KINETIC STUDY FOR DECOLORIZATION OF C.I REACTIVE BLACK-5 DYE

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ABSTRACT

Advanced oxidation processes (AOP's) hold great promise for the improved treatment of textile dye effluent. Attempt has been made to investigate the kinetics for decolorization of C.I Reactive Black-5 dye under strong oxidizing conditions in order to assess the effectiveness and feasibility for purification of water. The operating parameters such as hydrogen peroxide dosage, dye concentration, treatment time, UV light intensity. The degradation efficiency increased nonlinearly with increasing UV light intensity and hydrogen peroxide dosage. Dye was degraded under UV irradiation using H_2O_2 as oxidant to determine the optimum conditions. It has been estimated that this process can be used as an efficient and environmental friendly technique for effluent treatment of industrial wastewater containing organic compounds and dyes from textile industry.

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INTRODUCTION

Recent studies indicated that approximately 12% of synthetic dyes are lost annually during manufacturing and processing operations and that 20% of the resultant color enter the environment through effluents (Reife, 1993). Release of textile wastewater into the environment cause pollution. Major effect of it is on water. So, it causes water pollution.

The reduction of organic content and destruction of odor causing sulfur compound in wastewater can be done efficiently and simply with chemical oxidation treatment using oxidants, such as ozone, hydrogen peroxide, chlorine, chlorine dioxide (Goronszy, 1992). In 1876, Witt proposed that dye molecules contain two groups, the chromophore and auxochrome. The depth of color is related to the molecular structure of the dyes, which is related to the chromophores (-N=N- or >C=O) involved within the structure. In addition, visible and the UV irradiation electron transfer effects at varying wavelengths on the dye structures have been observed, supporting tautomeric capabilities of the dye molecules (Shore, 1990). An oscillation between the double and single bonds occurs along the conjugated molecular chain; therefore, as the chain becomes longer, the vibration rate

becomes slower resulting in a slower kinetic degradation rate (Shore, 1990).

The name azo comes from azote, the French name for nitrogen that is derived from Greek a (not) and zeo (to live). Azo dyes constitute the largest and the most important class of commercial dye extensively used in industrial applications such as textile etc. Azo dyes, characterized by the presence of one or more azo groups (—N═N—) bound to aromatic rings (R—N═N—R'), are the largest and most important class of synthetic organic dyes. It has been estimated that more than 50% of all dyes in common use are azo dyes because of their chemical stability and versatility.

Reactive azo dyes are the most commonly applied among more than 10, 000 dyes applied in textile processing industries (Van Der Zee et al., 2001). These dyes remain in industrial wastes and they have serious impact on environment due to their precursors and degradation products such as aromatic amines are considered carcinogenic (Ince, 1999).

Discharge of azo dyes is undesirable not only for aesthetic reasons but also because many azo dyes and their intermediate products are toxic to aquatic life (Chung and Stevens, 1993) and mutagenic to humans (Chung et al., 1992). Azo dyes are resistant to biodegradation under aerobic conditions (Goronszy, 1992) although anaerobic color removal was applied by many researchers successfully (O,Neill et al., 2000; Panswad and Luangdilok, 2000; Van Der Zee et al., 2001). Reactive dyes have been largely used in the textile industry for dying cellulose and cotton fibers. They form stable covalent bonds with the material they dye and impart the final product a bright and lasting color. However, this class of dyes present a low degree of fixation onto the fibers during dying, thus causing a loss of up to 50% dye in the generated effluent (Cooper, 1995).

Dye pollutants from the textile industry are a major source of environmental contamination. Color removal from textile wastewater has been a matter of considerable interest during the last two decades, not only because of the potential toxicity of certain dyes but also because of their coloring effect on the natural water (Grau, 1991). Textile reactive dyes were recalcitrant to biodegradation causing aesthetic, acute and chronic toxicity problems in receiving water (Kunz et al., 2002). For the removal of such recalcitrant pollutants, traditional physical and chemical techniques have been used extensively to treat textile wastewaters.

Most of the studies, such as chemical precipitation (Tuunay et al., 1996), adsorption by activated carbon (Al-Degs et al., 2000) and some natural absorbents (Morais et al., 1999), photo-catalytic oxidation (Arslan et al., 1999; So et al., 2002) ozonation (Lin and Lai, 2000; Liokou et al., 1997; Oolmez, 1999; Meric et al., 2004) coagulation, reverse osmosis and ultrafilteration etc can generally be used (Vandevivere, 1998). Nevertheless, these methods are generally non-destructive and expensive (Galindo and Kalt, 1998).

Advanced oxidation process is one of the potential alternatives to decolorize and reduce recalcitrant wastewater loads from textile dyeing. This process implies generation and subsequent reaction of radicals mainly hydroxyl radicals which are the most powerful oxidizing species after fluorine (O et al., 1993). The H_2O_2/UV process has the advantage of low capital cost and no considerable solid waste or vapor emission through or after the oxidation (Amin et al., 2008). A kinetic study was carried out taking into account

the contribution of the UV light alone and combined reaction of UV light and H_2O_2

(Malik and Sanyal, 2004; Zhou and Smith, 2002).
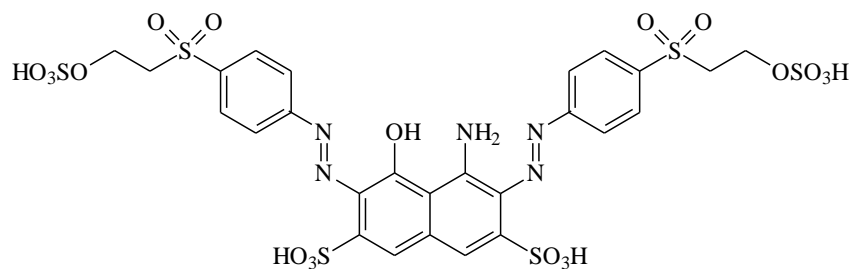
Fig. 1.1 structure of vinylsulphone C.I Reactive Black 5 azo dye

Molecular formula: $C_{26}H_{26}N_5O_{19}S_6$: Molecular weight: 899.8 g mol^{-1}

MATERIALS AND EXPERIMENTAL METHODS
Chemicals

The commercial Reactive Black 5 dye was taken from a local supplier named Haris Dyes and Chemicals Faisalabad. The dye was used as such and no further purification was done to assure the real conditions at which the dye industry works and the water residual should contain same kind of impurities as it is on commercial scale. Hydrogen peroxide (H_2O_2) which used was 35% $^V/_V$.

Determination of maximum wavelength λ_{max}

The maximum wavelength of the dye was determined by using HITACHI U-2800 double beam spectrophotometer. The spectrophotometer was calibrated using distilled water in both reference and sample cell. The dye solution was prepared using distilled water as solvent and introduced into the sample cell. Then scan the spectrophotometer through the range (800-200nm) of light. The peak of the graph plotted by spectrophotometer shows the wavelength at which the maximum light was absorbed by the sample. That was the λ_{max} of the used dye solution which is 594nm.

Measurement of absorbance of each dye sample at λ_{max}

To determine the absorbance of each dye sample at λ_{max} by using spectrophotometer, each solution was scanned at the λ_{max} of RB 5. The spectrophotometer was calibrated by using the distilled water in both reference and sample cells and then absorbance of dye sample at λ_{max} was measured by introducing the dye solution into sample cell instead of distilled water. The absorbance was noted as initial absorbance I_o.

Dye Concentration

Degradation of dye solution was observed by varying the dye concentration 50ppm(.05g/1000ml of water),60ppm(.06g/1000ml of water), 70ppm(.07g/1000ml of water),80ppm(.08g/1000ml of water),90ppm(.09g/1000ml of water), 100ppm(.01g/1000ml of water). Dye concentration was varied with respect to time during experiment.

UV light Intensity

To see how the UV light intensity effect the photo-degradation three UV-A tube rods of 6 W and of 254nm were used in UV chamber. When one light was switched on that means UV light intensity was of 6W

and when two lights were on that means UV light intensity was of 12W and same for three UV lights, intensity was of 18W.

Concentration of Hydrogen Peroxide

The concentration of H_2O_2 was varied and its effect on the %decoluration was observed. H_2O_2 concentration increases in %age with respect to the volume of dye solution that has been taken in china dish for UV Treatment and its effect on the %decoluration of dye was observed. As the H_2O_2 was added to the dye solution it must be immediately treated in UV reactor because reaction in the dye solution was

started just after the addition of H_2O_2 and decolorization was observed after the treatment of UV light for a fixed time and change in absorbance was observed using spectrophotometer.

UV Treatment Time

UV treatment time for dye sample varied from 10 minutes to 60 minutes, and further time as needed for complete decolorization of dye solution and its effect on the %age decolorization was continuously observed. Time also have significant role in dye decolorization.

Statistical Analysis

The data obtained was analyzed to check the efficiency of method.

1. The % decolouration can be observed by using the following formula:

    % Decoluration = $\dfrac{\text{Initial absorbance} - \text{Final absorbance}}{\text{Initial absorbance}} \times 100$

2. The standard deviation was calculated by using following formula:

$$\sigma = \sqrt{\frac{\sum(\bar{x} - x)^2}{n - 1}}$$

3. The work was the kinetic study of degradation of reactive Black 5 dye, so to find out the rate law, following formula was applied:

    Rate law $= \ln C_t/C_o$

RESULTS AND DISCUSSION

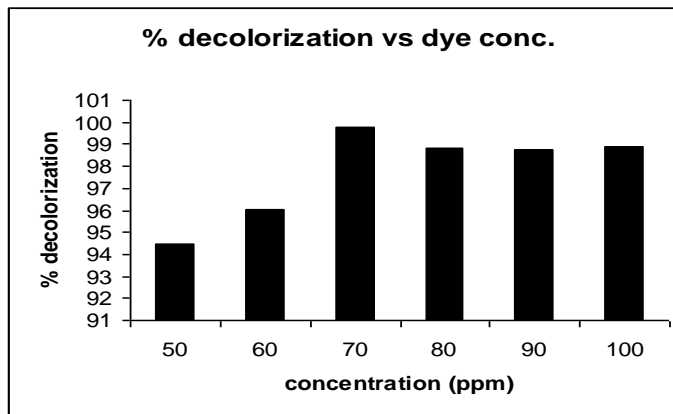**Effect of Dye Concentration on the Decolorization Efficiency**

Fig. 3.1 shows that when the dye concentration increases the efficiency rate will be decreased. Initially 0.005g/100ml of sample was decolorized up to 85 % in 40 minutes but as the dye concentration increases from 0.005 to 0.01/100ml the decolorization time become 70 minutes. Hence the time of decolorization was more when concentration was greater. It has been observed that the decrease of the

decolorization rate with the increase of the initial dye concentration (Aleboyeg et al., 2004). Rate of dye decolorization is directly proportional to the number of hydroxyl radicals, as the concentration of dye sample increases, the number of hydroxyl radicals remains constant, and so the decolorization efficiency was decreased. So, that an increase in dye concentration induces a rise of the internal optical density and the solution becomes more and more impermeable to UV radiation (Aleboyeg et al., 2004).
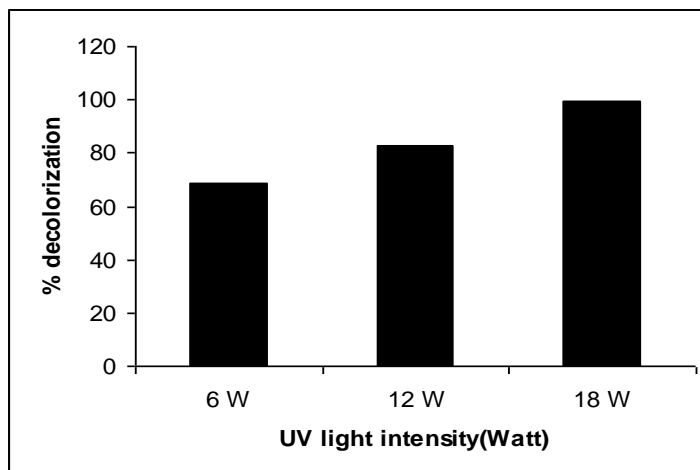
% decolorization vs dye conc.

Fig. 3.1 Effect of %age decolorization verses concentration of dye solution

Effect of UV Power

Fig. 3.2 shows the effect of UV power by varying the UV intensity as 6watt, 12watt, 18watt. By increasing the UV power the decolorization efficiency increases. When 50ppm-100ppm sample of C.I RB5 was treated with, 6watt, 94% decolorization was achieved in 90 minutes; when same sample was treated with 12watt the 97% decolorization was achieved in 70 minutes and treatment of same sample using 18watt UV intensity, 100% decolorization was achieved only in 40minutes. During this experiment all the other parameters were kept constant. More UV power, there was greater chance of the formation of hydroxyl radicals, that would increase the decolorization rate of dye sample (Colona and Marcandalli, 1999). It appears that with increasing the light intensity the decolorization rate increases. That increase was due to the enhanced production of hydroxyl radicals. At low UV power the rate of photolysis of H2O2 was limited and at high UV power more hydroxyl radicals were formed, upon the photo-dissociation of H2O2, hence decolorization rate increases (Behnajady and Modirshahla, 2006).
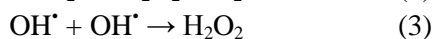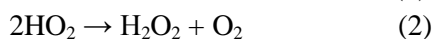

Fig. 3.2 Effect of %age decolorization verses UV light intensity at dye concentration of 70ppm
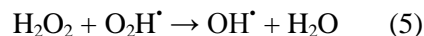
Effect of Hydrogen Peroxide Concentration on % Decolorization

Fig. 3.3 shows the effect of H_2O_2 dosage on % decolorization/decolorization efficiency by varying the H_2O_2 doses while keeping all other parameters constant. The H_2O_2 concentration varies from 0.4% to 1.6%. There was no observable loss of the color when the irradiation was applied in the absence of H_2O_2; the color removal was also negligible in the absence of UV radiation. The results reveal that a considerable decrease in the concentration of the dye occurs when the sample was irradiated with UV in the presence of H_2O_2. That loss was due to the formation of hydroxyl radicals, which are powerful oxidizing agents (Behnajady and Modirshahla, 2006). It was shown from results that the decolorization efficiency increases up to a certain point with hydrogen peroxide dose, and then it starts to decrease. This behavior was due the reason that hydrogen peroxide is scavenger for hydroxyl radicals (Amin et al., 2008). Hydrogen peroxide concentration was an important parameter for the degradation of the color in the UV/H_2O_2 photo-reactor. Indeed, the OH free radicals produced upon photolysis of H_2O_2 can react with dye molecules, but also with an excess of H_2O_2. Excess of hydrogen peroxide and high OH radical concentration result in competitive reactions, producing an inhibitory effect on the decolourization. OH radicals were prone to react or to recombine according to the following scheme (Baxendale and Wilson, 1957; Solecka et al., 2001; Wang et al., 2006).
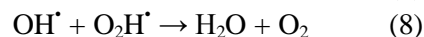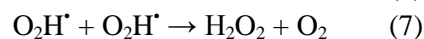
Initiation:

$$OH^. + H_2O_2 \rightarrow HO_2^. + H_2O \qquad (1)$$

$$2HO_2 \rightarrow H_2O_2 + O_2 \qquad (2)$$

$$OH^. + OH^. \rightarrow H_2O_2 \qquad (3)$$

Propagation:

$$H_2O_2 + OH^. \rightarrow O_2H^. + H_2O \qquad (4)$$

$$H_2O_2 + O_2H^. \rightarrow OH^. + H_2O \qquad (5)$$

Termination:

$$OH^. + OH^. \rightarrow H_2O_2 \qquad (6)$$

$$O_2H^. + O_2H^. \rightarrow H_2O_2 + O_2 \qquad (7)$$

$$OH^. + O_2H^. \rightarrow H_2O + O_2 \qquad (8)$$

When enough hydrogen peroxide was present in the solution, it starts to compete with the dye for reaction with hydroxyl radicals since $HO_2^.$ was less reactive than the $OH^.$ radical. Therefore, an important step in the optimization of the method was the determination of the adequate amount of $[H_2O_2]$, to avoid an excess of reagent that can retard the decolourization. At low H_2O_2 concentration, formation of $^.OH$ was the Kinetic determining step. H_2O_2 cannot generate enough hydroxyl radicals and the oxidation rate was logically slow. Further, most of the free radicals were directly consumed by the dye. In the presence of high concentration of H_2O_2, one could expect that more OH radicals would be produced. However, these radicals preferentially react with the excess of H_2O_2. This undesirable reaction competes with the degradation of the color (Baxendale and Wilson, 1957).Dyes are attacked by UV photon and by hydroxyl radical, which is a powerful oxidant generated from the photolysis of H_2O_2 by UV light, making possible the degradation of the dyes (Incee et al., 1997). The catalytic effect of hydrogen peroxide can be explained by the chain reaction mechanism proposed by Baxendale and Wilson 1957. This catalytic behavior of H_2O_2 has been observed by other authors (Benitez et al., 1996; Elkanzi and Kheng, 2000).

Fig. 3.3 reveals that when the amount of H_2O_2 was increased the %age decolorization was decreased. The dye solution shows maximum %age decolorization of 99.99% when 1% (.25ml) of H_2O_2 was used.
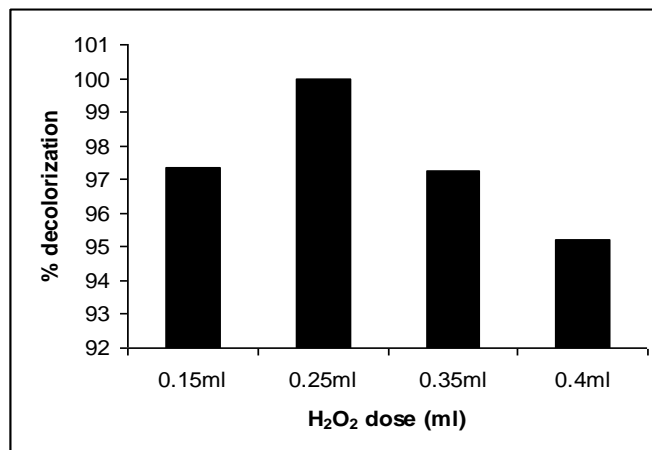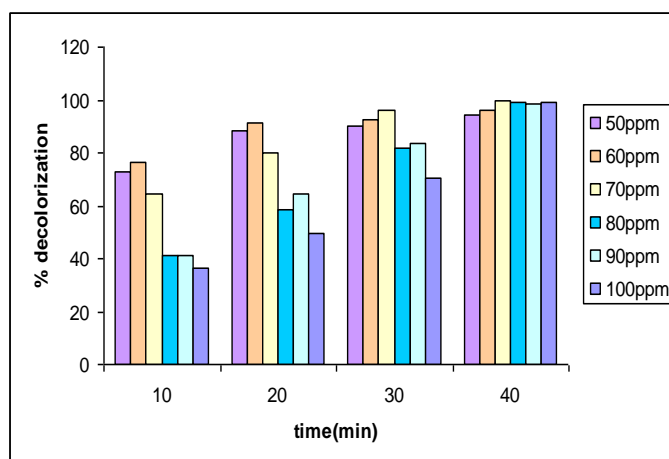
Fig. 3.3 Effect of % age decolorization verses Hydrogen Peroxide (H_2O_2) dose
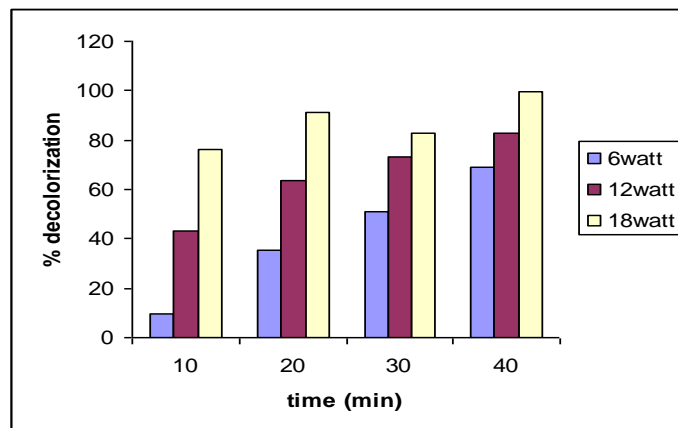
Effect of Time of on % Decolorization

The rate of % decolorization increases as the time was increased. Fig. 3.4a illustrates the effect of time on dcolorization of dye sample of different concentrations (50ppm-100ppm). It shows that when time increases the decolorization efficiency also increases. Fig. 3.4b shows the effect of time of UV treatment on the decolorization efficiency of dye sample. The increased time of treatment shows more decolorization. It was observed that the treatment time and % decolorizations both are in direct relation to each other (Amin et al., 2008).

Fig. 3.4a Comparison between % decolorization and time for different concentration of dye solution

Fig. 3.4b Effect of % age decolorization verses time at dye concentration of 70ppm at all UV lamps

CONCLUSION

The kinetics of decolourisation of azo dyes in wastewater was monitored by employing UV/H_2O_2 process. It can be concluded that the maximum decolorization efficiency for Reactive Black 5 dye was observed at following optimum conditions:

Concentration of dye solution $=$ 70ppm

H_2O_2 dose $=$ 1%

UV light intensity $=$ 18watt

Time $=$ 40 minutes

The decolorization process was modeled as reaction taking place: is the H_2O_2 catalyzed oxidation. The concentration of hydrogen peroxide was observed nearly constant during the course of the reaction. The decolorization occurs due to the chemical reaction in the dye solution. During the chemical reaction, a structural change takes place in the dye molecule. Reactive Black 5 dye is an azo dye and the chemical reaction involved the breakage of ─N═N─ in the dye structure. The color removal take place due to destruction/structural changes of chromophore which gives color to any compound and cause the absorbance of light. The structural changes cause decrease in absorbance of dye solution. The degradation of dye solution showed that the color removal from textile wastewater and results in purification of environment.

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Appendix I

Effect of %age decolorization verses concentration of dye solution

Sr. No.	Dye conc.	Absorbance		% decolorization	S.D
	(ppm)	Initial	Final(sample+UV+H_2O_2)		
1	50	0.902	0.050	94.46	0.007
2	60	1.070	0.040	96.04	0.007
3	70	1.280	0.003	99.76	0.003
4	80	1.109	0.013	98.82	0.007
5	90	1.226	0.015	98.77	0.003
6	100	1.374	0.016	98.86	0.003

Appendix II

Effect of %age Decolorization on UV light intensity

Sr. No.	UV light intensity	Time (mints)	Absorbance		% Decolorization	S.D
			Initial	Final		
1	6 W	40	0.843	0.263	68.80	0.001
2	12 W	40	1.083	0.186	82.83	0.002
3	18 W	40	1.280	0.003	99.76	0.003

Appendix III

Effect of % age decolorization verses Hydrogen Peroxide (H_2O_2) dose

Sr. No.	H_2O_2 dose	Time (mints)	Absorbance		% Decolorization	S.D
			Initial	Final		
1	0.15ml	100	1.861	0.049	97.36	0.005
2	0.25ml	100	1.861	0.001	99.99	0.001
3	0.35ml	100	1.861	0.051	97.25	0.005
4	0.4ml	100	1.861	0.089	95.22	0.004