

PHOTO DEGRADATION OF CRYSTAL VIOLET –A PARAMETRIC STUDY

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Abstract- There's no doubt that water is important. Aside from actually being part of the weather in the form of rain sleet and snow, large bodies of water can keep a region's temperature milder than a location even just a few miles inland. Now a days Water pollution is a major global problem. It has been suggested that it is the leading worldwide cause of deaths and diseases, and that it accounts for the deaths of more than 14,000 people daily. Water pollution has become a serious problem because of biomagnifications using water as a medium. Among the various processes (AOP) are promising, as complete destruction of the toxic organic substances can be achieved. AOP include photo degradation, electrochemical oxidation and biodegradation methods.

In this study solar assisted degradation of Crystal Violet in a synthetic effluent with varying parameters including dye dose, concentration of $[H^+]$, $[H_2O_2]$, $[Fe^{2+}]$, various metal oxides is presented.

Key words- Water pollution; AOP; Biomagnifications; solar degradation; Crystal Violet.

I. INTRODUCTION

Nobel laureate Sir.C.V.Raman said "Water the elixir of life". Water is the vital factor for the existence of organisms in the globe. It acts as a link between various biogeochemical cycles that exist in nature. Because of exploding population and extensive industrialization, water demand goes on increasing and existing water is also getting polluted. The high rate of consumption in one side and lack of protection of the existing water sources on the other side, water crisis is becoming a serious threat. Effects of water pollution may be acute or chronic. World community has witnessed some worst scenarios like Minamata Disaster and Love canal tragedy.

A. SOURCES OF POLLUTION

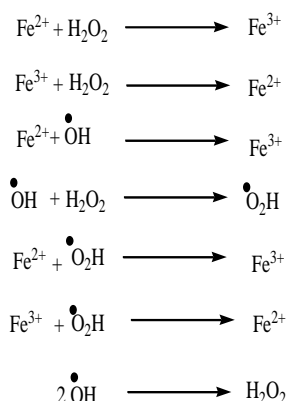
Water is getting polluted primarily by industrial effluents and domestic sewage which makes the water unusable in many cases. The pollutant may be inorganic salts, toxic organics,

suspended solids, radioactive materials or heat. Organic pollutants enter in to the water system through domestic sewage and rejects from paper mills, tanneries, pharmaceutical, textile and dyeing units. Synthetic dyes from the dyeing plants are one of the major pollutants those affect the aquatic system very seriously. They are deeply colored and contain dye assisting chemicals like NaOH, Na_2CO_3 and mordants which can totally modify the system. Majority of the dyes are toxic and non biodegradable, which cause lethal problems [1- 4]

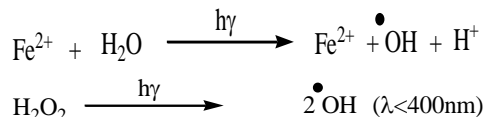
B. ADVANCED OXIDATION PROCESSES

Much attention is paid towards the advanced oxidation processes (AOP) for the treatment of the dye effluents. Methods like reverse osmosis(RO), electro chemical oxidation (ECO), adsorption are found to be of limited usage, either because of recuperation and resurgence or economical constraints. Homogeneous oxidation process employing H_2O_2 with UV light is found to be very effective in the oxidative degradation of dyes [5]. Complete decolourization and mineralization of the dyes by UV light in presence H_2O_2 had been reported [6-8]

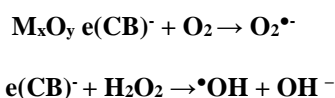
Fenton's and Photo Fenton's processes employ Fe^{2+} and H_2O_2 to produce $\bullet OH$, which attacks almost all organic compounds. Fenton reaction rates are increased by irradiation with UV or sunlight. When whole of the Fe^{2+} is converted in to Fe^{3+} eventually the reaction stops. In photo Fenton route Fe^{3+} is reduced back to Fe^{2+} photo chemically which continues the reaction cycle. The proposed mechanism involves following steps



The reason for the positive effect of irradiation on the degradation rate include the photo-reduction of Fe^{3+} to Fe^{2+} ions, which produce new HO^\bullet radicals with H_2O_2 according to the following mechanism,



In the recent time heterogeneous photo catalyzed degradation methods have gained importance which employ metal oxides. Due to semiconducting nature and photo activity, metal oxides are used as photo catalysts for removal organic pollutants. The main problem in the heterogeneous photo catalysis is, the separation of photo generated e^- - hole pair. This could be achieved by using electron acceptors or hole scavengers. According to Okamoto et al, oxygen is the primary acceptor of conduction band electron with formation of superoxide ion (O_2^-) [9]. Oxygen can be replaced by H_2O_2 and play the role of electron acceptor. It can trap the photo generated conduction band electron thus inhibiting the electron hole recombination as shown by the equation,



In the present work a synthetic effluent, containing Crystal Violet (CV) a triphenyl methane dye and a suspected carcinogen has been used to study the operational parameters of the photo Fenton degradation process.

II. MATERIALS AND METHODS

Crystal Violet was obtained from LOBA chemicals and used as such. Commercially available H_2O_2 (20 volume, 4M) was diluted freshly to prepare 0.4M solution every day. AnalaR grade H_2SO_4 , $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, MnSO_4 and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were used as

such. Double distilled water obtained by redistilling distilled water with a speck of KMnO_4 and NaOH was used to prepare all the solutions.

III. EXPERIMENTAL METHOD

A desired molar ratio of dye/ H_2O_2 / Fe^{2+} was prepared freshly before the experiments. In all cases 50ml of reaction mixture was irradiated in the sunlight between the times 11.00 a.m. to 3.30 p.m. on sunny days. At specific time of intervals 2ml of the sample was withdrawn and its absorbance at 582 nm was measured immediately.

For the degradation studies, decrease in the absorption peak at 582 nm was continuously monitored by using a single beam UV spectrophotometer (Elico - BL158). The time-dependent decrease in the dye concentration is shown in Fig. 1. The decrease in absorption at nm shows the destruction of aromatic moiety also. The absorption data of the dye solution was fitted to the first-order rate equation.

$$\log(A_t) - \log(A_0) = -2.303 kt$$

where k is the rate constant, t is the reaction time. A_0 and A_t are the initial and the final absorbance values of the dye solution, respectively. A plot of $\log(A_t)$ versus time generated a straight line with negative slope. Slope of the straight line multiplied by 2.303 gave the apparent rate constant.

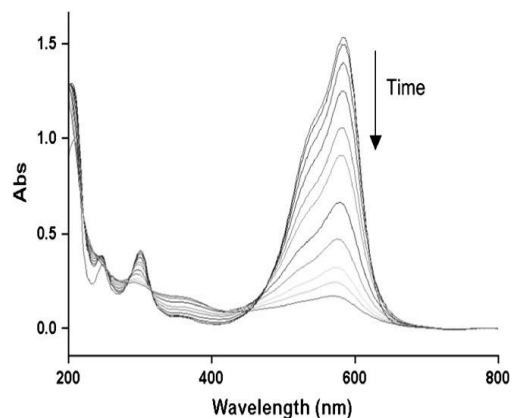


Fig.1. Degradation of crystal violet with time

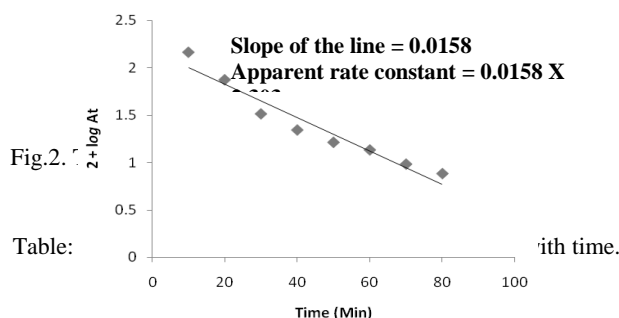


Table:

Time (min)	2 + log At
10	2.16
20	1.87
30	1.51
40	1.34
50	1.21
60	1.13
70	0.98
80	0.88

A. PHOTOCHEMICAL DEGRADABILITY

Before the photochemical oxidation reactions the photo stability of crystal violet should be ascertained. The dye solution of known concentration was exposed to sunlight and the absorbance was measured at the time intervals of 10 minutes. The dye undergoes photo degradation, but only 2.5% is decomposed in 120 minutes. So it was concluded that crystal violet is stable towards the sunlight.

Time (min)	% of dye remaining
20	98.8
40	98.4
60	98.1
80	97.8
100	97.6
120	97.5

Table 2. Direct solar irradiation of Crystal Violet

B. EFFECT OF PH

To investigate of effect of pH on the degradation reaction was run at various pH [3, 4, 5, 6]. The pH 1, 2 are avoided because crystal violet undergoes colour change between pH 1-2. Alkaline pH is avoided, since crystal violet is reduced to leuco-base by alkalis. It was found that in this working pH range, the degradation is not much influenced by pH.

C. EFFECT OF CONCENTRATION OF DYE

The dye concentration is one of the most important parameter to be considered in the degradation. The effect of initial concentration of dye was studied by taking varying amounts of dye under similar conditions. The results and figures show that increasing dye concentration decreases the rate of degradation. For further study the concentration of 0.14 m mol/lit was chosen.

D. Effect of H₂O₂

The standard kinetic run with varying amount of H₂O₂ showed that, the rate of degradation increases with increasing dose of H₂O₂ up to 40 m.mol only. Above the 40

m.mol concentration •OH are inhibited by H₂O₂ itself, according to the following equation,



E. EFFECT OF FE²⁺ CONCENTRATION

Increasing Fe²⁺ concentration produces more amounts of hydroxyl radicals leading to increased rate of degradation, reflected as the fivefold increase in the rate constant.

F. EFFECT OF CU²⁺ AND MN²⁺

When Fe²⁺ is replaced by Cu²⁺ and Mn²⁺ which are similar to Fe²⁺-H₂O₂ system in generating •OH, the rate of degradation is very low; even with a thirty fold higher concentration of Cu²⁺ or Mn²⁺.

G. EFFECT OF METAL OXIDES

The photo Fenton's process is compared with the degradation of the dye adsorbed on a semiconductor metal oxide surface. Appropriate quantity of metal oxides (ZnO, Fe₂O₃ and Cr₂O₃) were mixed with the dye + H₂O₂ mixture and irradiated with continuous aeration by a pump to avoid the sedimentation of the metal oxides. Initially the reaction mixture was kept in dark for 20 minutes for the attainment of adsorption – desorption equilibrium. The plots show that Fe₂O₃ is as efficient as the photo Fenton's process.

IV. CONCLUSIONS

The dye Crystal Violet which is fairly photo stable is completely degraded by the solar irradiation in presence of the Fe²⁺ - H₂O₂. In the chosen working range the rate of degradation is independent of pH and the reaction follows pseudo first order kinetics. Increasing dye concentration decreases the rate, which may be due to more number of competing molecules. Higher amount of H₂O₂ shows a limiting concentration of 800 m.mol/lit, above which the •OH are quenched, leading to lower rates of degradation. Increasing amount of Fe²⁺ produces more •OH, thereby increasing the rate of degradation. Single electron transfer systems like Cu²⁺/Cu³⁺ and Mn²⁺/Mn³⁺ in presence of H₂O₂ are not so efficient as the Fenton's system containing Fe²⁺/Fe³⁺. Semiconducting metal oxides activated by H₂O₂ also catalyze the degradation in which Fe₂O₃ is the most efficient. No colour resurges observed after the reaction, which showed that the dye molecule is completely degraded.

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