

Heterogeneous photo-Fenton degradation of mixture of Bismark brown-R and Azure-B dyes on copper loaded neutral alumina

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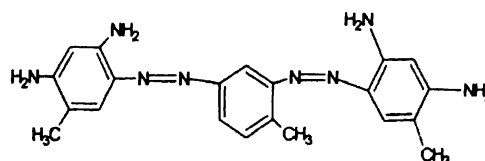
Abstract : In the present work, heterogeneous photo-Fenton degradation of mixture of two dyes has been investigated in aqueous medium under visible light. The selected two dyes are Bismark brown-R and Azure-B. The photocatalyst has been prepared by loading of Cu^{2+} ions on neutral alumina. The rates of photocatalytic degradation of dyes were monitored spectrophotometrically. The effect of operating parameters, such as amount of photocatalyst, light intensity, concentration of dyes, pH and amount of H_2O_2 on the rate of photocatalytic degradation has been studied. Photocatalyst has been characterized by ICP, IR, SEM and XRD. A tentative mechanism involving $\cdot\text{OH}$ radicals as an oxidant for the photocatalytic degradation of mixture of dyes has been proposed.

Keywords : Heterogeneous photo-Fenton, spectrophotometric, Bismark brown-R, Azure-B.

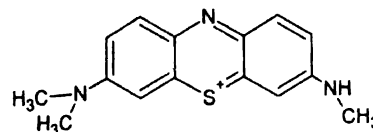
Introduction

Dyes make our world beautiful, but their increasing use and improper disposal of their effluents are creating pollution of the environment. Wastewaters originating from dyes production and application industries pose a major threat to surrounding ecosystems, because of their toxicity and potentially carcinogenic nature¹⁻³. Apart from the aesthetic problems relating to colored effluent, dyes also strongly absorb sunlight; thus, impeding the photosynthetic activity of aquatic plants and seriously threatening the whole ecosystem⁴. So, there is an urgent need to treat dye wastewater prior to its discharge into the nearby water bodies. Most of pollutants, except coloured pollutants (dyes), can be reduced by chemical, physical or biological methods. Therefore, the color problem of some textile wastewater caused by the residual dyes during the dyeing process needs more efforts to be studied and investigated^{5,6}.

The limitations of conventional wastewater treatment methods can be overcome by the application of the so-called advanced oxidation processes (AOPs)⁷; defined by



Bismark brown-R



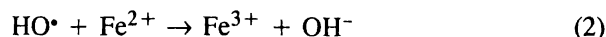
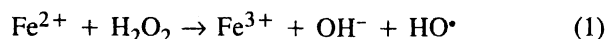
Azure-B

Glaze *et al.*⁸, which present a potential alternative to decolorize and to reduce recalcitrant colored wastewater loads⁷. Recently, advanced oxidation processes (AOPs) have been developed to oxidize organic contaminants into CO_2 , H_2O and inorganic ions or biodegradable compounds. These methods are environment friendly. Therefore, AOPs are considered as promising treatment methods for the treatment of wastewater.

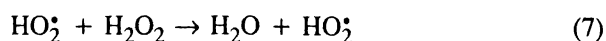
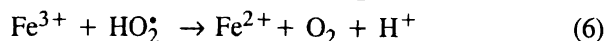
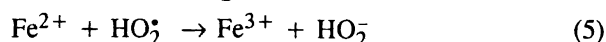
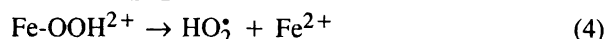
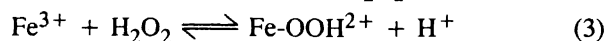
AOPs are based on the generation of very reactive hydroxyl radicals (OH^\bullet)⁹, which have a very strong oxidation potential [$E^\circ = +2.80\text{ V}$], next to fluorine. Hydroxyl radicals rapidly and nonselectively oxidize a broad range of organic pollutants¹⁰.

Fenton reagent is an established reagent for the degradation of dyes but the main drawback of the reagent is that the reaction becomes very slow after the consumption of Fe^{2+} ions, whereas in photo-Fenton reaction, Fe^{2+} ions are readily regenerated from Fe^{3+} ions with an additional requirement of light and water. This makes the process cyclic in nature and photochemical degradation proceeds smoothly.

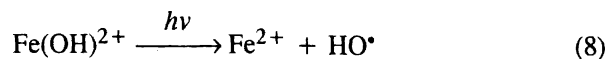
The generation of hydroxyl radicals during the catalytic cycle has been attributed to the following series of reaction¹¹.



In turn, Fe^{III} rapidly reacts with H_2O_2 forming Fe^{II} ¹²:



when UV/Visible light is added, Fe^{III} photoreduction regenerates Fe^{II} improving the effectiveness of the process due to the formation of new hydroxyl radicals¹³,



Although, photo-Fenton process has its own unique advantages as an oxidizing process because used reagents are relatively inexpensive, environmentally benign and easy to transport and handle. The homogeneous photo-Fenton process is efficient only in the pH range of 2–4 and is usually most efficient at around 2.5–3.0 but rather inefficient in the pH range of most natural and aluative water (pH 5–9). This is particularly due to the tendency for ferric oxyhydroxide precipitation, which has a low catalytic activity^{9,14}, while for heterogeneous photo-Fenton process, the source of iron used as a catalyst can be a solid surface, including iron-containing minerals or iron coated particles. The heterogeneous system has more advantages than the homogenous photo-Fenton reagent from

the viewpoint of the reaction pH range and the removal of iron ions. In addition, homogeneous photo-Fenton reactions need 50–80 ppm of Fe ions in solution, which is well above the European Union directive that allows only 2 ppm of Fe ions in treated water to dump directly into the environment¹⁵.

To overcome the disadvantages of the homogeneous Fenton process, and also considering the possibility of recovering the catalyst, some attempts have been made to develop heterogeneous catalysts, prepared by incorporating Fe ions or Fe oxides into porous supports^{16–18}. Photocatalytic degradation of phenol red using some transition metal complexes and hydrogen peroxide was examined by Punjabi *et al.*¹⁹. A study of catalytic behaviour of aromatic additives on the photo-Fenton degradation of phenol red was examined by Jain *et al.*²⁰. Photocatalytic degradation of sunset yellow FCF in presence of some transition metal complexes and hydrogen peroxide was examined by Lodha *et al.*²¹. Decolorization of reactive Brilliant red X-3B by heterogeneous photo-Fenton reaction using an Fe–Ce bimetal catalyst was examined by Zhang²². Heterogeneous photo-Fenton oxidation of reactive azo dye solution using iron exchanged zeolite as a catalyst was examined by Tekbaş²³.

In the present work, photo-Fenton degradation of mixture of Bismark brown-R and Azure-B dyes has been studied on copper loaded neutral alumina as heterogeneous photo-Fenton like catalyst. The mixture of two dyes has been used just to give it a shape of effluent; however, in actual practice, the effluents from dyeing and printing industries contain more than two dyes.

Experimental

Preparation of photocatalyst :

The photocatalyst has been prepared by wet impregnation method. The method involves impregnation from dilute solution of the precursors of active components on the support. The method led to the low loading of active component on solid support.

To start with, 50.0 g neutral alumina was taken in a beaker and 500.0 mL of $\text{Cu}(\text{NO}_3)_2$ (0.1 M) solution was added to it. The suspension was slowly stirred over a magnetic stirrer for 5–6 h. The suspension was filtered and washed with distilled water several times. Filtrate was tested for the NO_3^- ions till it gives negative test.

The residual Cu-loaded alumina was dried in an oven at 100 °C for 4–5 h.

Estimation of Cu ions in catalyst :

Estimation of copper ions was carried out by inductively coupled plasma optical emission spectroscopy using an instrument, Thermo Scientific, Model-iCap 6300 Duo. Amount of copper was found to be 1.24 ppm.

Characterization by SEM and FTIR :

Scanning electron microscopy (Model-Leo 430 Cambridge) has been used to observe the morphological changes caused by loading of copper ions on the surface of alumina. It has been observed that loading of copper ions leads to the formation of smaller and more regular particles of the catalyst. This factor has led to the increased surface area of catalyst and increased rate of photo-Fenton degradation. The SEM photographs of unloaded and loaded alumina are shown in Figs. 1 and 2, respectively. The particle size of Cu-loaded alumina and neutral alumina was measured with the help of SEM and it was observed that the average particle size is 181.36 μm and 245 μm , respectively.

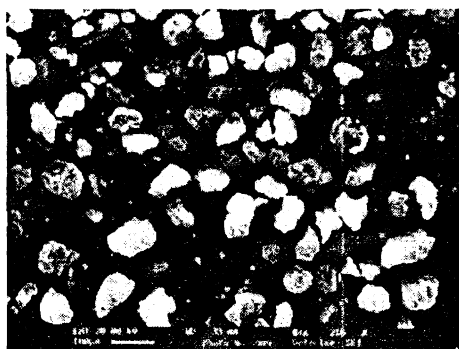


Fig. 1. SEM digram of neutral alumina.

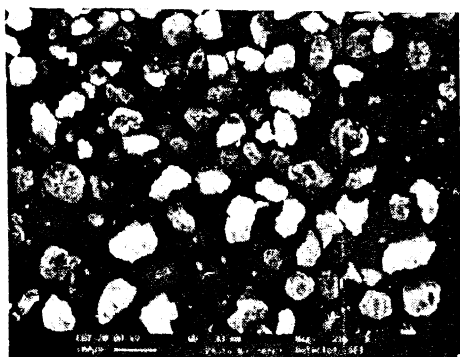


Fig. 2. SEM digram of Cu-loaded neutral alumina.

IR bands at 3611 and 3557 cm^{-1} in IR spectrum of unloaded alumina indicate that free -OH groups are present on the surface of neutral alumina, whereas these bands has shifted to lower frequency (3479–3362 cm^{-1}) in the Cu-loaded alumina indicating that OH groups have bonding interaction with copper ions. This has been further confirmed by the presence of a peak at 592 cm^{-1} due to the presence of Cu–O stretching vibration. The bands at 646 cm^{-1} and 661 cm^{-1} have been assigned for the Al–O–Al bond in loaded and unloaded alumina, respectively.

Characterization by AAS :

Stability of the catalyst was checked by Atomic Absorption Spectroscopy using ECTL 4129A Atomic Absorption Spectrophotometer. Even after one month, leaching of copper ions from the catalyst was found to be negligible (0.10 ppm). Thus, catalyst was found to possess good stability for its use as photo-Fenton like reagent under visible range.

X-Ray Diffraction studies :

XRD diffraction patterns of the samples were recorded on A18 KW X-Ray powder diffractometer using $\text{CuK}\alpha$ radiation. Diffraction pattern were recorded in the 2θ region of 10° to 90° , with a step size of 0.05° .

The Fig. 3 illustrates the indexed XRD patterns of the pure alumina and Cu-loaded alumina, all the Bragg reflections have been indexed in Al_2O_3 type rhombohedral structure in the hexagonal setting (Space group : R-3C No. 167). The presence of all the fundamental reflections and absence of any impurity phase confirms the purity of the two samples.

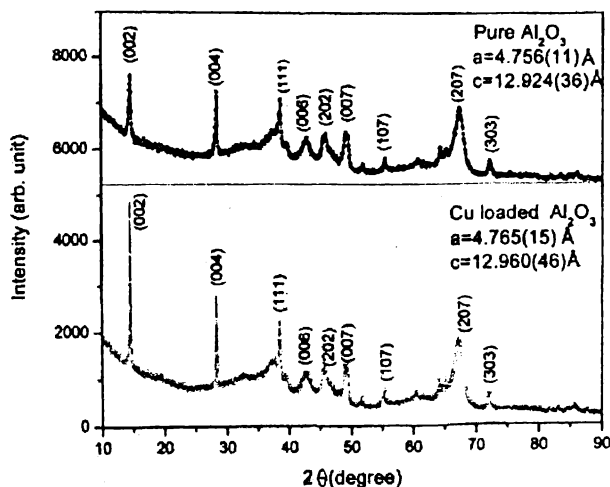


Fig. 3. The indexed XRD patterns of the pure alumina and Cu-loaded alumina.

The obtained values of the cell parameters for the pure alumina : $a = 4.756$ (11) Å, $c = 12.924$ (36) Å are in very good agreement with reported standard values $a = 4.759$ Å, $c = 12.993$ Å.

Relative changes in the peak positions and peak intensity in the Cu-loaded samples clearly indicate that Cu atoms are well incorporated in the alumina matrix.

The obtained values of the cell parameters for Cu loading in alumina are $a = 4.765$ (15) Å and $c = 12.960$ (46) Å. Thus, the unit cell slightly expands relative to pure Al_2O_3 , which is consistent with the substitution of larger cation Cu^{2+} (0.72 Å) on the Al^{3+} (0.51 Å) sites. The partial occupancy of the interstitial octahedral site would be expected to further increase in the expansion.

Stock solutions of Bismark brown-R (10^{-3} M, Himedia) and Azure-B (10^{-3} M, Himedia) were prepared in doubly distilled water. Degradation of mixture of dyes were observed by taking 40.0 mL mixture of 7.50×10^{-5} M of Bismark brown and 6.20×10^{-5} M of Azure-B dyes solution, 0.25 mL H_2O_2 (CBH, 30% vol.) and 0.25 g Cu-loaded neutral alumina. The reaction mixture was irradiated with a 200 W tungsten lamp (Philips). The intensity of light at various distances from the lamp was measured using a solarimeter (SM CEL 201). A water filter has been used to cut off thermal radiations. A digital pH meter (Model 232) was used to measure the pH of the reaction mixture. The pH of the solution was adjusted by the addition of previously standardized 0.1 N sulphuric acid and 0.1 N sodium hydroxide solution. The progress of the photo-Fenton degradation was monitored by measuring the absorbance of the reaction mixture at regular time intervals using UV-Visible spectrophotometer (Systronics, Model 106).

Results and discussion

An aliquot of 3.0 mL was taken out from the reaction mixture at definite time intervals and the absorbance was measured at 440 nm ($\lambda_{\text{max}} = 465$ nm) for Bismark brown-R and 650 nm ($\lambda_{\text{max}} = 645\text{--}655$ nm) for Azure-B. It was observed that the absorbance of the solution decreases with increasing time intervals, which indicates that the concentration of Bismark brown-R and Azure-B decreases with increasing time of exposure. A plot of $2 + \log A$ against time was linear and follows pseudo-first order kinetics (Fig. 4 : Typical runs, Table 1 : Typical runs).

The rate constants were measured with the expression

$$k = 2.303 \times \text{slope}$$

The photodegradation efficiency of the catalyst was calculated from the following expression :

$$\eta = \frac{\text{COD}_{\text{before}} - \text{COD}_{\text{after}}}{\text{COD}_{\text{before}}} \times 100$$

where, η = photodegradation efficiency (%), $\text{COD}_{\text{before}}$ = COD of dye of solution before illumination and $\text{COD}_{\text{after}}$ = COD of dye solution after illumination.

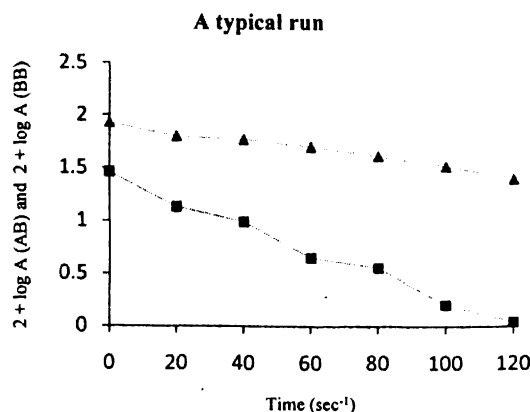


Fig. 4. Typical runs degradation of mixture of Bismark brown-R and Azure-B dyes : (■) Azure-B, (▲) Bismark brown-R.

Table 1. Typical run for dyes

pH = 7.5, $\text{H}_2\text{O}_2 = 0.25$ mL, Light intensity = 70.0 mW cm^{-2} ,
Photocatalyst = 0.30 g, [Bismark brown-R] = 1.50×10^{-4} M,
[Azure-B] = 1.25×10^{-4} M

Time (min)	Absorbance (AB)	Absorbance (BB)	$2 + \log A$ (AB)	$2 + \log A$ (BB)
0.0	0.845	0.288	1.9268	1.4593
20.0	0.628	0.136	1.7979	1.1335
40.0	0.585	0.098	1.7671	0.9912
60.0	0.500	0.045	1.6989	0.6532
80.0	0.410	0.036	1.6127	0.5563
100.0	0.328	0.016	1.5158	0.2041
120.0	0.248	0.011	1.3945	0.04131

$$(\text{AB}) k = 2.18 \times 10^{-5} \text{ s}^{-1}$$

$$(\text{BB}) k = 4.50 \times 10^{-5} \text{ s}^{-1}$$

Effect of pH :

The effect of pH (Fig. 5, Table 2.1) on the rate of photo-Fenton degradation has been investigated in pH

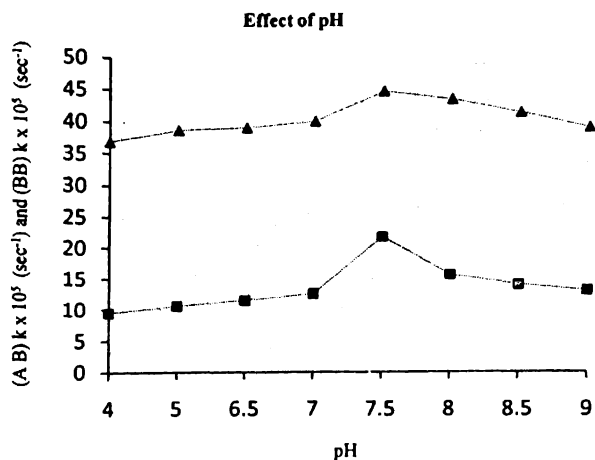


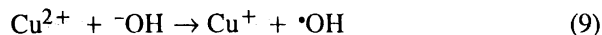
Fig. 5. Effect of pH on degradation of mixture of Bismark brown-R and Azure-B dyes : (■) Azure-B, (▲) Bismark brown-R.

Table 2.1. Effect of pH

[Bismark brown-R] = $1.50 \times 10^{-4} \text{ M}$, [Azure-B] = $1.25 \times 10^{-4} \text{ M}$, Photocatalyst = 0.30 g, H_2O_2 = 0.25 mL, Light intensity = 70.0 mW cm^{-2}

pH	(AB) $k \times 10^5 \text{ (s}^{-1}\text{)}$	(BB) $k \times 10^5 \text{ (s}^{-1}\text{)}$
4.0	9.45	36.89
5.0	10.56	38.78
6.5	11.47	39.24
7.0	12.56	40.24
7.5	21.84	45.00
8.0	15.63	43.70
8.5	13.96	41.60
9.0	13.00	39.21

range 4.0–9.0. It has been observed that with an increase in pH, rate of reaction increases and after attaining the maximum value at pH 7.5, rate decreases with increase in pH of reaction mixture. The optimum pH value for both the dyes was found to be at pH 7.5. A decrease in the degradation rate on decreasing pH of the medium from 7.5 to 4.0 may be explained by the fact that relative concentration of OH^- ions decreases as the pH was decreased from 7.5 to 4.0, which results in the generation of lesser number of OH^\bullet radicals by the following reaction.



In acidic medium, the surface of the catalyst gets a positive charge due to adsorption of H^+ ions. So, there is columbic repulsion between positively charged catalyst

surface and cationic dyes. Probably, these factors are responsible for the decrease in rate of degradation on moving from pH 7.5 to 4.0.

However, a decrease in rate of degradation has also been observed on increasing pH above 7.5. It may be due to the fact that dyes do not remain in their cationic forms because OH^- ions surround the dye molecules at much higher pH and therefore, there is repulsion between dye molecules and negatively charged catalyst surface (due to adsorption of OH^- ions). As a result, the rate of degradation decreases.

Effect of concentration of dyes :

The effect of variation of concentration of dyes (Fig. 6, Table 2.2) on rate of photo-Fenton degradation has been observed in the range from $0.50 \times 10^{-4} \text{ M}$ – $2.00 \times 10^{-4} \text{ M}$. It has been observed that the rate of degradation increases with increasing concentration of Bismark

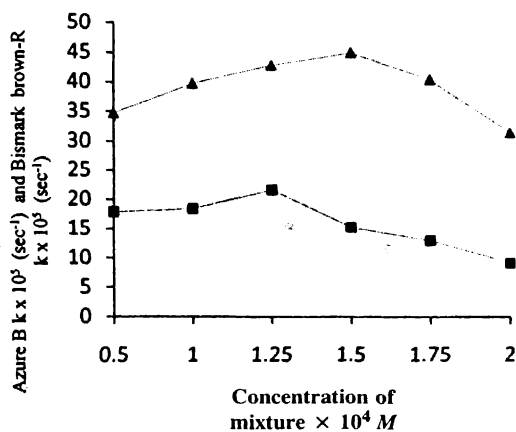


Fig. 6. Effect of concentration of dyes on rate of degradation of mixture of Bismark brown-R and Azure-B dyes : (■) Azure-B, (▲) Bismark brown-R.

Table 2.2. Effect of concentration of dye

pH = 7.5, Light intensity = 70.0 mW cm^{-2} , Photocatalyst = 0.30 g, H_2O_2 = 0.25 mL

Concentration of mixture $\times 10^{-4} \text{ M}$	Azure-B $k \times 10^5 \text{ (s}^{-1}\text{)}$	Bismark brown-R $k \times 10^5 \text{ (s}^{-1}\text{)} \times 10^{-4} \text{ M}$
0.50	17.90	34.73
1.00	18.50	39.79
1.25	21.84	42.90
1.50	15.41	45.00
1.75	13.12	40.49
2.00	9.20	31.57

brown-R and Azure-B up to $1.5 \times 10^{-4} M$ and $1.25 \times 10^{-4} M$, respectively. Further increase in concentration of Bismark brown-R and Azure-B beyond $1.5 \times 10^{-4} M$ and $1.25 \times 10^{-4} M$, respectively results in a decrease in the rate of degradation. This may be explained on the basis that initially, on increasing the concentration of dye, the reaction rate increases as more molecules of dyes are available for degradation. But further increase in concentration of Bismark brown-R and Azure-B beyond these limits causes retardation of reaction due to increasing number of collisions among dye molecules and corresponding collisions among dye molecules and $\cdot OH$ radicals decreases. As a consequence, rate of reaction is retarded. Unsuitable steric orientation is also one of the factors for a decrease in the rate of reaction.

Effect of amount of catalyst :

The effect of variation of amount of catalyst (Fig. 7, Table 2.3) has also been observed on the rate of photo-Fenton degradation.

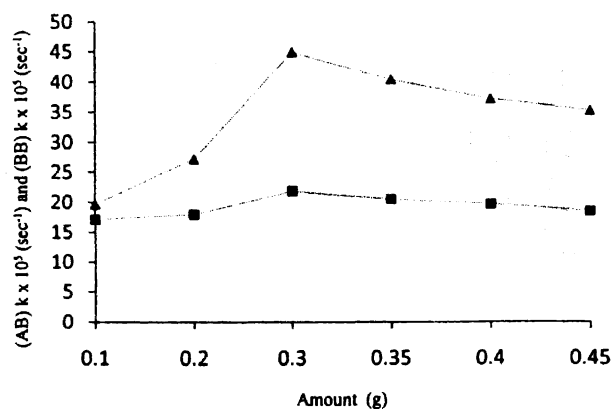


Fig. 7. Effect of amount of catalyst on the rate degradation of mixture of Bismark brown-R and Azure-B dyes : (■) Azure-B, (▲) Bismark brown-R.

Table 2.3. Effect of amount of photocatalyst

pH = 7.5, Light intensity = 70.0 mW cm^{-2} , $\text{H}_2\text{O}_2 = 0.25 \text{ mL}$, [Bismark brown-R] = $1.5 \times 10^{-4} M$, [Azure-B] = $1.25 \times 10^{-4} M$

Amount (g)	(AB) $k \times 10^5 \text{ (s}^{-1}\text{)}$	(BB) $k \times 10^5 \text{ (s}^{-1}\text{)}$
0.10	17.12	19.68
0.20	17.9	27.18
0.30	21.84	45.03
0.35	20.5	40.50
0.40	19.69	37.26
0.45	18.5	35.32

It has been observed that with an increase in the amount of catalyst, the rate of photo-Fenton reaction increases to a certain amount of catalyst (0.30 g), which may be regarded as a saturation point. Beyond this point, the rate of reaction decreases with increase in amount of catalyst. This may be explained by the fact that with an increase in the amount of catalyst, the exposed surface area of catalyst will increase. Hence, the rise in the rate of reaction has been observed. But after a certain limiting amount of catalyst (0.30 g), if the amount of catalyst was further increased, it would also increase the number of copper ions and then there is a possibility of short circuiting of cuprous and cupric ions. As a result, less number of hydroxyl radicals are formed and reaction rate is retarded.

Effect of H_2O_2 :

The effect of variation of amount of H_2O_2 (Fig. 8, Table 2.4) on the photo-Fenton degradation of Bismark

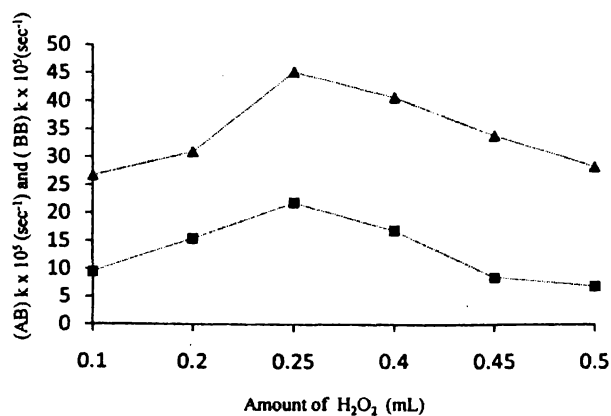


Fig. 8. Effect of amount of H_2O_2 on rate of degradation of mixture of Bismark brown-R and Azure-B dyes : (■) Azure-B, (▲) Bismark brown-R.

Table 2.4. Effect of amount of hydrogen peroxide

pH = 7.5, Light intensity = 70.0 mW cm^{-2} , Photocatalyst = 0.30 g, [Bismark brown-R] $1.5 \times 10^{-4} M$, [Azure-B] = $1.25 \times 10^{-4} M$

Amount of H_2O_2 (mL)	(AB) $k \times 10^5 \text{ (s}^{-1}\text{)}$	(BB) $k \times 10^5 \text{ (s}^{-1}\text{)}$
0.10	9.49	26.72
0.20	15.40	30.83
0.25	21.84	45.00
0.40	16.88	40.63
0.45	8.45	33.76
0.50	6.85	28.15

brown-R and Azure-B has been investigated in the range from 0.10–0.50 mL.

It has been observed that initially upon increase of H_2O_2 from 0.10–0.25 mL, the rate of degradation increases. However, from 0.25 to 0.50 mL, the rate of photo-Fenton degradation decreases for both the dyes. It may be attributed to the consumption of $\cdot\text{OH}$ radicals on reaction with increasing amount of H_2O_2 . The reaction generates hydroperoxy radicals ($\text{HO}_2\cdot$), which are less powerful oxidizing agent as compared to $\cdot\text{OH}$ radical.



As a result, a decrease in rate of degradation for both the dyes has been observed beyond 0.25 mL of H_2O_2 .

Effect of light intensity :

The data indicate that as the light intensity (Fig. 9, Table 2.5) increases, the rate of degradation also increases for both Bismark brown-R and Azure-B dyes and maximum rate has been found at 70.0 mW cm^{-2} . It may be explained on the basis that as the light intensity was increased, the number of photons striking per unit area also increases, resulting into higher rate of degradation. Further increase in the light intensity beyond 70.0 mW cm^{-2} results in a decrease in the rate of reaction. It may be probably due to thermal side reactions.

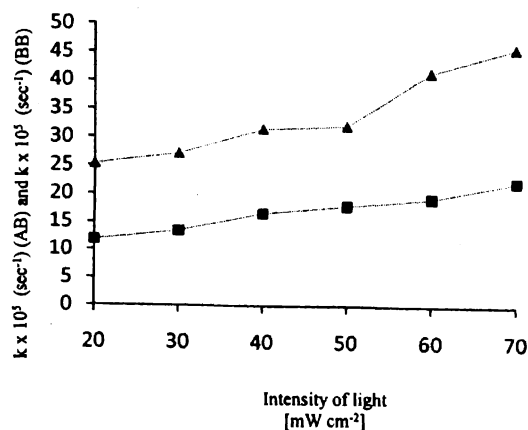


Fig. 9. Effect of light intensity on the rate of degradation of mixture of Bismark brown-R and Azure-B dyes : (■) Azure-B, (▲) Bismark brown-R.

Mechanism :

On the basis of the experimental observations and corroborating the existing literature, a tentative mechanism has been proposed for the degradation of Bismark brown-R and Azure-B by heterogeneous photo-Fenton like reagent.

pH = 7.5, Light intensity = 70.0 mW cm ⁻² , Photocatalyst = 0.30 g, [Bismark brown-R] = 1.5 × 10 ⁻⁴ M, [Azure-B] = 1.25 × 10 ⁻⁴ M		
Intensity of light (mW cm ⁻²)	(AB) <i>k</i> × 10 ⁵ (s ⁻¹)	(BB) <i>k</i> × 10 ⁵ (s ⁻¹)
20.0	11.83	25.31
30.0	13.45	27.10
40.0	16.51	31.32
50.0	17.82	31.81
60.0	19.10	41.00
70.0	21.84	45.00

The involvement of $\cdot\text{OH}$ radicals in the reaction has been confirmed by carrying out the reaction in presence of $\cdot\text{OH}$ radical scavengers like 2-propanol and butylated hydroxy toluene (BHT). In presence of both scavengers reaction rate has been found to be drastically reduced.

Chemical oxygen demand (COD) :

Chemical oxygen demand of solution of mixture of dyes before and after illumination has been determined by reflux method iodometrically. COD of mixture of dyes before and after exposure was found to be 145 and 44 mg/L, respectively. The photodegradation efficiency after 2 h of illumination has been found to be 70%.

Conclusions :

(i) Cu-loaded alumina catalyst has been prepared, by means of the incipient wet impregnation method, using neutral alumina and copper nitrate.

(ii) The amount of photo-Fenton catalyst required (Typically around 0.30 g in 40 mL) is much below than that usually used earlier.

(iii) The effects of the amount of the photo-Fenton catalyst, hydrogen peroxide, concentration of dyes, pH of the reaction medium and light intensity were analyzed in the present work. The results show appreciable degradation of mixture of Bismark brown-R and Azure-B. At optimal conditions, rates of degradation were obtained as $k = 2.18 \times 10^{-5}$ and $k = 4.50 \times 10^{-5}$ for Azure-B and Bismark brown-R, respectively in reaction mixture. During heterogeneous photo-Fenton process, $\cdot\text{OH}$ radicals react with dyes and degrade them into smaller products like H_2O , CO_2 , NO_3^- , SO_3^{2-} , SO_4^{2-} ions etc.

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