Kinetic Studies on Decolourization of Amaranth Dye by Solar/H$_2$O$_2$ Process

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ABSTRACT

Decolourisation of Anionic cum acidic azo dye Amaranth was carried out by an Advanced Oxidation Process Solar/H$_2$O$_2$. Dye samples of concentration 100 mg/L was taken in 250 mL conical flasks that were treated with 30% H$_2$O$_2$ and exposed to sun light in the intensity range of 60,000-90,000 lux. The impact of various parameters in decolourisation of dye like initial H$_2$O$_2$ concentration, initial dye concentration, initial pH, solar light intensity, additives and temperature was studied in view of kinetics. All the reactions carried out by the impact of system parameters follow pseudo-first order kinetics. Conditions were optimized, and the optimum pH was found to be 12 with an optimum H$_2$O$_2$ concentration of 650 mM to achieve 100% decolourization in 30 minutes. Impact of additives can be studied by adding chloride and dihydrogen phosphate ion of 1 M concentration. Then, mineralization is studied by COD removal. UV-Visible spectrometric analysis is done to study degradation level.

Keywords: Azo dye, Solar light assisted photodegradation, AOP, Advanced Oxidation Processes.

INTRODUCTION

Nowadays, there is an increase in the entry of many xenobiotic compounds into the environment because of the increase in production and usage of chemicals in various industries. Dyes are one of those xenobiotic chemical compounds which are required by various chemical-based industries like textiles, paints, food industries, cosmetics, plastics, pharmaceuticals, electronics, paper production, coloring solvents, inks, varnishes, drugs, and leather industries[1-5].

Dyes are chemical compounds with complex aromatic structures, and most of them are highly soluble in water[6]. Among them, synthetic azo dyes are found to be the most commonly used commercial textile dyes as they are reported to constitute about 30-40% of the total use. As of now,

we know more than two thousand azo dyes[5]. They can be identified by the azo groups (-N=N-) that are joined to two organic substituents[7].

Textile industries are one that release wastewater that is the significant source of entry of dyes into the environment[7-9]. A substantial amount of dye is lost in water during the dyeing process, and it is estimated to be around 1-20% of the world's dye production[2,4]. As a result, the textile industry becomes the largest consumer of water, and consequently, it produces a large amount of wastewater leads to water pollution[3-5,7,9,10].

Due to the presence of colour producing dyes and other chemicals textile industry wastewaters are distinguished by high TOC and COD values and their release into the aquatic environment affects the photosynthetic activity of aquatic plants and also causes environmental issues like eutrophication and aesthetic pollution[11]. Due to the complex structure, reactive azo dyes are non-biodegradable and toxic in a few kinds, mutagenic and carcinogenic, since their products, like amines after the breakdown, have also been found toxic to aquatic lives[2-4,9-12].

Hence, they become a significant concern for shielding the water environment. Hence it is essential from the ecological perspective to remove such dyes from textile industrial wastewater & to treat them so that they do not have any adverse impacts on the environment into which they are released[1,6,9].

The treatments of such organic dyes in wastewater are broadly classified into three types as physical, chemical, and biological treatment methods[1,11,13]. The most frequently used physical methods are ultrafiltration and adsorption on activated carbon. The most frequently used chemical methods are coagulation, RO and electrocoagulation. Each method has its own drawbacks[3-5,7,11,12]. The treatments such as Aerobic biological treatment and other similar techniques are not enough in breaking down the double bonds of reactive azo dyes[14]. The coagulation process only absorbs them up to some extent, and then the sludge formed from both coagulation and biological processes becomes more problematic to be disposed of[9-11,15]. The above discussed conventional treatment processes are not effective in achieving the complete mineralization of azo dyes. Thus, the elimination or removal of dyes

becomes a new challenge[3]. Therefore it is necessary to treat these dyes with appropriate methods.

Advanced Oxidation Processes are found to be suitable alternative methods to conventional water treatment processes, as they can decolourise, degrade dyes and other organic water contaminants completely[9,12,13]. They are characterized by high efficiency, low cost, and simplicity.[9]

Among AOPs, using Hydrogen peroxide in Ultra Violet radiation is a competent method[11]. It involves the generation of hydroxyl radicals, which are the most powerful oxidising species after fluorine, that quickly and effectively oxidize a wide range of organic pollutants[1,4,5,7-9,13,14].

The several advantages of UV/H_2O_2 treatment are the development of no sludge in the treatment and oxygen formation in the process, which is convenient for other aerobic biological decay processes. Simpler molecules like water, carbon dioxide and simple aliphatic carboxylic acids are obtained as final products by the process[5,7,8,11]. The usage of H_2O_2 has some advantages such as its complete miscibility with water, its commercial availability, no phase transfer problems, and lower investment costs. As a result, H_2O_2 becomes an environmentally friendly bleaching agent in all kind of industrial wastewater treatments[8,16].

This work's main objective is to use H_2O_2 as an oxidizer in presence of sun light for decolourisation of Amaranth dye without usage of any solid catalyst like TiO_2, MnO_2 and study the degradation in view of kinetics and effects of various system parameters[16]. The investigational work defined here assesses the photodegradation of model azo dye Amaranth. Usage of solar radiation and H_2O_2 without an artificial UV source is also an advantage as solar radiation is abundant in tropical countries like India[4].

Amaranth is a synthetically prepared azo dye that is dark red to purple. It is extensively used in the food and cosmetic industries as the significant coloring agent in cakes and jams[1,14]. It is also used in dyeing and colour photography[2]. Its usage is banned in many countries due to its toxic nature[1]. It is suspected to be carcinogenic and may cause a skin rash. It is recommended to avoid it for people who suffer from asthma or aspirin intolerance[2].

MATERIALS AND METHODS

Materials required

Spectrum Private Limited provided the amaranth dye, which was utilized without additional purification.

Experimental procedure

Deionized water was used to prepare amaranth dye solution of 100 mg/L concentration. 250 mL conical flasks were used to prepare the solution that were treated with 30 mL of 30% H_2O_2, which has 264 mM concentration, and then exposed to sun light with an average intensity of 60,000 to 90,000 lux. The lux meter of model UA 1010B was used to measure the intensity of sun light. Using a digital Spectrophotometer of type Shimadzu1800, the change in the absorbance values of the amaranth dye solution was determined to evidence decolourization.

The UV-Visible spectrometric analysis for dye solutions before and after degradation was also done as a part of the evidence for degradation.

The studies on impact of pH on decolourization of Amaranth was done by treating it with HCl, Citrate buffer, NaOH, Glycine buffer, Phosphate buffer, etc., each of which is of 0.1 M concentration. Dye solution in its own pH was also examined. All the studies were carried out in dye solution of concentration 100 mg/L treated with 30 mL of 30% H_2O_2, which is of concentration 264 mM. pH ranges from 2-10, and were used for the study. pH was measured by using digital pH meter of model AI-102. After studying the impact of pH in acidic, basic, and neutral conditions, pH was further optimized in basic pH by treating the dye solution with different volumes and different NaOH concentrations in the range 8-12 as its decolourization is more effective in basic pH.

Amaranth was treated with various doses of H_2O_2 ranging from 100mM to 1000mM at its optimal pH with dye concentration of 100 mg/L to analyze the impact of H_2O_2 concentration on the decolourization. Amaranth was treated with various dye concentrations ranging from 50 mg/L to 500 mg/L in its optimal pH and optimal H_2O_2 concentration to study the impact of dye concentration on decolourization.

The impact of additives like chloride and dihydrogen phosphate ion on the decolourization of Amaranth dye of 100 mg/L concentration was studied by treating them in concentration of 1 M in its optimal pH and optimal H_2O_2 concentration.

The impact of solar light intensities on the decolourization of Amaranth dye of 100 mg/L concentration was studied by treating it with different solar light intensities in its optimal pH and optimal H_2O_2 concentration.

Amaranth dye of 100 mg/L concentration was subjected to decolourisation at various temperatures while being maintained at its optimal pH and optimal H_2O_2 concentration.

Analytical methods

COD of Amaranth dye before and after degradation by Solar/H_2O_2 treatment was measured by acid digestion titration method and its reduction is accounted for mineralization.

Kinetic studies on the impact of initial pH, initial H_2O_2 concentration, initial dye concentration, additives, solar light intensity, and temperature can be done by studying its decolourization at certain time intervals by the decrease in its color. Regarding the dye concentration, the reaction is shown to be of pseudo-first order, which is,

$$ln[A_t]-ln[A_0]= -kt \qquad (1)$$

in which
k = rate constant of First order
t = Irradiation time
A_0 = Initial absorbance value before the start of the decolourization reaction
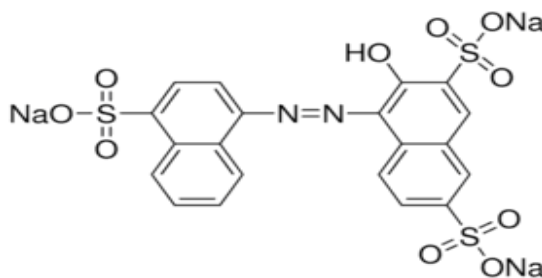A_t = Absorbance value at time t after the start of the decolourization reaction.[17]

Fig. 1. Structure of Amaranth

RESULTS AND DISCUSSION

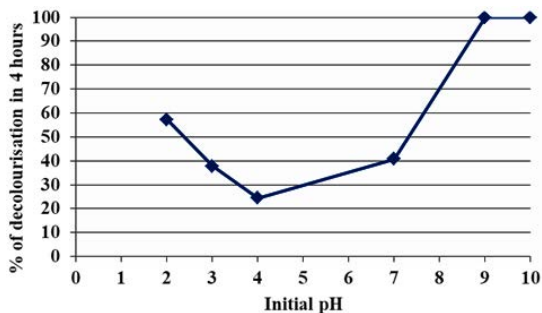### Impact of initial pH on decolourisation of dye

Fig. 2. Impact of initial pH on decolourization of Amaranth dye solution: Dye concentration = 100 mg/L, H_2O_2 concentration = 264 mM, pH range = 2 to 10
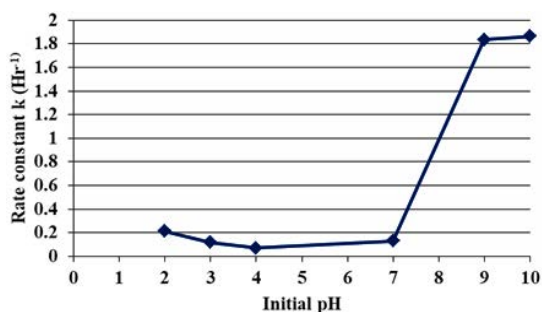

Fig. 3. Kinetic studies on impact of initial pH on decolourization of Amaranth dye solution: Dye concentration = 100 mg/L, H_2O_2 concentration = 264 mM, pH range = 2 to 10

Decolourization of azo dye Amaranth in different pH 2,3,7,9 and 10 was studied by treating it with HCl, citrate buffer, phosphate buffer, glycine buffer. Its decolourization in its own pH 4 was also studied.

It was evidenced that the decolourization in acidic pH 2 was only 57.24%. When pH was increased to 3, it was decreased to 37.82%, and when pH was increased to 4, it was further decreased to 24.5%. In neutral pH 7 decolourization was increased to 40.79%. In basic pH 9 decolourization was increased to 100%. On further increasing pH to 10, decolourization was maintained at 100%. Kinetic studies on the impact of pH have also provided evidence for that. The rate constants calculated for the decolourization reaction in the corresponding pH of 9, and 10 were maximum. Hence it was concluded that maximum decolourization was observed in basic pH of 9 and 10. So it was necessary to further optimize the basic pH from the range 8 to 12.

Decolourization of Amaranth was lower in acidic pH of 2, 3, and 4, and neutral pH of 7 was because of the following reasons:

At pH 7, H_2O_2 dissociated into the water and oxygen other than forming hydroxyl radical. Hence there will be very low concentration of hydroxyl radicals for attacking the molecules of dye, which results in lower decolourization[18,19].

$$2H_2O_2 \longrightarrow 2H_2 + O_2 \qquad (2)$$
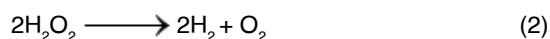
At pH 3 there was an increase in the concentration of hydroperoxy anions formed from H_2O_2. Hydroperoxy anion, a conjugate base of H_2O_2 reacts with H_2O_2 and reduces the generation of hydroxyl radicals results in lower decolourization[19].

$$H_2O_2 + HO_2^- \longrightarrow H_2O + O_2 + OH^· \qquad (3)$$

$$OH^· + HO_2^- \longrightarrow H_2O + O_2^- \qquad (4)$$
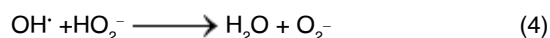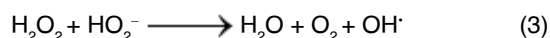
In acidic pH of 2 obtained by the addition of HCl to the dye solution, the concentration of the HCl's conjugate base, increases, which reacts with radicals, leading to inorganic radicals ions according to the following equation.

$$Cl^- + OH^· \longrightarrow ClO^·H \qquad (5)$$

These radical ions show a much lower reactivity than hydroxyl radicals. It leads to a decrease in dye decolourization as there arises a rivalry among the anions and dye concerning reaction with hydroxyl radicals[18,20].

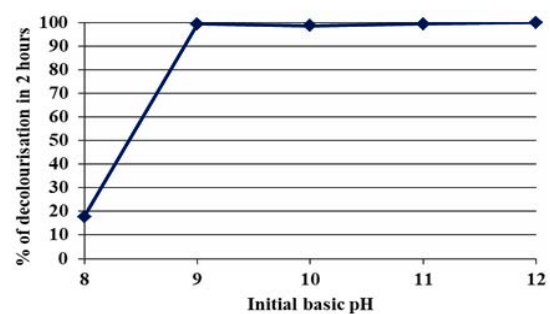### Impact of initial basic pH on decolourisation of dye

Fig. 4. Impact of initial basic pH on decolourization of Amaranth dye solution. Dye concentration = 100 mg/L, H_2O_2 concentration = 264 mM, pH range = 8 to 12
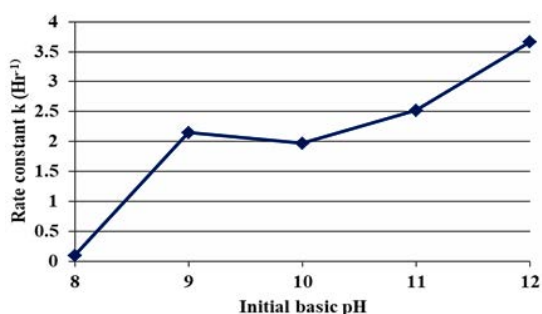
Fig. 5. Kinetics on impact of initial basic pH on decolourization of Amaranth dye solution. Dye concentration = 100 mg/L, H_2O_2 concentration = 264 mM, pH range = 8 to 12

On further optimizing the pH for decolourization of azo dye Amaranth in primary condition, it was treated with different NaOH concentrations to get pH ranges from 8 to 12. It was observed that the decolourization was increased from 17.81% to 99.29% on increasing pH from 8 to 9. Decolourization was decreased to 98.66% on further increasing pH from 9 to 10. The decolourization was increased from 98.66 to 99.36% on increasing pH from 10 to 11. The decolourization reached the maximum extent of 100% when pH was increased from 11 to 12. Hence it was concluded that 12 was the optimal pH for decolourization of the dye.

Kinetic studies also proved that. The rate constant calculated for the corresponding pH 12 for decolourization reaction was the maximum.

Tanja Kurbus *et al.,* have reported similar results in the treatment of vinyl sulphone dyes by UV/H_2O_2 as all of them had their decolourization in basic pH of 12. A. Riga *et al.,* have reported in the case of degradation of Procion H-excl dyes by UV/H_2O_2. Also, the degradation of dyes took place effectively in basic pH of 12 and above. Abbas Rezaee *et al.,* have also reported the same result in reactive blue 19 by UV/H_2O_2, which had its effective degradation in basic pH of 11[21-23].

In basic medium, there is an increase in the concentration of the formation of the conjugate base of H_2O_2, HO_2^-. HO_2^- absorbs solar radiation more powerfully than the H_2O_2, leading to a rise in the concentration of OH. radicals, resulting in a higher decolourization reaction[18].

$$H_2O_2 \longrightarrow HO_2^- + H^+ \tag{6}$$

$$HO_2^- + H^+ + hv \longrightarrow 2OH^* \tag{7}$$
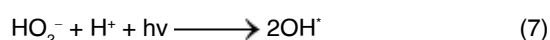
Impact of H_2O_2 concentration on decolourisation of dye
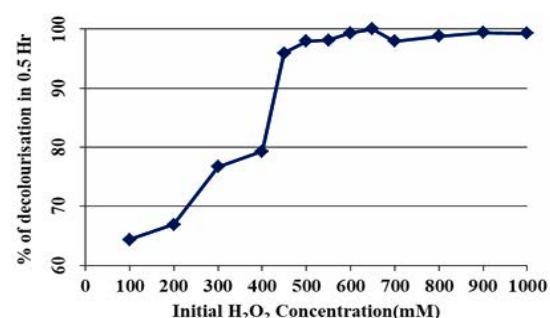

Fig. 6. The impact of initial H_2O_2 concentration on decolourization of Amaranth dye. Dye concentration = 100 mg/L, H_2O_2 concentration range = 100 mM to 1000 mM, optimal pH = 12

Fig. 7. Kinetic studies on impact of initial H_2O_2 concentration on decolourization of Amaranth dye. Dye concentration = 100 mg/L, H_2O_2 concentration range = 100 mM to 1000 mM, optimal pH = 12
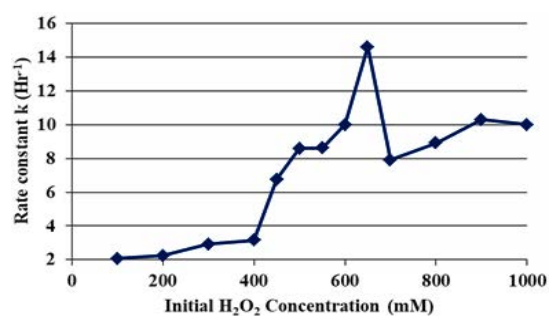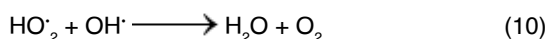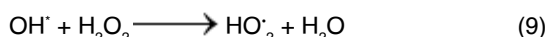
A dye solution with a concentration of 100 mg/L was treated with various concentrations of H_2O_2 ranging from 100 mM to 1000 mM in its optimal pH 12 to study the impact of initial H_2O_2 concentration on decolourization of the dye. It was found that 100% decolourization was achieved in the shortest time duration of 0.5 h (30 min) in the H_2O_2 concentration of 650mM. Rate constants calculated based on Pseudo-first order kinetics also proved that. Hence it was concluded that 650mM was the optimized concentration of H_2O_2.

The lower rate of decolourization of Amaranth dye below and above the optimized concentration of 650mM was attributed to the following reasons:

H_2O_2 produces hydroxyl radicals on photolysis reaction that takes place in presence of solar radiations. The radicals formed by the reaction react with excess of H_2O_2 molecules that forms oxygen and water. Therefore, it leads to lower availability of hydroxyl radicals. Hence the probability of reaction of hydroxyl radicals with dye molecules to degrade them becomes very low. Therefore in a higher concentration of H_2O_2, the decolourization rate was low[18,24-26].

$$H_2O_2 + hv \longrightarrow OH^\cdot \qquad (8)$$

$$OH^\cdot + H_2O_2 \longrightarrow HO_2^\cdot + H_2O \qquad (9)$$

$$HO_2^\cdot + OH^\cdot \longrightarrow H_2O + O_2 \qquad (10)$$

The generation of hydroxyl radicals was also reduced when H_2O_2 concentration was decreased. Due to the high concentration of dye molecules, there was an extremely low concentration of hydroxyl radicals to react with and destroy them[18,24–26].

Similar results have been reported by A. Riga *et al.,* in the case of Procion H-excl dyes which were treated by $TiO_2/UV/H_2O_2$, Xuanmo Liu in the case of Reactive Black 5 dye treated by Fenton and Fenton-like system, Reza Marandi *et al.,* in the case of Reactive Black B dye treated by UV/H_2O_2/biosorbent system, Hang Xu *et al.,* in case of Reactive Red SBE treated by Fenton process, Azam Aleboyeh *et al.,* in case of Acid Blue 74 treated by UV/H_2O_2 process, Fatima H. Al Hamedi *et al.,* in case of Rhodamine B treated by UV/H_2O_2 process, Silvia Gabriela Schrank *et al.,* in case of Vat Green 01 dye treated by UV/H_2O_2 process, Raja *et al.,* in case of Reactive Red-180 by solar/H_2O_2 process, etc.,[17,18,20,22,24,26-28]

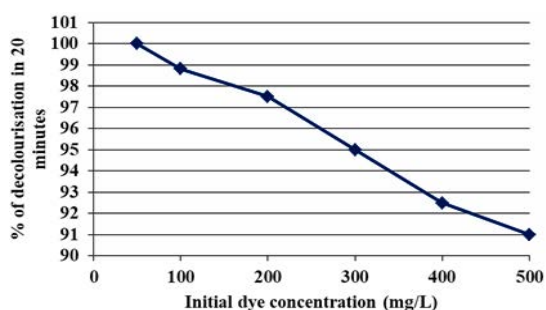**Impact of initial dye concentration on decolourisation of dye**

Fig. 8. The impact of initial dye concentration on decolourization of Amaranth dye: Dye concentration range = 50 mg/L to 500 mg/L concentrations, optimal H_2O_2 concentration = 650 mM, optimal pH = 12
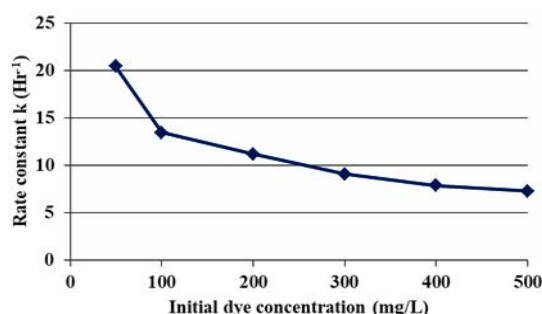

Fig. 9. Kinetic studies on impact of initial dye concentration on decolourization of Amaranth dye: Dye concentration range = 50 mg/L to 500 mg/L concentrations, optimal H_2O_2 concentration = 650 mM, optimal pH = 12

Treatment of various dye solution concentrations ranging from 50 mg/L to 500 mg/L with the optimal H_2O_2 concentration of 650mM at the optimal pH 12 was done to examine the impact of initial dye concentration on the decolourization of Amaranth. It was found that when dye concentration increases, the percentage of decolourization decreases. That was also evidenced by the rate constants determined by Pseudo-first kinetic studies.

The rate of decolourization of Amaranth dye decreases with an increase in dye concentration. It may be because of the following reasons:

The internal absorbance increased as the dye concentration increased, making the dye solution increasingly resistant to solar rays. However, only a specific fraction of the H_2O_2 in the reaction mixture can be irradiated, which reduces the amount of hydroxyl radicals that are produced. As a result, there was no enough concentration of hydroxyl radicals to react with the surplus dye molecules as the concentration of the dye solution increased and breakdown them. Additionally, the concentration of intermediate molecules, which include highly reactive free radicals, rises. Competition for the ability of dye molecules and intermediate compounds to react with hydroxyl radicals increases. It reduced the bleaching impact of H_2O_2, which results in a slower rate of decolourization in dye solutions with increasing concentrations[19,24,26,29].

Similar results have been reported by M. Muruganandham *et al.,* in the case of Reactive Yellow 14 treated by UV/H_2O_2, Xuanmo Li *et al.,* in the case of Reactive Black 5 treated by Fenton and Fenton like system, Hideyuki Katsumata *et al.,* in the case of Reactive Yellow 86 treated by the solar-assisted photo-Fenton process, Montaser

Y. Ghaly *et al.,* in the case of Maxoline Navy 2 RM 200% basic dye treated by solar/TiO_2 process, Amrit Pal Toor *et al.,* in the case of Direct Yellow 12 dye treated by UV/TiO_2 process, Hang Xu *et al.,* in the case of Reactive Black B dye treated by UV/H_2O_2/biosorbent system, B. Neppolian *et al.,* in case of Reactive Yellow 17, Reactive Red 2, Reactive Blue 4 treated by UV/TiO_2 process, Hang Xu *et al.,* in case of Reactive Red SBE treated by Fenton process, Azam Aleboyeh *et al.,* in case of Acid Blue 74 treated by UV/H_2O_2, Fatima. H. Alhamedi *et al.,* in case of Rhodamine B treated by UV/H_2O_2, Raja *et al.,* in case of decolourization of Reactive Red 180 dye by solar/H_2O_2, etc.,[17-19,25-31].

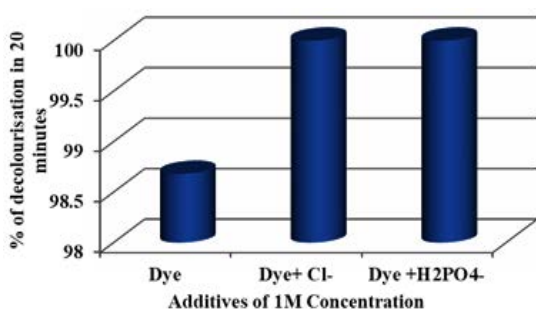## Impact of additives on decolourisation of dye

Fig. 10. Impact of additives on decolourization of Amaranth: Reaction conditions: (i) Dye solution concentration = 100 mg/L, optimal H_2O_2 concentration= 650 mM, optimal pH = 12. (ii) Dye solution concentration = 100 mg/L, optimal H_2O_2 concentration = 650mM, optimal pH = 12, Chloride ion =1 M concentration (iii) Dye solution concentration = 100 mg/L, optimal H_2O_2 concentration = 650mM, optimal pH = 12, Dihydrogen phosphate ion = 1 M concentration
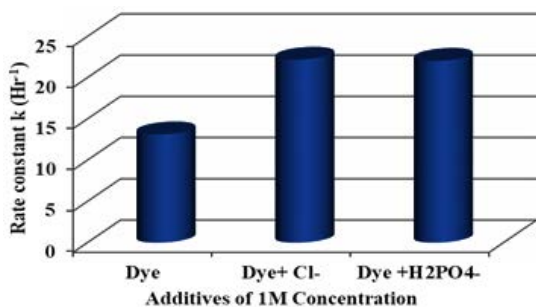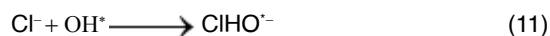

Fig. 11. Kinetic studies on impact of additives on decolourization of Amaranth: Reaction conditions: (i) Dye solution concentration = 100 mg/L, optimal H_2O_2 concentration = 650 mM, optimal pH = 12. (ii) Dye solution concentration = 100 mg/L, optimal H_2O_2 concentration = 650mM, optimal pH = 12, Chloride ion = 1 M concentration (iii) Dye solution concentration = 100 mg/L, optimal H_2O_2 concentration = 650 mM, optimal pH = 12, Dihydrogen phosphate ion = 1 M concentration

Amaranth dye with concentration of 100 mg/L in the optimal pH 12 and optimal H_2O_2 concentration of 650mM was treated with additives such as chloride and dihydrogen phosphate of concentration of 1 M to evaluate the impact of them in the decolourization of the dye.

It was observed that both the Chloride ion and Dihydrogen phosphate ion has an enhancement impact on decolourization. The decolourization of dye alone in 20 min time duration was only 98.68%, whereas 100% decolourization was achieved by adding Chloride ion and Dihydrogen phosphate ion of 1 M concentration. The rate constants calculated based on kinetic studies also proved that.

In high concentrations like 1 M of Chloride ion, intermediate radical ions may dissociate to form hydroxyl radical, which readily attacks the dye molecules, leading to an increase in dye decolourization reaction, which was not possible in low concentrations like 0.001 M, 0.1 M[32].

$$Cl^- + OH^\bullet \longrightarrow ClHO^{\bullet-} \qquad (11)$$

$$ClHO^{\bullet-} \longrightarrow Cl^- + OH^\bullet \qquad (12)$$

$$H_2PO_4^- + OH^\bullet \longrightarrow HPO_4^- + H_2O \qquad (13)$$

Dihydrogen phosphate ion reacts with hydroxyl radical to form intermediate radical ion which acts as radical scavengers. It actually leads to inhibition in decolourization reaction. Similar results were obtained in case of Xiang-Rong Xu *et al.,* in case of Orange G degradation by persulphate/Fe^{2+} process and Miljina D. Radovic *et al.,* in case of decolourization of Reactive Blue 19 by UV/H_2O_2 process[32,33]. But the results obtained show that there was an enhancement in decolourization of Amaranth dye instead of inhibition in decolourization. It may be attributed due to the following reason.

The inhibition impact in decolourization reaction of any dye by both Chloride ion and Dihydrogen phosphate ion occurs in acidic medium and neutral medium. But decolourization of Amaranth took place in a basic medium, and the enhancement by both the ions may be attributed to the fact that generation of more number of hydroxyl radicals from H_2O_2 in a basic medium, which also observed by Alnuaimi *et al.,* in the case of decolourization of Neutral Red by Photocatalytic TiO_2 process[34]. Similar results were obtained

by Jiangang Qu *et al.,* in the case of Reactive Black 5 dye degraded by UV/H_2O_2 and Taha M. Elmorsi *et al.,* in the case of Mordant red 73 azo dye degraded by UV/H_2O_2, which had also had its increase in photodegradation which contains NaCl as an additive in the concentration above 0.2 M.[35,36]

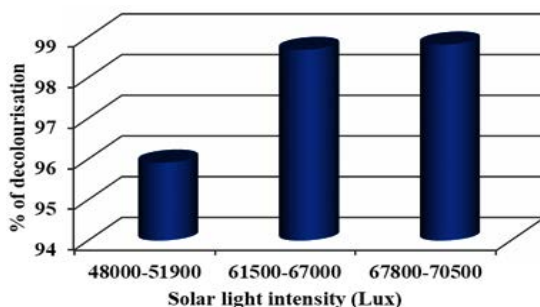**Impact of solar light intensity on decolourisation of the dye**

Fig. 12. Impact of solar light intensity on decolourization of Amaranth: Reaction conditions: Dye solution concentration = 100 mg/L, optimal H_2O_2 concentration = 650 mM, optimal pH = 12, solar light intensity range = 48000-70500
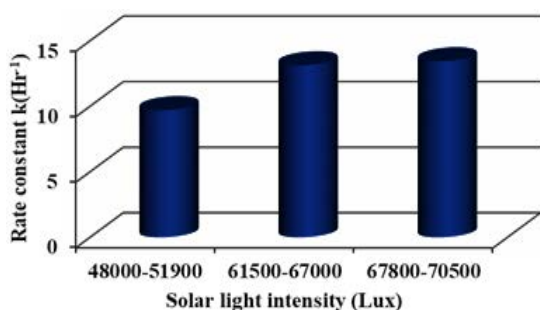

Fig. 13. Kinetic studies on impact of solar light intensity on decolourization of Amaranth: Reaction conditions: Dye solution concentration = 100 mg/L, optimal H_2O_2 concentration = 650 mM, optimal pH = 12, solar light intensity range = 48000-70500

By comparing the percentage of decolourization of the dye at a concentration of 100 mg/L in various solar light intensities with an optimised concentration of H_2O_2 at 650mM and the optimal pH 12, the influence of solar light intensity on decolourization of Amaranth was explored. It was found that an increase in solar light intensity caused an increase in the decolourisation of Amaranth. That was also evidenced by rate constants derived from Pseudo-first order kinetic investigations.

Similar results were observed by M. Muruganandham et al. in Reactive Yellow 14 treated by the solar/H_2O_2 method[19].

The increased generation of hydroxyl radicals causes the dye to decolorize more frequently. The quantity of photons absorbed by the H_2O_2 molecules depends on the intensity of the solar light. H_2O_2 molecules absorb more photons when the intensity of sun light rises, increasing the amount of hydroxyl radicals. The photolysis of H_2O_2 in solar/H_2O_2 is a direct function of incident light intensity. At low intensity, photolysis of H_2O_2 produces less hydroxyl radicals, which results in less decolourization, whereas at high intensity, photolysis of H_2O_2 produces more hydroxyl radicals, which results in more decolourization. All of the photons produced were efficiently employed because it appears that the solar power tested is in the linear range[19,29].
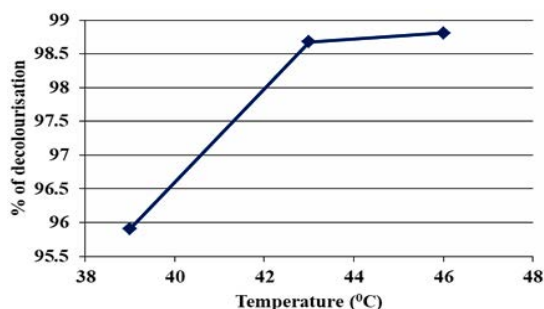
Impact of temperature

Fig. 14. Impact of temperature on decolourization of Amaranth: Reaction conditions: Dye solution concentration = 100 mg/L, optimal H_2O_2 concentration = 650mM, optimal pH = 12, Temperature range = 38-46^{0}C
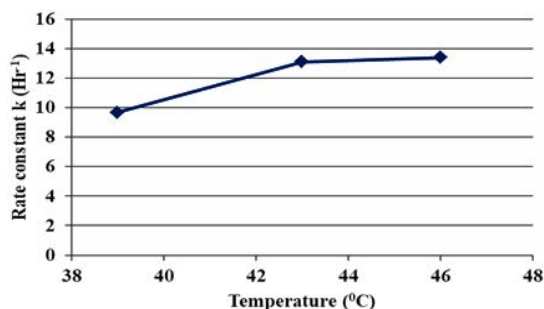

Fig. 15. Kinetic studies on impact of temperature on decolourization of Amaranth: Reaction conditions: Dye solution concentration =100 mg/L, optimal H_2O_2 concentration = 650 mM, optimal pH = 12, Temperature range = 38-46^{0}C

By comparing the percentage of decolourization of the dye at a concentration of 100 mg/L in different temperatures with the optimal concentration of H_2O_2 of 650mM at the optimal pH 12, the impact of temperature on decolourization of amaranth was studied.

It was found that the increase in temperature has led to an increase in the decolourization percentage of Amaranth. Rate constants calculated based on kinetic studies also proved that.

It can be explained on the basis that the decolourisation reaction induced by increase in temperature which leads to an increase in the generation of hydroxyl radicals. Therefore, it enhances the degradation of the dye. This phenomenon can be explained as on increasing temperature up to a certain extent (i.e.) up to 50°C it increases dissociation of H_2O_2 in the solar-assisted photodegradation process which leads to the generation of more number of hydroxyl radicals. But above 50°C dye degradation decreases because of the decrease in the concentration of Dissolved Oxygen and spontaneous decomposition of hydrogen peroxide into water and oxygen in the dye solution reaction mixture.

Similar results were obtained by Meric *et al.,* in the case of decolourization of Remazol Red dye treated by Fenton process[10] and Pare *et al.,* in the case of degradation of Neutral Red by Visible light/ZnO in which 45°C was found at the optimum temperature, in case of decolourization of Reactive Red 120 dye treated by UV/H_2O_2 by Mansoorian *et al.,* and in case of decolourization of Reactive Blue 19 and Reactive Red 198 treated by Fenton and revised Fenton methods by Rishi Ananth Shankar *et al.,*[37-39]
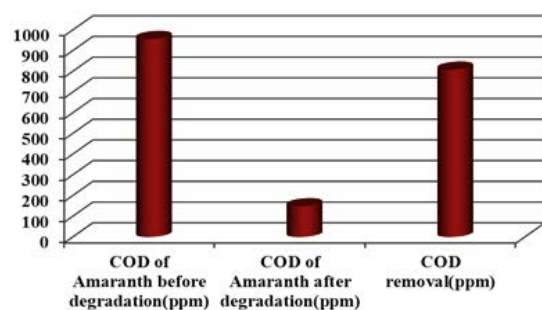
COD removal

Fig. 16. COD values of Amaranth dye before and after degradation: Reaction conditions: Dye solution concentration = 100 mg/l, optimal H_2O_2 concentration = 650 mM, optimal pH = 12

The COD values denote the quantity of oxygen needed for oxidation of substances present in the sample completely by chemical means. The COD values will depend on the dye's initial concentration, chemical structure, and decolourization time. The COD value of Amaranth dye before degradation was 956 ppm and reduced to 148ppm after degradation. Hence the COD removal was 84.52%, and it was observed that oxidation was done virtually[21].

It is known that complete mineralization of a dye does not mean that it is completely decomposed into smaller and simpler molecules like CO_2, H_2O, etc.; there may be some longer-lived reaction intermediates in the degraded and mineralized product. The obtained results were found to be satisfactory and mineralization done by solar/H_2O_2 occurred effectively. Thus, it was concluded that solar light was more effective in generating hydroxyl radicals by the photolysis process of H_2O_2. It also activates the bonds of organic molecules to degrade further[21].

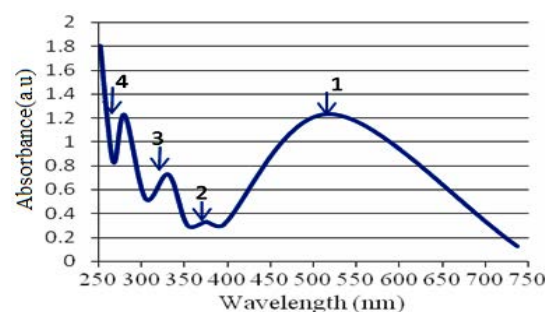**UV-Visible spectrometric analysis**

Fig. 17. UV-Visible spectrum of Amaranth dye: Before degradation by Solar/H_2O_2 treatment
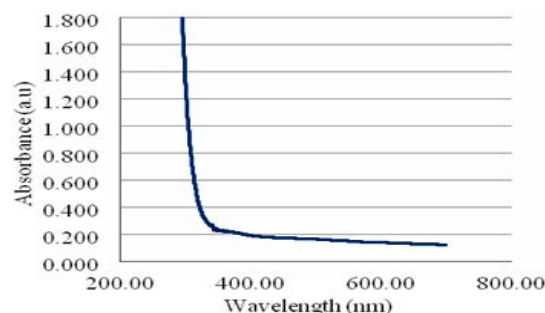

Fig. 18. UV-Visible spectrum of Amaranth dye: After degradation by Solar/H_2O_2 treatment

The UV-Visible spectrum of Amaranth dye shows four absorption peaks at 521nm, 375nm,

331nm, and 279nm respectively. Peak at 521nm corresponds to the Azo group and peaks at 375 nm, 331nm and 279nm correspond to aromatic groups like alcohol, naphthalene, sulphonic acid, etc.,after the treatment by solar/H_2O_2 process, the spectrum shows no absorption peak at all. Hence we conclude that the degradation of Amaranth dye was done effectively.

Rashmi Padhye observed similar biodegradation of Amaranth by the Ligninolytic culture of Phanerochaete Chrysosporium and Eric da Cruz Severo al the case of Amaranth degradation through the photo-Fenton process of heterogeneous by $FeWO_4$ catalyst prepared through microwave irradiation[2,14].

CONCLUSION

This solar-assisted photodegradation process using H_2O_2, also known as solar/H_2O_2, was proved to be an suitable method for decolourization of Amaranth dye of 100 mg/L concentration within the shortest period of 30 min completely with the optimum conditions of pH = 12 and H_2O_2

concentration of 650 mM. UV-Visible spectrometric analysis was provided as a piece of evidence for complete decolourization of dye. COD removal done by this method was also found to be 84.52%. Among the literature surveys done among degradation of Amaranth dye by various methods, it also proved that it was an efficient method as best results obtained among all those. This method's various advantages are also that it does not form any sludge as formed by Fenton and Photo-Fenton method. It does not form any suspension that has to filter after treatment as formed using TiO_2 and ZnO photocatalysts. It is not so harmful as ozone, which is toxic and not so costlier also uses UV light irradiation in combination with H_2O_2. Hence we can conclude that it is an effective method for the decolourisation and degradation of Azo dyes like Amaranth.

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