

# A Comparative Study On Gamma Radiolytic And Oxidative Degradation Of Aqueous Solution Of Methyl Violet 6B

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**Abstract:** In textile industry, Advanced Oxidation Processes (AOP's) are used for degrading and removing colour which allows wastewater reuse. In this study, radiolytic degradation and chemical oxidation process ( $K_2S_2O_8/Fe^{2+}$ ) were investigated for decolourisation of Methyl Violet 6B (MV) dye. The effects of operating parameters such as potassium persulphate (KPS) dosage, ferrous ion ( $Fe^{2+}$ ) dosage, pH and gamma radiation on decolourisation have been evaluated. About 52% dye removal was observed by chemical oxidation ( $K_2S_2O_8/Fe^{2+}$ ) in dark condition while 82.5% by synergistic effect of persulphate (PS) and gamma radiations (dose = 0.078 kGy). Greater removal efficiency was noted at low concentrations of KPS,  $Fe^{2+}$  and low gamma dose. G (-dye) was found to decrease with increase in  $\gamma$ -dose.

**Keywords:** Methyl violet 6B, persulfate, ferrous ions, gamma radiation, degradation, G (-dye).

## I. INTRODUCTION

Due to the extensive use of dyes in industries, they have become an integral part of industrial effluent. Most of these dyes are toxic and potentially carcinogenic in nature and their removal from industrial effluents is a major environmental problem. Various methods have been suggested to handle the dye removal from water these include the biodegradation, coagulation, adsorption, advanced oxidation and the membrane processes [1]. Among these techniques, the Advanced Oxidation Processes (AOP's) appear to be promising field of study, which have been reported to be effective for the near ambient degradation of soluble organic contaminants in water and soils because they can provide an almost total degradation [2]. AOPs are based on the generation of highly reactive oxidants and are able to oxidize a wide range of compounds that are otherwise difficult to degrade [3].

PS oxidation chemistry is an emerging technology in the field of AOPs to degrade organic contaminants. PS is relatively stable like permanganate. Moreover, it could be activated to generate reactive sulphate radicals and secondary radicals like  $OH^\bullet$ , similar to activation of  $H_2O_2$  to produce radicals for degradation of a wide range of contaminants. Thus PS remains impressive because it offers advantages of both permanganate and  $H_2O_2$  [4]. It has been reported that PS anion can be activated thermally or chemically by the transition metal ions, such as  $Fe^{2+}$  to generate a strong oxidant sulphate free radical ( $SO_4^{\bullet-}$ ,  $E^0=2.5-3.5$  V). The overall stoichiometric reaction between PS and  $Fe^{2+}$  is expressed by Eq. (1) through two steps of Eq. (2) and (3) as follows [5].



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Activated PS combined with ultrasound is reported to have synergistic effect on dye degradation [6]. Photochemical oxidation of reactive dyes by UV/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> process has also been reported to have an enhanced rate of degradation [7].

On the other hand, the use of ionizing radiation for the treatment of textile dye effluents seems to be promising. This is because, the effect of gamma radiations can be intensified in aqueous solution by the primary products formed from the radiolysis of water. The irradiation dose necessary for complete decomposition of a dye depends principally on its molecular structure and reactivity towards the primary water radiolysis products, the presence of oxygen or oxidizing agents, temperature, pH as well as concentration of the solution [8].

The aim of this study was to analyze the possibility of using gamma rays to degrade or decolourize MV in the presence and absence of K<sub>2</sub>S<sub>2</sub>O<sub>3</sub> in water. The change of spectra, pH, dye concentration and degree of decolouration (percent reduction in optical density) were examined as a function of irradiation dose. Synergistic effects resulting from additives such as K<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and Fe<sup>2+</sup> on degradation process were investigated. The reaction intermediate if any were identified using HPLC.

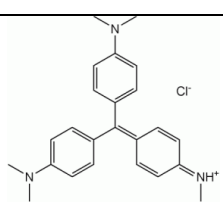
## II. EXPERIMENTAL

### A. Materials

MV was obtained from National Chemicals and used without further purification. The characteristics of the dye are given in Table 1. KPS and sodium azide were obtained from S.D. Fine. Ferrous ammonium sulphate, HCl and NaOH were obtained from Merck. Doubly distilled water was used to prepare dye solutions of desired concentrations. Methanol (HPLC grade) and Acetonitrile (HPLC grade) were obtained from Fisher Scientific.

TABLE I.

CHARACTERISTICS OF METHYL VIOLET 6B (MV) DYE.

Name of dye	Molecular formula	Molecular weight	Class of dye	$\lambda_{\max}$	Structure
Methyl Violet 6B	C <sub>24</sub> H <sub>28</sub> N <sub>3</sub> Cl	393.958 g/mol	Basic dye (pentamethyl-pararosaniline dye)	582 nm	

### B. Methods

#### 1) Experiments with persulphate.

Batch experiments were performed for persulphate reaction in dark and at room temperature. Reaction mixtures were obtained by taking appropriate amount of MV stock solution, adding ferrous sulphate and adjusting the pH value with HCl and NaOH. The reactions were initiated by adding calculated amounts of KPS. During the experiment, samples were collected after various reaction times and immediately quenched by adding NaN<sub>3</sub> solution to the reaction mixture and change in concentration was evaluated with a spectrophotometer. Similar reactions were performed in presence of gamma radiations.

#### 2) Radiolysis experiments

The gamma radiolytic experiments were carried out using a <sup>60</sup>Co irradiation facility with a dose rate of 0.5418 kGyh<sup>-1</sup> as determined by Fricke dosimetry [G (Fe<sup>2+</sup>) = 15.6 (100eV<sup>-1</sup>)]. The solutions were irradiated in borosilicate glass tubes with B24 joint. Different concentrations of MV were used for radiolysis experiments

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with and without oxidising agent and the results were compared. The radiolysis experiments were performed at room temperature.

### 3) Analytical methods

The degradation efficiency of PS and gamma radiolysis was evaluated using a Spectronic 20 D+ UV-Vis spectrophotometer. Prior to the measurement, a calibration curve was obtained by using the standard MV solution with known concentration. The solutions were analysed before and after the reaction by using Shimadzu HPLC (LC 20AT) with an SPD 20 A detector and C18 column. The mobile phase used for analysis was methanol.

## III. RESULTS & DISCUSSION

### A. Effect of pH

The effect of the initial pH value of solutions on the decolourisation of MV by PS and gamma radiations was studied at three different pH values, 3, 7 and 9. It was observed that the degradation of MV at all pH values followed first order kinetics (Fig. 1). With increase in pH, the efficiency of MV degradation decreased indicating that the acidic pH is more favourable for MV degradation than the neutral and alkaline pHs.

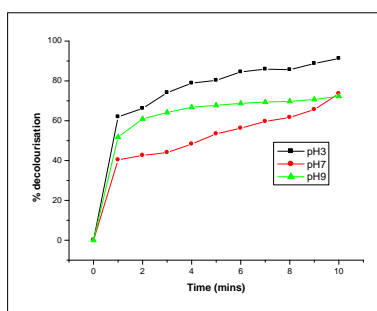
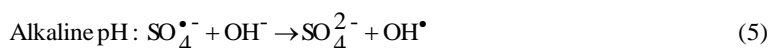
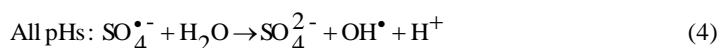


Fig. 1. Effect of pH on degradation of MV; [MV] =  $4 \times 10^{-5}$  M; [Fe<sup>2+</sup>] = 2 mM; [K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 10 mM and gamma radiations at dose rate 0.5418 kGy<sup>-1</sup>.

In aqueous solution there exist both sulphate and hydroxyl radicals and an inter conversion reaction occurs which produces hydroxyl radicals having an oxidation potential of 2.7 V. The inter conversion reactions are described in the following Eq. (4) and (5).



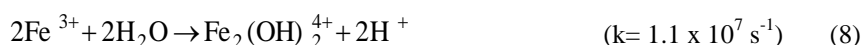
Thus, the pH of solution determines whether the sulphate radical or the hydroxyl radical predominates. Sulphate radical usually participates in electron transfer while, hydroxyl radical participates in hydrogen abstraction or hydrogen addition reaction. Thus, the sulphate radical predominates in acidic conditions. A decrease in MV degradation at neutral and alkaline pH can be attributed to the precipitation of iron (Fe<sup>2+</sup> and Fe<sup>3+</sup>). The soluble Fe<sup>2+</sup> species is stable between wide ranges of pH from 2 to 9 while Fe<sup>3+</sup> precipitation occurs above pH 4. Thus, when the pH value of an aqueous solution is above 4, the amount of soluble Fe<sup>2+</sup> could be decreased due to the formation of Fe<sup>3+</sup> complexes which hinder the further reaction of Fe<sup>2+</sup> with PS [5]. The reaction can be described as follows in Eq. (6-8)



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The production of turbidity above pH 7 confirmed precipitation. Thus, all experiments were performed at pH 3.

### B. Effect of ferrous sulphate concentration

The efficiency of MV degradation is influenced by the presence of  $\text{Fe}^{2+}$ . With increase in the concentration of  $\text{Fe}^{2+}$  from 2 mM to 10 mM an increase in MV degradation was observed, probably, due to a rise in production of sulphate radicals in the reaction. However, with further increase in  $\text{Fe}^{2+}$  concentration the degradation efficiency decreased (Fig. 2). This, indicates that  $\text{Fe}^{2+}$  can also act as sulphate radical scavenger as expressed in Eq. (9).

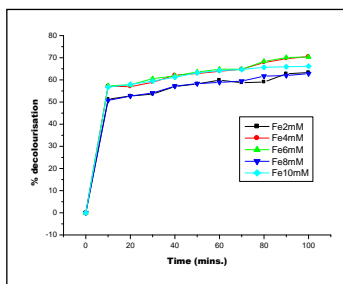


Fig. 2. Effect of ferrous sulphate on degradation of MV; [MV] =  $4 \times 10^{-5}$  M;  $[\text{K}_2\text{S}_2\text{O}_8]$  = 10 mM; pH= 3.

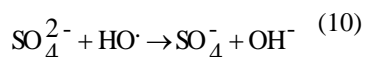
Thus, while an essential amount of  $\text{Fe}^{2+}$  is required to activate PS and generate a sufficient amount of sulphate radicals in the reaction solution, an excess amount of  $\text{Fe}^{2+}$  would decrease the degradation efficiency. An increase in  $\text{Fe}^{2+}$  concentration may not result in a proportional increase of PS decomposition and no increase in the degradation may occur [7].



### C. Effect of PS concentration

Oxidation of dyes is carried out by  $\text{SO}_4^{\bullet-}$  produced between PS and  $\text{Fe}^{2+}$  reaction (Eq.1-3). As seen from Fig. 3 the degradation efficiency of the dye was found to increase with increase in the concentration of PS. However, with further increase in PS dose only a slight increase was observed. This was in agreement with observations by other researchers [5], who applied  $\text{Fe}^{2+}$  to activate PS to degrade other pollutants. This was also reported in Fenton reaction where excessive amount of hydrogen peroxide had a detrimental effect on the degradation efficiency [9] and [10].

With increase in PS concentration there may be an increase in the sulphate ions which causes a decrease in the percentage degradation of the dye. This is because these ions can react with  $\text{OH}^{\bullet}$  radicals in solution and result in their depletion as follows.



The sulphate radicals can also react with water molecules to produce more sulphate ions as follows

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Since sulphate radical is less reactive than hydroxyl radicals, therefore sulphate ion concentration increases in solution which leads to less dye degradation [1].

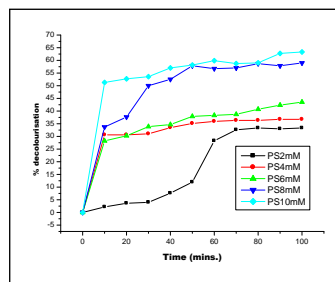


Fig. 3. Effect of persulfate concentration on degradation of MV; [MV] = 4 x 10<sup>-5</sup> M; [Fe<sup>2+</sup>] = 2 mM; pH = 3.

### D. Effect of initial dye concentration

It is important from an application point of view to study the dependence of removal efficiency on the initial concentration of the dye. The effect of MV concentration on dye removal efficiency was investigated at different concentrations from 4 x 10<sup>-5</sup> to 6.2 x 10<sup>-5</sup> M. It has been observed that the extent of degradation decreased with an increase in the initial concentration of MV as shown in Fig. 4. This is because of a lower concentration of sulphate radical which resulted due to increasing concentration of MV while the dose of PS and Fe<sup>2+</sup> remained the same.

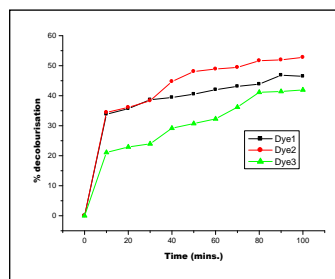


Fig. 4. Effect of MV concentration; [Fe<sup>2+</sup>] = 2 mM; [K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 10 mM; pH=3; [Dye 1] = 4 x 10<sup>-5</sup>M; [Dye 2] = 5.3 x 10<sup>-5</sup>M; [Dye 3] = 6.2 x 10<sup>-5</sup>M

### E. Effect of gamma radiations

The efficiency of degradation of MV dye for PS reaction was found to be 52.78% in dark, whereas 61.95% was achieved for gamma radiations alone (dose = 0.078 kGy) and 82.5% for combined effect of PS and gamma radiations (dose = 0.078 kGy) as shown in Fig. 5.

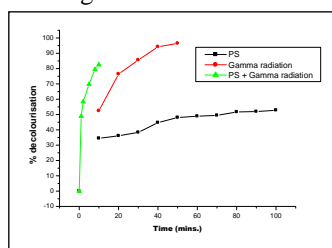


Fig. 5. Degradation of MV in presence of persulfate, gamma radiations and persulfate in synergism with gamma radiations.

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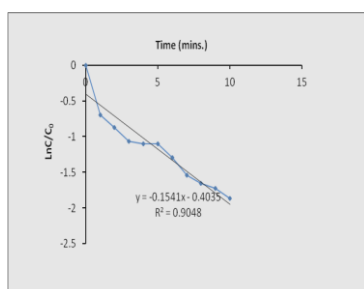
The G (-dye) showed a significant decrease, thus indicating spontaneous degradation of the dye. The rate constant and G (-dye) for different concentrations of MV are given in **Table 2**.

**TABLE 2.**

G(-dye), rate constants and % decolouration of MV at different concentrations.

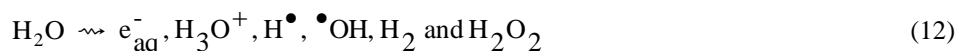
<b>Methyl Violet 6B</b>			
<b>Concentration of MV</b>	4 x 10 <sup>-5</sup> M	5.3 x 10 <sup>-5</sup> M	6.2 x 10 <sup>-5</sup> M
<b>G(-dye) Dose = 0.079 kGy</b>	0.321	0.43	0.448
<b>Rate constant (min<sup>-1</sup>)</b>	0.184	0.187	0.173
<b>% decolouration of dye in presence of gamma radiation (dose = 0.079 kGy) &amp; persulfate/Fe<sup>2+</sup></b>	81.41	82.5	81.25

The semi-logarithmic graph of the concentration of MV in the presence of PS and gamma radiations versus irradiation time gave a straight line indicating pseudo- first order reaction (Fig. 6).



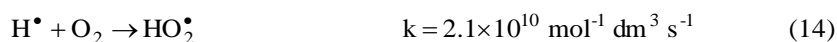
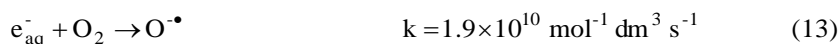
**Fig. 6.** Pseudo- First order plot of dye degradation using persulfate and gamma radiations.

In the radiolysis of water the transients and products are e<sup>-</sup><sub>aq</sub>, H<sub>3</sub>O<sup>+</sup>, H<sup>•</sup>, H<sub>2</sub>, and H<sub>2</sub>O<sub>2</sub>



The products formed in radiolysis of water are extremely reactive and disappear in very fast self termination reactions in ultra pure water. However, in the presence of proper solutes in the solution like dye molecules, they readily react with these compounds [11].

In practical systems O<sub>2</sub> is always present, with a molar concentration of 0.25 mmol/dm<sup>3</sup> at room temperature. It reacts with e<sup>-</sup><sub>aq</sub> and H<sup>•</sup> rapidly to form superoxide radical anion (O<sup>2•-</sup>) or perhydroxyl radical (HO<sup>2•</sup>) in reactions 13 and 14.



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The hydrogen peroxide formed in water decomposition and also in the reaction of two superoxide radical anion / perhydroxyl radicals under certain conditions play an important role in the degradation of dye molecules. The iron ions present in aqueous solutions during irradiation may induce Fenton reactions since in the direct decomposition of water and in the presence of dissolved oxygen in the self termination reactions of the  $O_2^{\bullet-}/HO_2^{\bullet}$  radicals hydrogen peroxide is constantly formed in the system as shown in equations 15-17.  $Fe^{2+}/Fe^{3+}$  ions react with  $H_2O_2$  and  $HO_2^{\bullet}$  and forms  $HO^{\bullet}$  radicals. These  $HO^{\bullet}$  radicals accelerate the decomposition of the dye.



MV showed maximum absorption at four peaks (206, 250, 305 and 582 nm). The peaks at 305 and 582 nm were prominent. The former absorption was considered to be of substituted aromatic rings and the latter can be assigned to the conjugated system of the dye molecule. After irradiation the intensity of the peak at 582 nm decreased. The peak intensity in the visible region decreased in presence of PS/ $Fe^{2+}$  at zero minutes of gamma irradiation while the peak intensity at the UV region hardly showed a difference. After 10 minutes of gamma irradiation the intensity of the visible region decreased further but the peaks at UV region merged and were still seen. After 20 minutes of gamma irradiation both the intensities of visible and UV region diminished (Fig. 7). The intensity in the UV region is due to the presence of aromatic rings in the dye molecule which is hard to degrade. The further decrease in the intensity is due to the destruction of the aromatic rings of the dye molecules due to radicals formed from radiolysis of aqueous solutions

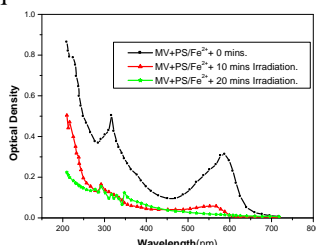


Fig. 7. Absorption spectra of MV in presence of persulfate and gamma radiations; [Gamma radiation dose rate = 0.5418 kGyh<sup>-1</sup>].

The degradation product if any were analysed by HPLC. With increase in the time of irradiation the intensity of the MV peak decreased but after 20 minutes of irradiation although the main peak diminished no additional peaks were obtained (Fig. 8). It was however not feasible for us to separate the degradation products by HPLC.

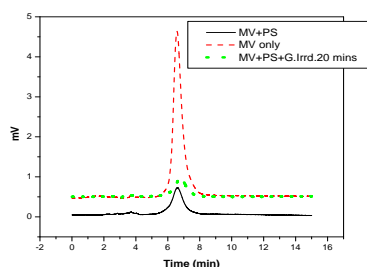


Fig. 8. HPLC chromatogram of MV dye.

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## IV. CONCLUSIONS

The degradation of MV using PS activated by  $\text{Fe}^{2+}$  and gamma irradiation was found to be feasible. The decolouration efficiency of the aqueous dye solution showed dependence in change of pH, initial concentration of dye, PS and gamma radiation dose. 61.95% degradation was achieved for a gamma dose of 0.078 kGy whereas, 82.5% degradation was achieved at a gamma dose of 0.078 kGy in presence of PS. The study reveals that the combining effect of PS and gamma radiation significantly increases the rate of reaction. These results are quite interesting for no sludge disposal and maximum decolouration was obtained in lesser time at very low doses of both oxidant and gamma radiations.

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