

Photocatalytic Degradation of Methylene Blue by Using $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ Nano Composite under Visible Light

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Abstract

Photocatalytic degradation of methylene blue from aqueous solution has been carried out using $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ photo catalyst under visible radiation. Effect of various parameters like pH, concentration of dyes, amount of semiconductor and light intensity has been studied on the rate of reaction. Various control experiments were carried out, which indicated that semiconductor $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ played a key role in photocatalytic degradation of dye. A suitable tentative mechanism has been proposed for photocatalytic degradation of dye.

Keywords: Methylene blue; Nano composite; Photo catalyst; Sol-gel

Introduction

Waste water from textile, paper and some other industrial processes are usually highly colored, toxic, carcinogenic or mutagenic [1]. These colored compounds are not only aesthetically displeasing but also inhibiting sunlight enetration into the stream and affecting aquatic ecosystem. Dyes usually have complex aromatic molecular structures which make them more stable and difficult to biodegrade. Some dyes are reported to cause allergy, dermatitis, skin irritation, cancer and mutations in humans [2].

Among many organic pollutants, methylene blue (MB) is one of pollutant color for environment undesirable which effects on aesthetic of environment [3]. Thus, environmental contamination by these toxic chemicals has emerged as a serious global problem. On the contrary, bleached dye after degradation of solution is relatively less toxic and almost harmless. Secondly, dye containing coloured water is almost no practical use, but if this coloured solution is bleached to give colorless water, then it may be used for some useful purposes like washing, cooling, irrigation and cleaning. Recently, photocatalytic reactions induced by illumination of semiconductors in suspension have been shown to be one of the most promising processes for the wastewater treatment [4]. Nano sized semiconductors such as TiO_2 , ZnO , ZnS , WO_3 and Fe_2O_3 are often used as catalytic agents because of their high stability, low costs, high efficiency and no toxicity [5]. Among various semiconductor photo catalysts, iron oxide (Fe_2O_3) nanomaterials exhibit promising photocatalytic activities due to their environmental friendly behavior, low catalyst cost, high specific surface area, high crystallinity and solar energy application [6-8] and thus, could be an alternative material for environmental application and wastewater treatment [9-11]. Moreover, hematite is the most stable iron oxide under ambient condition and has significant scientific and technological importance, due to stability and interesting band gap of 2.2 eV, for absorption under visible light irradiation. However, the photocatalytic activity of the iron oxide is depending on the particle size, which is difficult to synthesize nano-sized iron oxide by conventional method and to control its crystal size in the photo catalyst [12]. This is due to the agglomeration of nano-particles in the aqueous solution, which causes the reduction of photocatalytic efficiency. One certain way to overcome this drawback is to apply innovative synthetic method of iron oxide nanoparticles of the catalysts that can be easily dispersed in organic medium and homogenously loaded on to the supported materials. Many studies have continuously tried to improve the photocatalytic activity of iron oxide by coupling of different semiconductor oxide nanoparticles [13-16]. Therefore, in this work, binary $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ nanocomposite was used as photo catalyst under visible radiation for degradation of MB

dye in aqueous solution and investigates the effects of catalyst loading, initial concentration, induced light and pH.

Experimental

Synthesis of photo catalyst

The $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ binary mixed nanoxide powder was prepared by sol-gel method. The sol was corresponded to total volume ratio of metal, Butanol, deionized water and nitric acid ratio of 1:20:4:0.1. In each case, ferric nitrate nanohydrate and aluminum nitrate nanohydrate were dissolved in stoichiometric amounts of water, 69% HNO_3 and Butanol then mixed with vigorous stirring at room temperature (25°C). The prepared sol was left to stand for the formation of gel. After the gelation was completed, the gel was aged for 5 days at room temperature and sample was dried at 75°C for 36 h. After grinding the dried samples, they were calcined at 400°C for 3 h. Nano sized materials of the catalyst were analyzed and the procedure was indicated in my previous work [17].

Photocatalytic degradation studies

Photocatalytic activities of the as-synthesized powder were evaluated by decolorization of Methylene blue dye in aqueous solution. The experiments were carried out in the presence of visible light irradiation without any catalyst (blank), with catalyst in dark and in the presence of $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ photo catalyst. The photocatalytic reactor consists of a Pyrex glass beaker with an inlet tube for provision of air purging during photo catalysis and outlet tube for the collection of samples from the beaker. Reaction was set up by adding 0.2 g of the as-synthesized powder into 100 mL of MB solution (25 mg/L) in the Pyrex glass beaker of 250 mL volume and the suspension was magnetically stirred in dark for 30 min to obtain adsorption/desorption equilibrium before irradiating the light in the beaker. Before illumination of the samples by visible radiations, air/oxygen was purged into the solution with the help of a porous tube at hand purging in order to keep the suspension of the reaction homogenous.

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During the reaction, the solution was maintained at room temperature and the distance of the lamp from the solution was 9 cm. Then the light source was activated, 10 mL of the sample was withdrawn at 15 min time interval over irradiation time for 90 min. The suspension was centrifuged at 3000 rpm for 10 min and filtered to remove the catalyst particles before measuring absorbance. The absorbance of the clear solution was measured at a λ_{\max} of 665 nm for quantitative analysis. The incandescent bulb was used as visible light source with a definite power of 40 W, 220 V and 60 Hz frequency. Percentage degradation of MB dye was calculated using the following relation:

$$\% \text{ degradation} = \frac{A_0 - A_t}{A_0} \times 100$$

Where A_0 is absorbance of dye at initial stage A_t is absorbance of dye at time t.

Results and Discussion

Photocatalytic degradation study

The photocatalytic activity of as-synthesized nanomaterial was evaluated by the degradation of MB dye in aqueous solution. The decolorization of the MB dye was examined under three different conditions (treatments): visible light irradiation without any catalyst (blank solution), in the presence of catalyst without light irradiation (in dark) and in the presence of Al₂O₃/Fe₂O₃ photo catalyst under visible light irradiation, respectively. For the blank experiment (in the absence of the catalyst) under visible light irradiation, almost insignificant degradation of the dye was observed with only 5.95%. The corresponding plots of percent degradation as a function of time under visible light irradiation without catalyst are shown in Figure 1.

In the presence of photo catalyst (Al₂O₃/Fe₂O₃), but without irradiation, only 14.81% decolorization efficiency was observed throughout in the 90 min. This result confirms that degradation of the MB in the presence of the photo catalyst, but without light irradiation is insignificant. The fact is that no electron-hole pair could be generated in the semiconducting material without assistance of light irradiation. The formation of electrons-holes pairs are responsible for enhancing the oxidation and reduction reactions with the MB dye, which might be adsorbed on the surface of the semiconductor to give the necessary products. The corresponding plots of percent degradation as a function of time in the presence of catalyst without light irradiation are shown in Figure 2.

Actually, the experimental results show that when the dye solution is exposed to visible light irradiation for 90 min in the presence of Al₂O₃/Fe₂O₃ photo catalyst, about 75.10% of the MB dye could be degraded under visible light irradiations. The corresponding plots of percentage degradation of MB dye as function of time under visible irradiation in the presence of Al₂O₃/Fe₂O₃ photo catalyst are shown in Figure 3. Accordingly, the degradation efficiency of MB dye under the visible light was found to be much larger than the degradation efficiency as compare to blank and dark treatment. This enhancement under visible light in the presence of Al₂O₃/Fe₂O₃ photo catalyst could be explained from two reasons. The first one could be the fact that the Al₂O₃/Fe₂O₃ photo catalyst prepared by the sol gel method has a high specific surface area, that could give more active surface sites to absorb water molecules and to form active •OH and HOO• radicals by trapping the photo generated holes. This free active radical drive the photo degradation reactions and eventually leads to the decomposition

of organic pollutants in aqueous solution [8]. The higher surface area also facilitates the absorption of dye molecules on the surfaces of Al₂O₃/Fe₂O₃ photo catalyst. Under visible light irradiation, MB molecules are absorbed on the surfaces of nano composite and produced electrons. These electrons are captured by the surface adsorbed O₂ molecules to yield O₂^{-•} and HO₂• radicals, which makes more chance to touch with dye molecules and giving a faster reaction speed then, the MB molecules could be mineralized in time by the super oxide radical ions. Therefore, it can be concluded that the smaller crystalline size of nano composite are favorable for the reduction of O₂ and oxidation of H₂O molecules by trapping electrons and holes, which improves the photocatalytic activity of the nano composites photo catalyst under visible light region. However, the photocatalytic activity of Al₂O₃/Fe₂O₃ nano composite is still not satisfactory for degradation of organic pollutants in wastewater

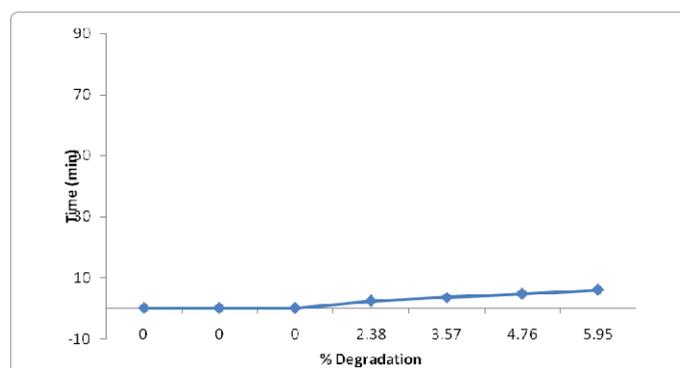


Figure 1: Plots of percentage degradation of MB dye as function of time under visible light irradiations in blank solution (without catalyst).

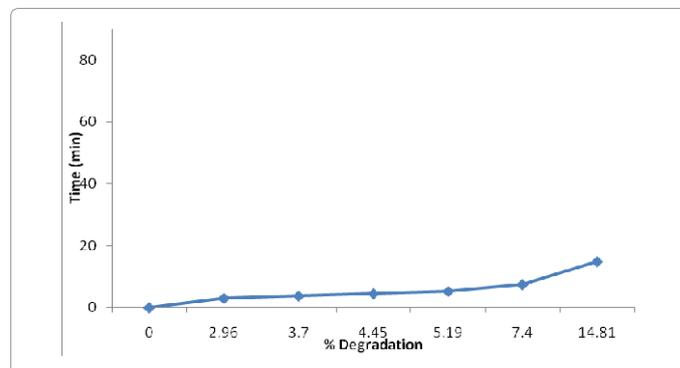


Figure 2: Plots of percentage degradation of MB dye as function of time in the presence of Al₂O₃/Fe₂O₃ photo catalyst under without irradiation.

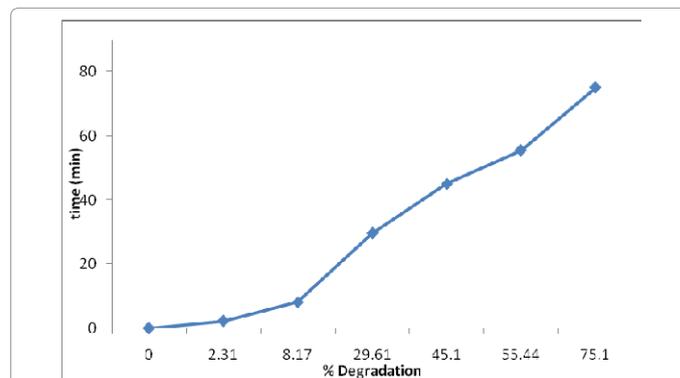


Figure 3: Plots of percentage degradation of MB dye as function of time under visible irradiation in the presence of Al₂O₃/Fe₂O₃ photo catalyst.

as compare to other binary nano composite. This may be due to that, the similar ionic radii and same charge of the materials of iron (III) and aluminum (III) oxide. Subsequently complete substitutions occur between aluminum (III) oxide and iron (III) oxide nanoparticles and no structural defect could be expected [18].

Effect of pH of solution

The pH of the solution is likely to affect the degradation of MB dye in aqueous solution and therefore, the rate of degradation of the dye was studied in the pH range of 4.0 to 9.0. It has been observed that the rate of photo catalytic degradation of MB dye was increased as pH was increased from 4.0 to 5.0 and it got an optimum value at pH 5.0. On further increasing the pH, the rate of the reaction was decreased. This behavior may be explained on the basis that when pH was increased, attraction between cationic dye molecules and hydroxyl ions increases and accordingly the rate of photocatalytic degradation of the dye was increases. But above pH 5.0 value rate of photocatalytic degradation of the dye was decrease, this may be due to the fact that amphoteric nature of catalyst and the surface becomes negatively charged for higher pH values. This causes the electrostatic repulsion between the catalyst and negatively charged MB dye in aqueous solution. On other hand, the zero point charge (pHzpc) of $\alpha\text{-Fe}_2\text{O}_3$ is the main parameters that controlling the degradation of MB on composite Fe_2O_3 , which are about 4.4. As the solution pH increases from an acidic region to an alkaline region, MB ions in solution exist mainly as acidic form. When the pH is below the isoelectric point of composite Fe_2O_3 catalyst, the surface of $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ will be positively charged. Methylene blue dye solutions are easily adsorbed on the Fe_2O_3 hierarchical microspheres surface in the low pH range due to strong electrostatic attraction between dye and $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$. As pH increases, the Fe_2O_3 surface becomes less positively charged, and the interaction between $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ and dyes becomes less and changes to a repulsive force at $\text{pH} > \text{pHzpc}$, resulting in a significant decrease of degradation efficiency [19] (Figure 4).

Effect of initial MB concentrations

The effect of initial dye concentration on the degradation efficiency was investigated by varying the initial dye concentration. Different initial concentrations of MB with rang from $0.5 \times 10^{-5} \text{ M}$ to $1.4 \times 10^{-5} \text{ M}$ were used to evaluate the photo catalytic activity as shown in Figure 5. As a result the photo degradation efficiency was decreased with concentration of MB dye more than $1.1 \times 10^{-5} \text{ M}$ after 90 min irradiation time. This fact explain as, the adsorption capacity is higher at lower concentration because more active site is available for MB molecules to be adsorbed on the surface $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ photo catalyst. At higher concentration which the more and more molecules of MB adsorbed on the surface $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ photo catalyst, which have hinder the photo generation of hydroxyl radicals of OH^- ions ($\text{H}^+ + \text{OH}^- \rightarrow \cdot\text{OH}$), which causes the decreasing rate of photo degradation reaction of the catalyst [20,21]. Therefore, much longer time is required to reach the complete degradation of higher concentrations of MB as compared to low concentration of the dye. These results confirm that the Beer-Lambert law: as the initial dye concentration increases, the path length of photons entering the solution was decreases. This results in the lower photon absorption on the catalyst particles, and consequently decreases the photocatalytic reaction rate at higher concentration of MB dye [22].

Effect of amount of catalyst

The amount of semiconductor also affects photo degradation efficiency of the catalyst. Different amounts of photo catalyst were

used (0.02 g to 0.11 g) for degradation of MB dyes under visible light irradiation and the results are given as shown in Figure 6. It has been observed that as the amount of photo catalyst of $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ was increased, the rate of photo degradation of dye increases but ultimately, the reaction rate become virtually constant after a certain amount (0.05 g) of the semiconductor. This may be due to the fact that as the amount of photo catalyst was increases the number of active sites on the photo catalyst surface and the exposed surface area also increases, but when the concentration of the catalyst increases above the optimum value, the degradation rate decreases due to the interception of the light by the suspension [22,23]. And also excess catalyst prevent the illumination, $\cdot\text{OH}$ radical, a primary oxidant in the photocatalytic system decreased

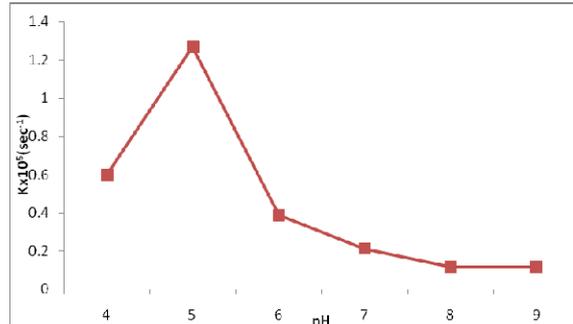


Figure 4: Effect of initial pH on photocatalytic degradation of MB on the presence of catalyst.

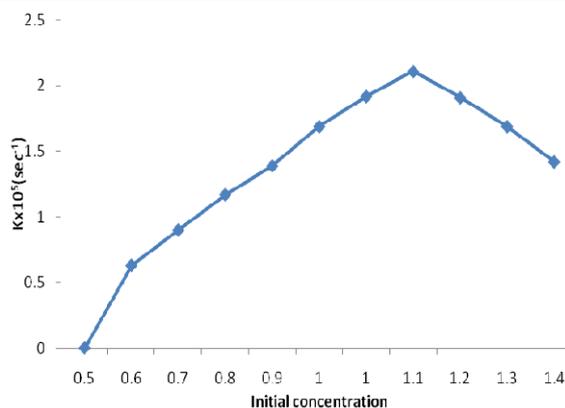


Figure 5: Effect of initial concentration of MB on degradation efficiency.

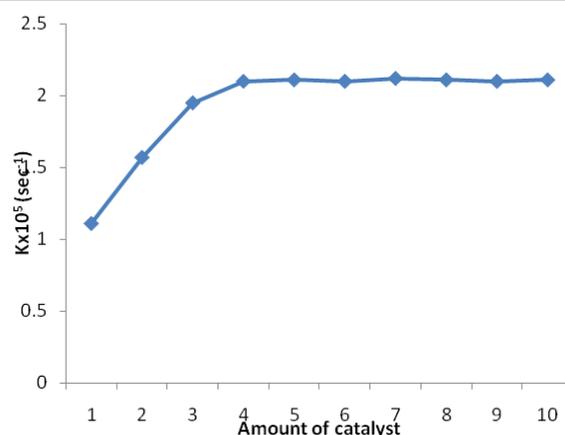


Figure 6: Effect of amount of photo catalyst.

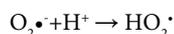
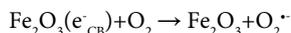
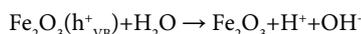
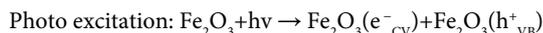
and the efficiency of the degradation reduced accordingly [24]. Furthermore, the increase of catalyst concentration beyond the optimum may result in the agglomeration of catalyst particles, hence more catalyst surface become unavailable for photo absorption, and degradation rate of catalyst became decrease [25].

Effect of light intensity

The effect of light intensity on the photocatalytic degradation of MB was also investigated. The light intensity was varied by changing the distance between the light source and the exposed surface area of semiconductor and observation results were reported in Figure 7. These data indicate that photocatalytic degradation of methylene blue was enhanced with the increase in intensity of light, because an increase in the light intensity will increase the number of photons striking per unit area per unit time of photo catalyst surface. There was a slight decrease in the rate of reaction as the intensity of light was increased beyond 50.0 mWcm⁻². Therefore, light intensity of medium order was used throughout the experiments.

Degradation mechanism of methylene blue

Methylene blue is a heterocyclic aromatic compound with the molecular formula C₁₆H₁₈N₃SCl [26]. The primary photocatalytic oxidation mechanism is believed to proceed as follows:



Degradation pathway of methylene blue provided by -OH radical makes the main contribution to degradation of methylene blue and its intermediates [27] (Figure 8). Since the MB is cationic and not electron donor, the initial step of MB degradation can be ascribed to the cleavage of the bonds of C-S⁺=C functional group in MB:



The sulfoxide group can undergo a second attack by an OH[·] Radical and producing the sulfone, which causes the definitive dissociation of two benzenic rings:



and/or



Subsequently, the sulfone can be attacked itself by a third OH[·] radical for giving a sulfonic acid:



Finally release of SO₄²⁻ ions can be attributed to a fourth attack by OH[·]



The amino group in MB can be substituted by an OH[·] radical, forming the corresponding phenol and releasing a NH₂ radical which generates ammonia and ammonium ions, estimated to be primary products?



The other two symmetrical dimethyl-phenyl-amino groups in MB undergo a progressive degrading oxidation of one methyl group by an attack from OH[·] radical, producing an alcohol, then an aldehyde, which is spontaneously oxidized into acid, decarboxylates into CO₂ by photo-Kolbe reaction.

Conclusion

Heterogeneous photo catalysis on semiconductor nanoparticles has been shown to be effective methods to removing organic pollutants from wastewater as a complete mineralization of dyes in to CO₂, H₂O and other oxides. The identification of reaction intermediates allowed us to propose a reaction pathway of the degradation which involves breakdown of the cleavage bonds of C-S⁺=C functional group in MB bond by hydroxylation of the aromatic ring, leading at the end to ring opening and formation of carboxylic acids and aldehyde which undergoes oxidation to form CO₂ and water. The photocatalytic degradation of MB dye using Al₂O₃/Fe₂O₃ photo catalyst depends on the initial concentration of MB dye pH, amount of catalyst, and light intensity. Nevertheless, sol-gel method is widely used because the method facilitates the synthesis of nano sized crystallized binary Al₂O₃/Fe₂O₃ oxide catalysts for the degradation of organic pollutants powder of high purity at relatively low temperature.

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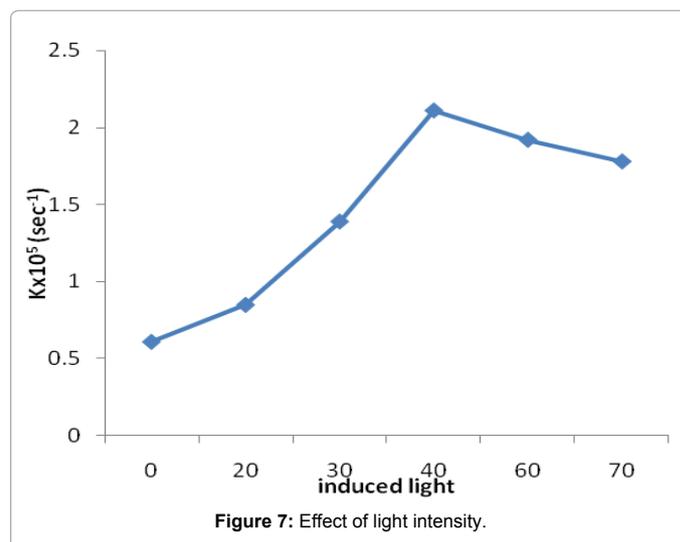


Figure 7: Effect of light intensity.

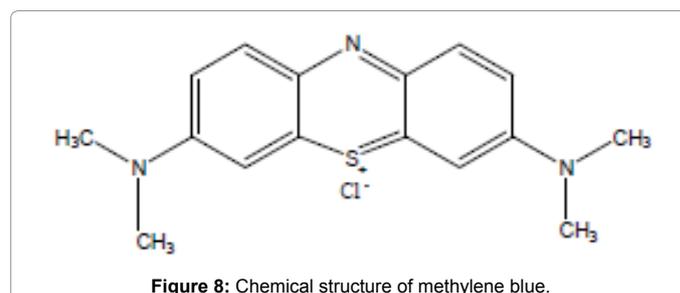


Figure 8: Chemical structure of methylene blue.

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