MB retained as function of time) were plotted as shown in Fig. 5. The degradation rate increased from 0.5 to 2 mL/L of H₂O₂. Further increase in H₂O₂ loading reduced the degradation rates. Higher concentration of H₂O₂ rendered reaction solution acidic affecting reduced rates, while higher rates are obtained in alkaline media.

Bubbles were evolved from the photolysis of H₂O₂ or CO₂ produced from the complete mineralization of MB. The production of the bubbles increased with the increase in H₂O₂ concentration. Higher concentration of H₂O₂ liberated more of hydroxyl free radicals, which cause the dye discolouration. However, increase in the H₂O₂ concentration beyond certain limits (critical concentration) does not increase the reaction rates as it tends to act as a hydroxyl radical scavenger instead of a free radical generator. From Fig. 5 it is inferred that 2 mL/L can be considered to be an optimum value of H₂O₂ loading for the discolouration in the presence of UV.

A Pseudo first-order kinetic model was used to fit the experimental data

\[ -\frac{dC_{\text{MB}}}{dt} = kC_{\text{MB}}C_{\text{OH}^*} \]  \( \ldots (1) \)

where \( C_{\text{MB}} \) represents the dye concentration, ppm; and \( C_{\text{OH}^*} \) represents the hydroxyl radical concentration, ppm.

By the pseudo-stationary hypothesis (i.e. the \( C_{\text{OH}^*} \) can be considered to be a constant in the presence of excess H₂O₂), the rate expression (1) can be simplified to fit an equation following the first order kinetics,

\[ -\frac{dC_{\text{MB}}}{dt} = kC_{\text{MB}} \]  \( \ldots (2) \)

Integrating the above equation; from \( C_{\text{MB}0} \) to \( C_{\text{MB}t} \) on the left hand side, and \( 0 \) to \( t \) on the right,

\[ \int_{C_{\text{MB}0}}^{C_{\text{MB}t}} -dC_{\text{MB}} = k \int_0^t dt \]

\[ \ln(C_{\text{MB}0}/C_{\text{MB}}) = kt \]  \( \ldots (3) \)

where \( C_{\text{MB}0} \) represents the initial dye concentration in ppm, \( C_{\text{MB}} \) represents the final dye concentration in ppm.
The experimentally obtained data were verified to fit the above equation (Fig. 6).

The fairness of the fit is indicated by the fact that linear regression ($R^2$) values are always greater than 0.95. Therefore, the model is in good agreement with the experimental data. The values of the first order rate constant are indicated in the Table 1. The value of $k$ is maximum at $H_2O_2$ dosage of 2 mL/L.

**Degradation using $H_2O_2/UV/BaTiO_3$**

Discolouration tests were further carried out using 0.05% catalyst loading and varying $H_2O_2$ dosage. The results are shown in the Fig. 7. It is observed that 2 mL/L of $H_2O_2$ gives better degradation as compared to higher dosages of $H_2O_2$ for 12 ppm methylene blue concentration. It has been concluded earlier that this represents the optimum dosage of $H_2O_2$. To prove the effectiveness of catalyst addition, and for comparison, rate curves pertaining to dosage of 2 mL/L of $H_2O_2$ and 2 mL/L $H_2O_2$ with 0.05% catalyst loading, are shown in Fig. 8. There has been an enhancement in the rate of degradation with catalyst addition and a consequent reduction in time to decolourize the solution.

**Conclusions**

Heterogeneous photocatalysis has proved to be very effective in the removal of toxic pollutants from the industrial waste waters owing to its ability to convert them into innocuous end products such as CO$_2$, H$_2$O etc. Synthesis of semiconductor photocatalyst for degradation of the azin dye (MB) was accomplished and characterized using scanning electron microscope (SEM), and X-ray diffraction (XRD) analysis. It revealed the existence of fine powders of nano scale BaTiO$_3$. In order to study the optimum conditions for catalyst loading; comparative studies were carried out by varying the pH of the solution. Alkaline medium gives better degradation compared to neutral or acidic medium for similar catalyst loadings. For $H_2O_2/UV$ system, the reaction rate increases up to a critical value (2 mL/L) and then decreases as $H_2O_2$ added beyond the critical value begins to act as a scavenger for the hydroxyl radicals. The degradation kinetics of methylene blue with $H_2O_2$
(which represents a homogenous system) follows a pseudo-first-order kinetics. Presence of the catalyst in UV/H₂O₂ system resulted in increased degradation as compared in its absence.

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