

Photocatalytic Efficiency of Mill Scale for the Degradation of Textile Dye by Photo Fenton and Photo-Ferrioxalate System Under UV and Sunlight

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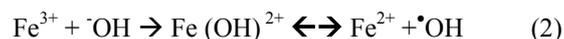
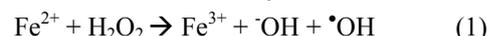
Abstract The aim of the study was to investigate the photocatalytic efficiency of mill scale (waste iron oxide collected from local steel plants) for the degradation of textile dyes. The photodegradation on methylene blue (MB) in natural environment with co-existence of mill scale and oxalic acid/ H₂O₂ under UV or sunlight were studied. Some effecting factors such as mill scale content, oxalate ion, H₂O₂ and MB concentration were also investigated. Dye decomposition rate was found to increase with an increase in the amount of mill, reached a maximum and then decreased with increasing mill scale concentration. The decomposition rate decreased with increasing dye concentration. Faster dye degradation was observed by mill scale/H₂O₂ than with mill scale/oxalic acid system. Photocatalytic performance of mill scale (a solid waste) was found as an interesting alternative for the degradation of dyes (liquid waste).

Keywords Advanced Oxidation Processes (AOPS), Photo-Fenton, Fenton, Methylene Blue, Degradation

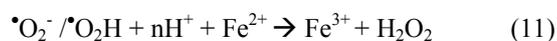
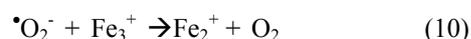
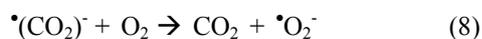
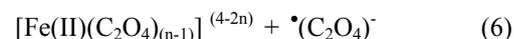
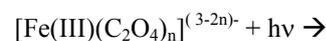
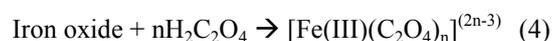
1. Introduction

The textile dyeing industries of Bangladesh generate large amount of effluents, sewage sludge and solid waste materials everyday which are being directly discharged into the surrounding channel, agricultural fields, irrigation channels, surface water and these finally enter into river. The presence of dyes in surface and subsurface water is making them not only aesthetically objectionable but also causes many water borne diseases, viz. mucous membrane, dermatitis, perforation of nasal septum and severe irritation of respiratory tract. Various options have been being employed to treat such wastes. These include chemical treatment such as chlorination and ozonation [1, 2], electrochemical treatment [3], physical treatment such as adsorption by activated carbon and membranes [4, 5], biological treatment and advanced oxidation processes (AOPs) [6].

AOPs have attracted wide interests in wastewater treatment since the 1990s. In principle, AOPs are based on the generation of hydroxyl radicals in water, which are highly reactive and nonselective oxidants being able to oxidize organic compounds particularly unsaturated organic compounds such as azo dyes. Among AOPs, two of the most important processes to generate hydroxyl radicals are using the photo-Fenton and photo-ferrioxalate (Fe²⁺/H₂O₂/UV and Fe²⁺/OA/UV) systems [7]. The photo-Fenton process starts with the combination of H₂O₂ with Fe²⁺ or Fe³⁺ shown in below. The reactions involved are briefly described as:



The reaction process starts again using photo generated Fe²⁺ [8]. During the photochemical reaction of Fe(III)-oxalate complexes under illumination by UV and/or visible light, superoxides hydroperoxy radicals ([•]O₂/[•]O₂H) [Eqs (5) - (9)] are formed as the key intermediates. H₂O₂ thought to be formed from [•]O₂/[•]O₂H [Eqs. (10) and (11)] participates in a classical Fenton reaction with Fe(II), formed by photo-reduction of Fe(III), producing [•]OH [Eq. (12)] [9]:



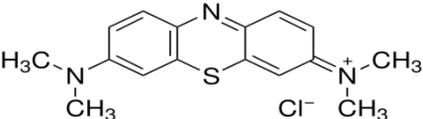
Semiconductor- photocatalysis evokes interest because of its potential to utilize natural sunlight, and studies on semiconductor- catalyzed environmental remediation using artificial UV light are numerous. TiO_2 , ZrO_2 , V_2O_5 , MoO_3 , Fe_2O_3 , Co_3O_4 , CuO , ZnO , ZnS , CdO , CdS , Al_2O_3 , SnO_2 , PbO , Pb_2O_3 , PbO_2 , Sb_2O_3 , Bi_2O_3 , La_2O_3 , CeO_2 , Pr_6O_{11} , and Eu_2O_3 are employed as photocatalyst [10-13]. In the present study we report the photocatalytic efficiency of cheap, commercially available metal oxide-mill scale (waste iron oxide generated in steel re-rolling plants) under natural sunlight and UV light. Methylene Blue(MB) is selected as model pollutant which is extensively used in textile, foodstuff and pharmaceutical industries as a thiazine dye. The optimal conditions of experimental parameters for the removal of MB have also been determined.

2. Experimental

2.1. Samples

Mill scale was collected from local steel industries. The molecular structure and other properties of MB are shown in table 1. All the chemicals were used without further purification.

Table 1. Properties of MB

Methylene Blue (MB)	
Nature	Cationic dye
λ_{max} (nm)	664
Molecular weight (g/mol)	319.85
Molecular structure	

2.2. Characterization

The crystalline phase of mill scale was determined by X-ray powder diffraction with monochromated $\text{Cu K}\alpha$ radiation.

2.3. Photodecomposition Experiments of MB

The experiments were carried out by adding varying amounts of mill scale to 100ml of aqueous solution containing MB and H_2O_2 or oxalic acid. Before photo reaction, the suspension was magnetically stirred in the dark for half an hour to establish absorption-desorption equilibrium. The various aqueous suspensions were then illuminated by UV or solar illumination with magnetic stirring. The photodegradation was carried out under two 8W UV lamps with the main emission at 365 nm. Solar illumination of the magnetically stirred sample suspension was carried out in a room beside a window. At a given time of intervals, the analytical samples were withdrawn from the suspension and then stored in the dark for needed analysis. The absorbance spectrum was determined with a UV-vis spectrophotometer (optizen 3220UV, Korea) and degradation of MB was monitored by recording the absorbance at $\lambda_{\text{max}} = 664$ nm as a function of illumination time. The percent decolorization and rate constant values were calculated as follows [14-15]: %Decolorization = $100 \times (C_0 - C_t)/C_0$, Rate constant, $k = (\ln(C_0/C_t))/(-t)$; where C_0 is the initial concentration of dye, and C_t is the concentration of dye at reaction time t (min).

The photodecomposition experiments were performed under the following experimental conditions, MB concentration (C_0) = 0.01 - 0.1 mM, mill scale content = 0.1-1.3 g/100mL, oxalic acid concentration 0.5-3.0 mM and H_2O_2 concentration 1-4 mL/100mL aqueous suspension.

3. Result and Discussion

3.1. XRD and Phases of Mill Scale

The crystalline phase of mill scale, determined by X-ray powder diffraction shown in figure 1. The phases found were wustite, magnetite, & hematite.

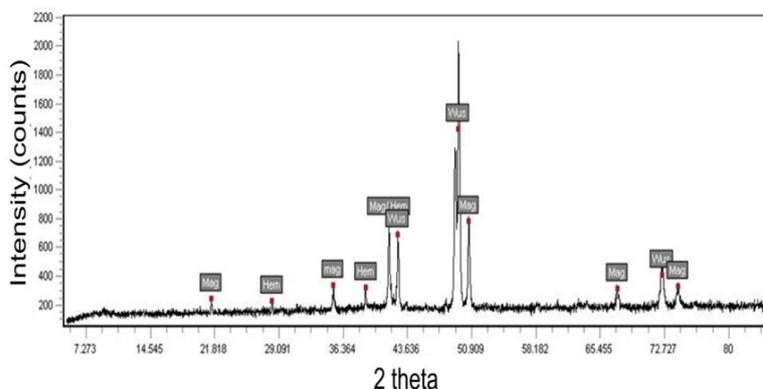


Figure 1. XRD pattern of mill scale

3.2. Effect of Variables on MB Degradation

Figure 2 shows the MB degradation under different experimental conditions. Curve a represents MB degradation in presence of 1.0mM oxalic acid and UV light. Degradation was only 11% at this condition. Curve b represents the degradation experiment under UV irradiation only and it was 12.5%. The degradation increased to 20% when experiment was carried out in presence of 2 ml H₂O₂ (curve c).

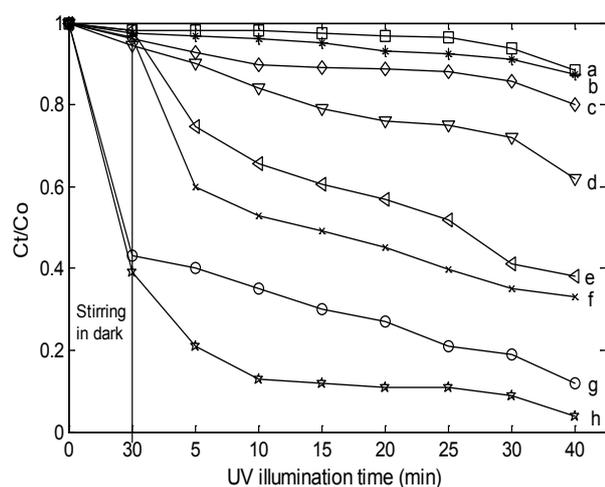


Figure 2. Degradation of 0.05mM MB under different condition (a) 1.0 mM OA (b) UV (c) 2mL H₂O₂ (d) UV + 0.8gm mill scale (e) UV + 1mM oxalic Acid (f) UV + 2mLH₂O₂ (g) UV + 1mM oxalic Acid + 0.8 gm mill scale (h) UV + 2mLH₂O₂ + 0.8 g mill scale

Then MB degradation increased to 38% under UV and in presence of 0.8 g mill scale (curve d). The degradation of MB was 61.9% under UV light irradiation and 1mM oxalic acid. Another experiment showed degradation of 67% under UV irradiation and in presence of 2 ml H₂O₂ (curve f). Degradation was found to be 88% under UV light and 0.8gm mill scale with 1mM oxalic acid (curve g). Finally when 2.0mL H₂O₂, 0.8g mill scale and UV irradiation were used combined, the removal percentage of MB significantly increased upto 98%(curve h). Thus it was observed that either the combination of UV light, mill scale and H₂O₂ or the combination of UV light, mill scale and OA are required for complete degradation of MB.

3.3. Effect of Mill Scale Content on MB Degradation

A set of experiments were carried out to observe the dependence of MB photodegradation with the mill scale variation under UV light irradiation in presence of H₂O₂ (photo-Fenton) and OA (photo-ferrioxalate system) per 100ml aqueous solution. Mill scale content was taken as 0.1g, 0.3 g, 0.5 g, 0.8 g, 1.0g and 1.3 g for 100 mL of solution. The corresponding rate constant values for both of these experiments are shown in figure 3.

Optimum mill scale content was found 0.8g for photo Fenton and 0.5g for photo-ferrioxalate system under UV illumination. When the Fe ion concentration is too low, e.g.,

0.1 g/100 ml, the decolorization rate is slow because there are not sufficient ions available for dye degradation. With increasing mill scale content upto 0.8g in case of photo-Fenton and 0.5g in case of photo-ferrioxalate, the decolorization rate also increased. Because when Fe ion concentration increases, the catalytic effect also accordingly increases and when its concentration become higher, a great amount of Fe ion is produced. Fe ion undergoes a reaction with hydroxyl ions to form Fe(OH)²⁺ which in turn produces more •OH radicals (Eqs. 1-3) [16, 17]. This •OH radical increases the rate of decomposition.

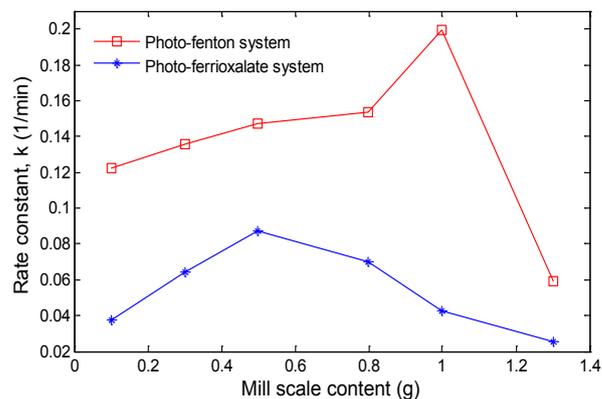


Figure 3. MB photodecomposition rate constant (k) under various mill scale contents.

On the other hand, when the iron powder concentration is too high, e.g., 1.3 g/100mL, the reaction suspension became more turbid with excessive oxide loading, and this suppressed the penetration of UV light and hence photoactivated volume of suspension decreases. This in turn decreased the formation of •OH radicals, lowering the photodecomposition ability. Thus it can be said that higher dose of catalyst may not be useful both in view of aggregation as well as reduced irradiation field due to light scattering.

3.4. Effect of H₂O₂ Variation on MB Degradation in Photo Fenton System

In a photo-Fenton-based system, the oxidant concentration is a key factor that can significantly influence the degradation of organics. The H₂O₂ concentration is directly related to the number of hydroxyl radicals generated, and thus to the performance achieved.

Figure 4 displays the effect of the hydrogen peroxide dosage, in this case for decolorizing MB over mill scale. MB degradation was carried out with 1ml, 2ml and 4ml H₂O₂. The observed effect of the H₂O₂ concentration was clear: the higher the H₂O₂ concentration, the faster the colour removal. As it can be observed from figure 4, using concentrations of H₂O₂ = 1 ml, colour degradation rate was 0.044, 0.041, 0.020 for 0.01, 0.05, 0.1 mM MB respectively. and it was increased to 0.058, 0.043, 0.025 when H₂O₂ = 2ml and finally it was 0.103 and 0.057 with 4ml H₂O₂ when 0.05 and

0.1 mM MB used respectively. But the result was undefined when 0.01 mM MB was used in this case of 4 mL H₂O₂. This is due to the fact that at higher H₂O₂ concentrations scavenging of HO[•] radicals will occur, as expressed by the following equations [18,19]:

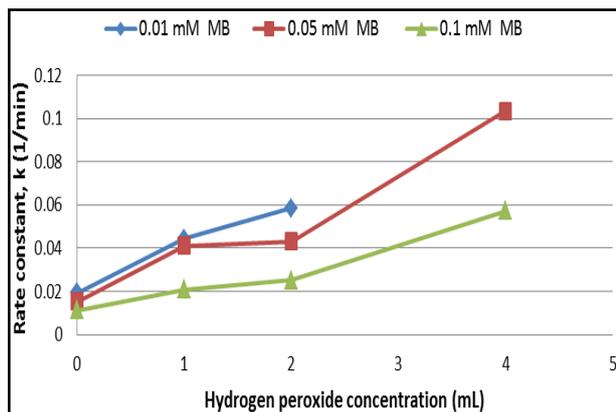
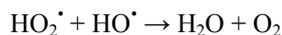
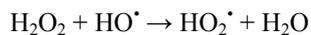


Figure 4. Photodecomposition rate constants (*k*) of various concentration of MB for H₂O₂ (1, 2, 4) mL concentrations in the presence of 0.8 g mill scale under UV illumination

It is important to remark that HO₂[•] is less reactive than HO[•], and thus an increased amount of hydrogen peroxide has a diminishing return on the reaction rate [20]. From figure 4 it was clear that degradation of MB was increased with increasing H₂O₂ concentration and best photo-degradation was possible at 4 mL H₂O₂. But due to very fast degradation of MB it was difficult to determine the rate constant for low concentration of MB. So, 2 mL H₂O₂ per 100 mL solution was used for further experiment.

3.5. Effect of Initial Concentration of Dye on MB Degradation

After optimizing the catalyst dose, the photocatalytic degradation of MB was carried out by varying the initial concentrations of the dye from 0.01-0.1 mM. Here, various concentrations of MB (0.01 mM, 0.05 mM and 0.1 mM) were decomposed in presence of 2 mL H₂O₂ under UV illumination with different amount of mill scale (0.3 g, 0.8 g and 1.3 g/100 mL solution) as shown in figure 5. From the results it can be seen that for all cases decomposition rate decreased with increasing concentration of MB. When 0.3 g mill scale was used, the rate constant values were 0.19, 0.10 and 0.08 for 0.01, 0.05 and 0.1 mM MB respectively. When 0.8 g mill scale was used the rate constant values were 0.35, 0.27 and 0.10 for 0.01, 0.05 and 0.1 mM MB respectively. And when 1.3 g mill scale was used the rate constant values were 0.28, 0.13 and 0.08 for 0.01, 0.05 and 0.1 mM MB respectively.

3.6. Effect of OA Variation on MB Degradation in

Photo-Ferrioxalate System

A series of experiments were performed to examine the effect of the initial oxalic acid concentration under the following conditions; MB concentration = 0.05 mM, mill scale content = 0.5 g/100 mL and UV light illumination. The degradation of MB concentration at various oxalate concentrations are shown in figure 6 as a function of the UV illumination time for oxalic acid concentrations of 0.5, 1, 2 and 3 mM, respectively. This result clearly shows the enhancement of MB photodecomposition in oxalate solution. Previously it was shown that (figure 2) without OA the degradation was 38% in presence of (UV + 0.8 g mill scale). The optimal oxalate concentration is 1 mM under these experimental conditions. Balmer and Sulzberger [14] reported that Fe³⁺ is present mainly as [Fe(III)(C₂O₄)₂]⁻ and [Fe(III)(C₂O₄)₃]³⁻ in the Fe(III)-oxalate system when the concentration of oxalate is > 0.18 mM. On this basis, Fe(III)(C₂O₄)₂⁻ and Fe(III)(C₂O₄)₃³⁻ are thought to be formed under the present experimental conditions, and may be much more efficiently photolyzed than other Fe³⁺ species, greatly enhancing MB photodecomposition in the presence of oxalic acid. However, any excess oxalic acid will occupy the adsorption sites on the surface of mill scale, and will also compete with MB in the photodecomposition reaction.

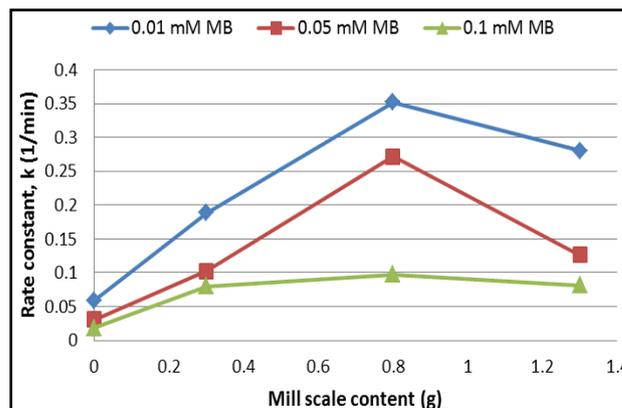


Figure 5. Photodecomposition rate constants (*k*) of various concentration of MB

3.7. Effect of Solar/UV Irradiation on MB Degradation

The photocatalytic degradation of MB using mill scale as photocatalyst and solar/UV irradiation as light source has been carried out under 2 mL H₂O₂ concentration per 100 mL solution and the results are presented in figure 7. About 95% degradation is achieved within 60 minute under UV irradiation whereas same degradation requires more than 120 minute in solar irradiation of MB dye. The difference in the rate of degradation is attributed to difference in the input energy. The energy of UV irradiation is large compared to band gap energy of the catalysts. Hence, the problem of electron-hole recombination is not fully but largely avoided with UV source.

But in sunlight only 5% of the total radiation possesses the

optimum energy [21] for the band gap excitation of electrons. Hence, the percentage degradation is found to be less in solar radiation. Although sunlight has only 5% of optimum energy for photocatalytic excitation and ultimately degradation of dyes, it could be safe and cost effective source. UV source is not only hazardous but also expensive because of large input of electric power to generate UV irradiation. In tropical countries intense sunlight is available throughout the years and, hence, it could be effectively used for photocatalytic degradation of pollutants in wastewater. In case of large surface demanding photocatalytic degradation, sunlight would be the ultimate source. Moreover there is no material deterioration in case that sunlight is used as a radiation source. But UV light source may effect the catalyst decomposition [22].

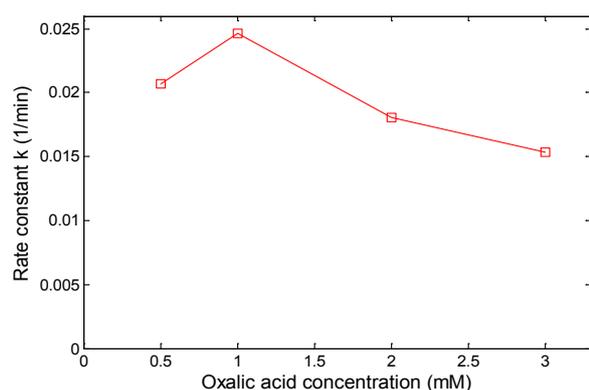


Figure 6. MB photodecomposition rate constants, k in various oxalic acid concentrations

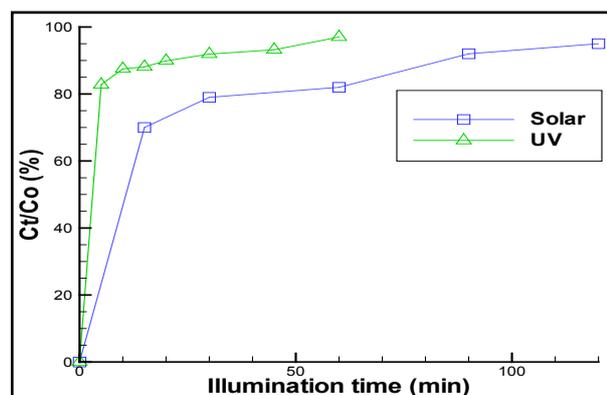


Figure 7. Effect of solar/UV light source on the degradation of MB

4. Conclusions

Experimental results indicated that the decolorization of MB is facilitated in the presence of mill scale. The combination of mill scale, hydrogen peroxide or oxalic acid and light illumination (UV or Solar) is essential for the photodecomposition of MB. The optimum mill scale content was found to be 0.8 g/100 ml solution in presence of H_2O_2 and 0.5 g/100ml solution in presence of OA under UV illumination. Degradation of MB was increased with

increasing H_2O_2 concentration and decreased with increasing dye concentration. Optimum oxalic acid concentration was 1mM for the degradation of MB. The MB photodecomposition was found higher under UV than solar illumination. Among the Photo-Fenton and photo-ferrioxalate system, photo-Fenton route showed the highest degradation rate.

Last but not the least, it can be concluded that mill scale can effectively be used as a photocatalyst for the degradation of dyes.

Acknowledgements

The authors are grateful to Ministry of Science and Technology, Government of the Peoples Republic of Bangladesh for providing fund and Bangladesh University of Engineering and Technology for providing facilities to carry out this research work.

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