Photocatalytic Degradation of Azo Dye using Ferric Oxide Nanoparticle

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Abstract: The growth of the world population, the development of various industries and the use of fertilizers and pesticides in modern agriculture have overloaded not only the water resources but also the atmosphere and the soil with pollutants. Textile industry which is one of the largest water consumer in the world, produces wastewater comprising of various recalcitrant agents such as dye, sizing agents and dying aid. Therefore utmost care has to be taken in releasing these types of wastewater to the environment. In disposal of wastewater, color is very important due to aesthetic deterioration as well as the abstruction of penetration of dissolved oxygen and sunlight to natural water bodies. The sunlight penetration and reduction of dissolved oxygen into natural water sources affects the aquatic life. The dye precursors and the degradation products of the dye are proven to be carcinogenic in nature. Catalysts are used to convert environmentally hazardous materials into harmless compounds. In the present work ferric oxide nanoprticles are used for the photocatalytic degradation of azo dye. The influence of hydrogen peroxide and the effect of various photocatalysts on photocatalytic degradation was carried out.

Keywords: Photocatalytic Degradation, Azo Dye, Ferric Oxide Nanoparticle.

Introduction

Large quantities of dyes are manufactured annually worldwide and are used in a variety of applications such as textiles, paper, foodstuffs and cosmetics. Textile dyes are of environmental interest because of their widespread use, their potential for formation of toxic aromatic amines and low removal rate during waste treatment. The toxicity and potential carcinogenic nature of these dyes and their manufacturing precursors pose a specific threat to the environment. The colour of waste is the most apparent indication of pollution. Such coloured dye effluents pose a major problem for the manufacturing plant itself as well as municipal treatment plants down the line. Removing of colour from waste is often more important than other colourless organic substances[1-8]. Methods to decolourize dye effluents have therefore acquired increasing attention[9-14].

Results and Discussion

Photocatalytic oxidation experiments

Initially, the experiments were carried out under the following conditions:

Dye +UV, Dye +sunlight, Dye+ H_2O_2+ dark, Dye+ H_2O_2+ sunlight, Dye+ H_2O_2+UV, Dye+Fe_3O_4+Sunlight, Dye+Fe_3O_4+UV, Dye+ZnO+Sunlight and Dye+TiO_2+Sunlight. The results of photocatalytic decolourisation of an azo dye are shown in the Figure 1 and Table 1. From the decolourisation results it is clear that the dye is resistant to direct photolysis of UV light and irradiation in the presence of sunlight alone. Photochemical decolourisation of azo dye under different conditions [Dye] = 1×10^{-4} M.

Table 1: Photochemical decolourisation of azo dye under different conditions

| Time, min	Percentage remaining	
	Sunlight	**UV**
0	100	100
30	99.8	97.6
60	99.5	96.6
90	99.1	94.18
120	99.0	92.48
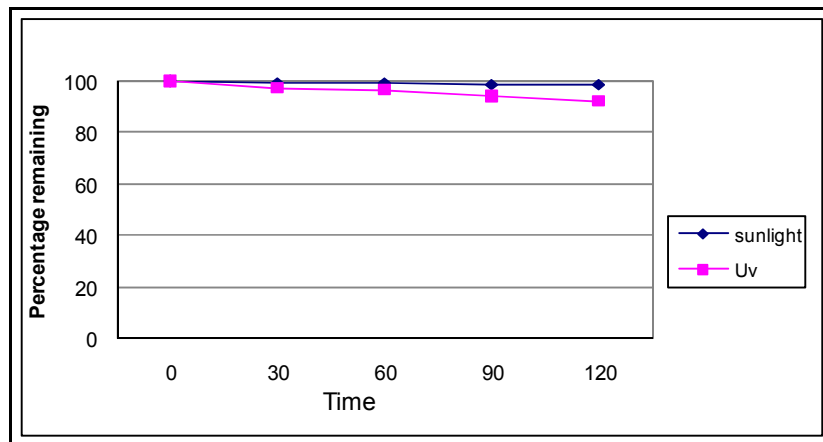
Figure-1 Photochemical decolourisation of azo dye under different conditions, [Dye] = 1×10^{-4} M

For H_2O_2 (5 mmol) with dye, in dark 3.51% decolourisation was observed whereas the decolourisation was found to be 5.03% in the presence of sunlight for the same concentration of H_2O_2 at 120 min and is shown in table 2 and figure 2.

Photochemical decolourisation of azo dye under different conditions and in presence of H_2O_2
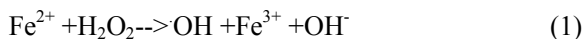
Table 2: Photochemical decolourisation of azo dye under in presence of H_2O_2

| Time, min	Percentage Remaining		
	Sunlight	**Dark**	**UV**
0	100	100	100
30	99.42	99.68	98.91
60	99.08	99.54	97.23
90	96.05	97.21	95.27
120	94.97	96.49	92.13
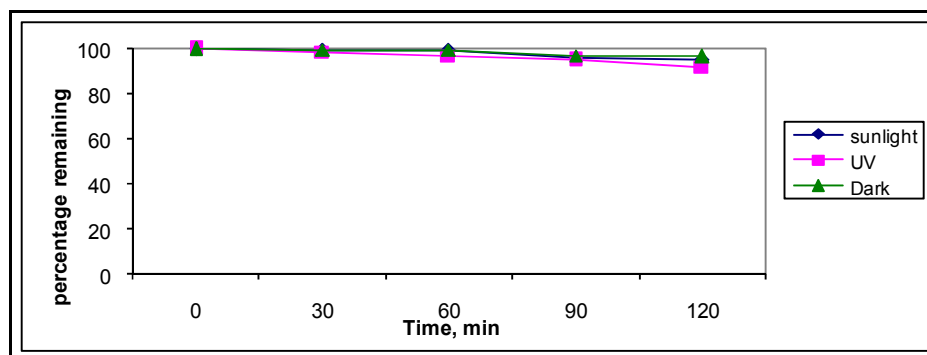
Figure-2 Photochemical decolourisation of azo dye under different conditions [Dye] =1×10^{-4} M, [H_2O_2] = 5 mmol

The combined action of UV and H_2O_2 caused 75.00% of decolourisation for 75 mmol of H_2O_2 at 40 min and the decolourisation was found to be 7.87% for 5mmol of H_2O_2 at 120 min. It is clear from the Figures 2 and 3, that decolourisation of dye is mainly due to hydroxyl radical generated by chemical and photochemical reactions of each process. Azo bonds are more active in these dyes. Congo red contains two azo bonds and decolourisation of dye is due to the initial electrophilic cleavage of its chromophoric azo bond attached to naphthalene ring.

$$Fe^{2+} + H_2O_2 \longrightarrow {}^{\cdot}OH + Fe^{3+} + OH^- \qquad (1)$$

In the photo Fenton's process, in addition to the above reaction the formation of hydroxyl radical also occurs by the following reactions and

$$H_2O_2 + UV \rightarrow {}^{\cdot}OH + {}^{\cdot}OH \qquad (2)$$

$$Fe^{3+} + H_2O_2 + UV \rightarrow {}^{\cdot}OH + Fe^{2+} + H^+ \qquad (3)$$
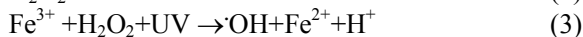
Photochemical of decolourisation azo dye under different conditions
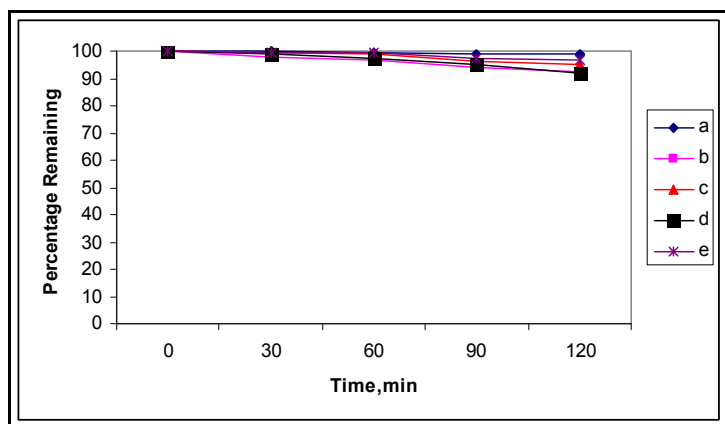
Figure-3 photo chemical decolourisation of an azo dye under different conditions.

At 60th minute, colour removal was 84.49%, 55.22%, 16.4% for ZnO, Fe_3O_4, TiO_2 respectively and is displayed in the Figure 4 and Table 3. Azo bond are more active in these dyes. Congo red contains two azo bonds and decolourisation of dye is due to the initial electrophilic cleavage of its chromophoric azo(-N=N-) bond and they are oxidized by positive hole, hydroxyl radical and reduced by electron in conduction band. The degradation of aromatic part of the dye molecule produced a number of intermediate compounds and removal of these intermediates took long time. The degradation of aromatic part of the dye molecule was not complete. This shows that some of the intermediates produced are resistant to photocatalytic oxidation reaction.
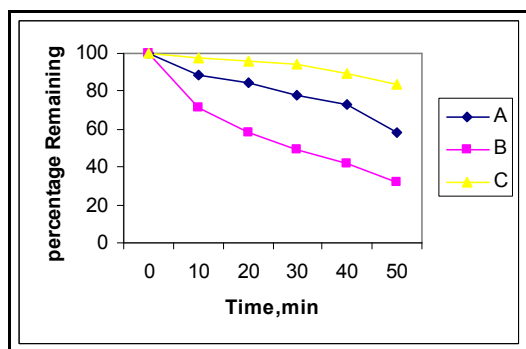
Figure-4 Photocatalytic decolourisation of the dye as a function of irradiation time in the presence of other catalysts. [Dye] = 1×10^{-4} M, [Photocatalyst] =0.2g

Table 3: Photocatalyst decolourisation of the dye in the presence of other catalysts.

Time ,min	Percentage remaining		
	Fe_3O_4	ZnO	TiO_2
0	100	100	100
10	88.62	71.65	97.9
20	84.37	58.17	96.3
30	78.02	49.22	94
40	72.55	41.98	89.5
50	58.12	32.13	83.6

Effect of Fe_3O_4 dosage

The optimum amount of Fe_3O_4 has to be added in order to avoid excess catalyst and also to ensure total absorption of radiation photons for efficient photodegradation. It depends on type of photocatalyst, pollutant concentration, characteristics of UV radiation(power, wavelength), photoreactor geometry, etc. The effect of photocatalyst (Fe_3O_4) concentration on the degradation of azo dye was investigated from 0.05 to 0.2g,the effect of Fe_3O_4 loading on an initial rate on the decolourisation and degradation.

As the concentration of the catalyst is increased from 0.05 to 0.2g, the decolourisation increases from 51.97 to 58.66% at 60 min irradiation time.

The enhancement of removal rate is due to-

(i) the increase in the amount of catalyst weight which increase the number of dye molecules absorbed and

(ii) the increase in the density of particles in the area of illumination. Further increase of the catalyst loading makes the removal rate constant. By the addition of catalysts above 0.2g the number of active sites on the surface may become almost constant because of the decreased radiation penetration, the increased radiation scattering and the loss in surface area by agglomeration. These reduce the specify activity of the catalyst.

From these results it is clear that the optimum catalyst loading is not common for all photocatalytic reaction and it is dependent on various experimental parameters. The optimum amount of catalyst loading is found to be 0.2g for the degradation and decolourisation of azo dye. Hence 0.2g was used as the catalyst dosage for the photocatalytic reactions.

Photo degradation efficiency of photo catalysts (ZnO, Fe_3O_4 and TiO_2)

The photo oxidation by other photocatalysis such as TiO_2, ZnO and Fe_3O_4 has been investigated in the presence of sunlight. ZnO and Fe_3O_4 are found to be more efficient when compared to TiO_2. The decolourisation efficiencies of ZnO, Fe_3O_4, and TiO_2 are respectively 84.49%, 58.66%, and 16.4% respectively at the time of 60 min. Generally semiconductors having large band gap and have strong photocatalytic activities. The order of activities of the photo catalyst are ZnO> Fe_3O_4>TiO_2. ZnO is found to be more efficient than TiO_2 and Fe_3O4. The higher efficiency of ZnO than the TiO_2 has also been reported in the treatment of pulp mill bleaching waste water and dye waste water.

The photocatalytic activity of semiconductors is also dependent on the crystallinity, particle size, surface are and concentration of the impurities in the catalysts. ZnO has the disadvantage of undergoing photocorrosion under acidic condition on illumination. The TiO_2 permits rapid recombination of electron hole and so conduction band electron in these semiconductors cannot move into the electron acceptors in the solution rapidly. Hence, a negligible photocatalytic activity for decolouristion and degradation is observed in this catalyst. Its higher surface are resistant to photo corrosion, biological immunity and its low cost.

Conclusion

The photocatalytic decolourisation and degradation of an azo dye in aqueous solution with Fe_3O_4 as photo catalyst in slurry form have been investigated using solar light and UV. The study of the effect of various photo catalysts ZnO, Fe_3O_4, TiO_2 on the decolourisation and degradation. The effects of various parameters such

as catalyst loading and initial dye concentration on decolourisation and degradation have been investigated to find out optimum conditions. The azo dye decolourised by Fe_3O_4 nano particle assisted photo catalysis in aqueous dispersion under irradiation by solar light and UV. The dye is resistant to direct photolysis. A photocatalytic decolourisation and degradation obey pseudo-first order kinetics at low initial concentrations. The presence of auxiliary chemicals such as Na_2CO_3 and NaCl decreases the photocatalytic decolourisation and degradation.

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