



## Decolourization of Congo Red Dye using Solar/H<sub>2</sub>O<sub>2</sub> Process

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The Congo red dye was decolourized by advanced oxidation process using solar/H<sub>2</sub>O<sub>2</sub> method and the effect of various parameters on decolourization like pH, H<sub>2</sub>O<sub>2</sub> concentration, dye concentration, solar light intensity, additives, COD and TOC removal studies and kinetic studies were investigated. The photodegradation process was done by exposing dye solutions with the concentration of 100 mg/L treated with 50% H<sub>2</sub>O<sub>2</sub> to sunlight with the lux intensity range of 60,000-90,000 lux. The best possible pH 2 with an optimal H<sub>2</sub>O<sub>2</sub> concentration of 1000 mM to achieve 100% decolourization within the period of 5 h. The kinetic studies done on H<sub>2</sub>O<sub>2</sub> concentration also proved that the high solar light intensity leads to higher decolourization and low solar light intensity leads to lesser decolourization. Addition of additives like H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and Cl<sup>-</sup> leads to a decrease in the rate of decolourization. The removal of COD and TOC removal was found to be 83.26% and 5.18%, respectively.

**Keywords:** Congo red dye, Solar/H<sub>2</sub>O<sub>2</sub>, Photodegradation process, Advanced oxidation processes, Decolourization.

### INTRODUCTION

In the modern world of digital and technological advancements, urbanizing the rural areas to industrialization leads to many job opportunities and became disaster for the environment. As industries generate industrial wastes and deploying its hazardous chemicals to water sources causing a polluted region. In particular, the textile industries produce more pollution by discharging the carcinogenic chemicals to the rivers, ponds and nearby agricultural areas [1,2]. Several factors will be considered while estimating the water contamination levels like colour intensity of dye, salt concentration and the main ingredients used in the textile industry are directly discharged into the water streams. This can be estimated by the biological oxygen demand (BOD) chemical oxygen demand (COD) values [1,3].

A range of nearly 42 groups of different dyes are available and majority of them are used in the textile industries are quite toxic and carcinogenic in nature. Among the variety of dyes,

majority of the azo dyes are commercially used containing the azo groups with two nitrogen [4,5]. Congo red is an azo type dye used for the diagnostics of the Sheela Flexner serotype 2a, commercial and staining of specimens and also used as an indicator in acid base titrations. In contrast, Congo red dye decomposes in water much slower than other dyes, so it is necessary to degrade the dye almost completely to prevent forming the toxic aromatic amines as degraded products [1,6,7]. In order to remove the dye, COD can be utilized as one of the factors for its degradation, with other treatment processes like coagulation, flocculation and adsorption. Generally, the physical/chemical process are considered as non-destructive modes of degradation as they possess lower efficiency. Employing the absorbent materials are not cost effective and can be processed only after the biological treatment of water [8]. On the other hand, biological processes are sustainable methods but not effective in decolourizing the desired effluents containing dyes [2,3].

Advanced oxidation processes (AOP) method is one of the best alternative ways to decolourize the dyes with the existing

methods as well as decompose the chromophores. In this method, solar light, UV light, ozone or Fenton's reagent can be employed in order to activate the H<sub>2</sub>O<sub>2</sub> and produce hydroxyl radicals. These hydroxyl radicals can also be produced from photolysis of H<sub>2</sub>O<sub>2</sub> on various organic compounds, even though it is not very selective by nature but they manage to degrade different recalcitrant compounds [1]. Hydroxyl radicals have a greater oxidation potential of 2.8 V than H<sub>2</sub>O<sub>2</sub>, which makes the decolourization more feasible [3]. In terms of degrading toxic substituents, AOPs are more potent than biological processes as they degrade the dye before the treatment and their versatility can be improved by hydroxyl radicals in several different ways [9].

Among the AOP methods, UV/H<sub>2</sub>O<sub>2</sub> method is found more effective as it transforms dyes into lesser complex structures enabling them to biodegradable more easily [6]. The obtained products after oxidation will be organic compounds with lower molecular weight leading them to decompose easily into water and carbon dioxide [5]. This method can also convert aromatic amines into harmless products [10]. Hydrogen peroxide is an environmentally adequate reagent for AOPs as used as bleaching agent in both domestic and industries [11]. Employing H<sub>2</sub>O<sub>2</sub> with UV or solar light can be advantageous in several ways as completely miscible with water and also cost effective method [12]. Moreover, employing the UV/H<sub>2</sub>O<sub>2</sub> will be a better choice for the treatment of dyes and textile industrial wastewater as it does not produce any sludge or require additional treatment process [5,13].

The usage of solar light instead of UV light in AOPs enabled the opportunity to minimize the usage of costly artificial light energy sources such as UV lamps requires high electrical power which is expensive and hazardous. Therefore, one can opt for natural solar energy, which is abundant in tropical country like India [9]. It has more advantages than the other methods of degradation, in which usage of reagents like Fenton will be limited which produces toxic sludge forcing to further disposal after treatment [14].

## EXPERIMENTAL

Congo Red dye was obtained from Spectrum and used as such without further purification.

**Experimental procedure:** Congo red dye solution of 100 mg/L concentration was prepared using double distilled water in 250 mL conical flasks treated with 30 mL of 50% H<sub>2</sub>O<sub>2</sub> (w/v) which is of concentration 526 mM. Dye solutions treated with H<sub>2</sub>O<sub>2</sub> were irradiated with sunlight in the lux intensity range of 60,000-90,000 lux. Lux intensity was measured using a lux meter of model UA 1010B. Decolourization was evidenced by measuring the change in absorbance values of Congo red dye solution using a digital photo colorimeter of model IR 506 C.

**pH studies:** The digital pH meter of model AI-102 was used to measure the pH. The effect of pH in decolourization was studied by adding HCl and NaOH to dye solution of a concentration of 100 mg/L treated with 30 mL of 50% H<sub>2</sub>O<sub>2</sub>. The pH was studied in the ranges 2, 7 and 9 by adding small amounts of HCl and NaOH of various concentrations to avoid the volume change [13].

The effect of H<sub>2</sub>O<sub>2</sub> concentration in decolourization was studied by treating dye solution of a concentration of 100 mg/L in optimized pH with various concentrations of H<sub>2</sub>O<sub>2</sub> ranging from 100 to 1200 mM. The effect of dye concentration in decolourization was studied by treating different concentrations of dye solution ranging from 50 mg/L to 500 mg/L in optimized pH and with optimized H<sub>2</sub>O<sub>2</sub> concentration. The effect of solar light intensity was investigated by comparing the decolourization percentage of dye solution in optimized conditions in high and low solar intensities. Effect of additives like H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and Cl<sup>-</sup> in decolourization was also studied.

**Analytical methods:** Chemical oxygen demand (COD) was measured by acid digestion method and total organic carbon (TOC) was measured by TOC-LIQUID method.

## RESULTS AND DISCUSSION

### Effect of various parameters on decolourization of Congo red

**Effect of pH:** The decolourization efficiency and reaction rate of decolourization can be strongly affected by pH [14]. The effect of pH on decolourization of Congo red dye was studied by mixing the dye solutions of concentration 100 mg/L treated with H<sub>2</sub>O<sub>2</sub> of concentration 526 mM (30 mL of 50% H<sub>2</sub>O<sub>2</sub> w/v) with small amount of HCl or NaOH to maintain in the pH range of 2, 7 and 9 and exposed it to sunlight. Decolourization was confirmed by observing the decrease in absorbance values, which was measured using photo colourimeter. It was observed that the rate of decolourization was a maximum of 100% in case of an acidic pH of 2 in 6 h. The rate of decolourization was a minimum of 54.13% in neutral pH of 7 in 10 h. In basic pH of 9, it was found to be 66.96% in 10 h (Fig. 1).

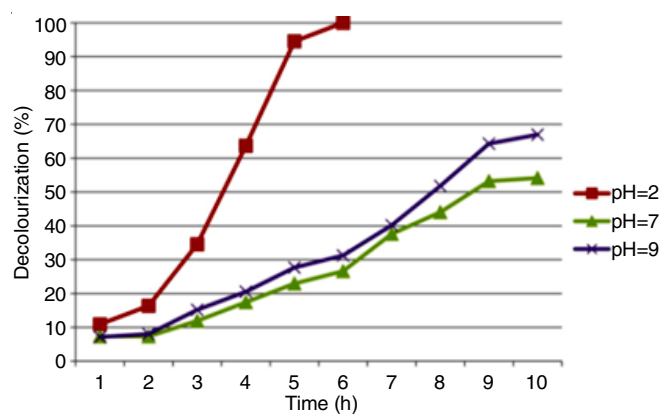


Fig. 1. Effect of pH on decolourization of Congo red dye (Reaction conditions: pH = 2, 7 and 9, [Dye] = 100 mg/L, [H<sub>2</sub>O<sub>2</sub>] = 526 mM)

It was observed that the rate of decolourization was more effective in acidic medium. The effect of pH in decolourization of Congo red dye in the range of 1 to 6 was studied by adding HCl of various concentrations. The rate of decolourization of dye was maximum at pH 2 (100% in 6 h). At pH 1, the rate of decolourization was slightly less than that of pH 2 (100% in 7 h). On increasing the pH to 3 and 4, the time taken for the decolourization was occurred even at longer time (100% in 13 h). On further increasing the pH to 5 and 6, the rate of decolouri-

zation was further longer time period (96.3% in 13 h for pH 5 and 69.15 in 13 h for pH 6) (Fig. 2). Thus, it was concluded that the optimum pH was 2.

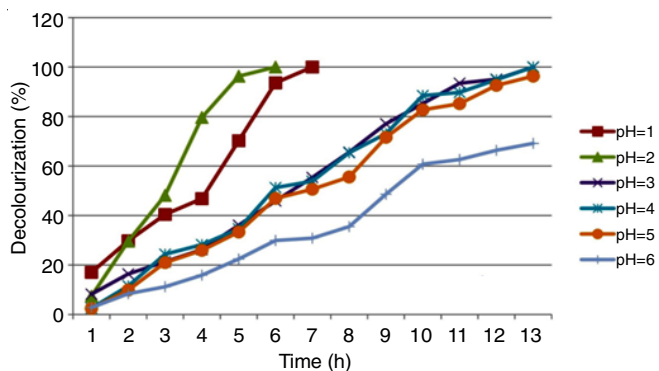


Fig. 2. Effect of acidic pH on decolorization of Congo red dye (Reaction conditions: pH = 1-6, [Dye] = 100 mg/L, [H<sub>2</sub>O<sub>2</sub>] = 526 mM)

**Effect of H<sub>2</sub>O<sub>2</sub> concentration:** Effect of H<sub>2</sub>O<sub>2</sub> concentration on the decolorization of Congo red dye was studied by treating dye solutions of concentration of 100 mg/L at the optimum pH 2 with different concentrations of H<sub>2</sub>O<sub>2</sub> from 100 to 1200 mM. It had been found that maximum decolorization of 100% in the shortest period of 5 h in the case of 1000 mM H<sub>2</sub>O<sub>2</sub> concentration and 900 mM H<sub>2</sub>O<sub>2</sub> concentration. But the rate of decolorization was maximum in the case of 1000 mM concentration of H<sub>2</sub>O<sub>2</sub>. Hence, the optimum concentration of H<sub>2</sub>O<sub>2</sub> was found to be 1000 mM (Fig. 3). The rate of decolorization of Congo red dye was minimum in lower and higher concentrations of H<sub>2</sub>O<sub>2</sub> due to the photolysis reaction of H<sub>2</sub>O<sub>2</sub> with sunlight which results in the formation of the hydroxyl radicals. They react with an excess of H<sub>2</sub>O<sub>2</sub> to form oxygen and water, which makes an inhibitory effect on decolorization of Congo red because there is lower availability of hydroxyl radicals for reaction with dye molecules to degrade it. Therefore, at a high concentration of H<sub>2</sub>O<sub>2</sub> it occurs only a lesser extent of decolorization. Similarly, the generation of hydroxyl radicals is also lower than expected at a lower concentration of H<sub>2</sub>O<sub>2</sub>. Hence, its ability to react with dye molecule is also very low [13].

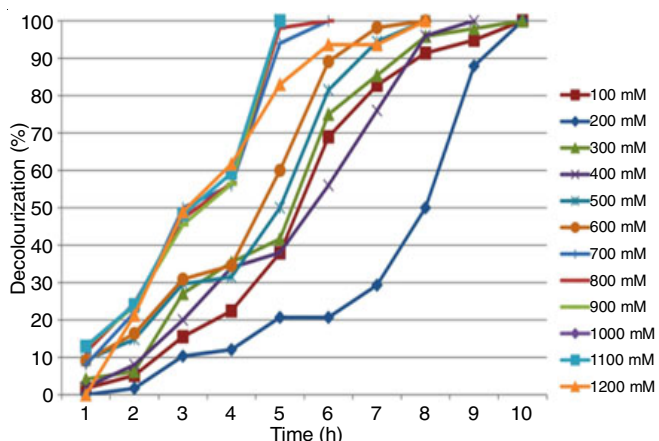


Fig. 3. Effect of H<sub>2</sub>O<sub>2</sub> on decolorization of Congo red dye (Reaction conditions: pH = 2, [Dye] = 100 mg/L, [H<sub>2</sub>O<sub>2</sub>] = 100-1200 mM)

**Effect of dye concentration:** Effect of dye concentration on decolorization of Congo red was studied by treating dye solutions of different concentrations from 50 to 500 mg/L in optimized pH 2 and H<sub>2</sub>O<sub>2</sub> concentration of 1000 mM. It was found that the rate of decolorization was maximum at 50 mg/L dye concentration and minimum at 500 mg/L dye concentration. It was observed that lower time was taken for decolorization of Congo red dye solution at lower concentration (Fig. 4).

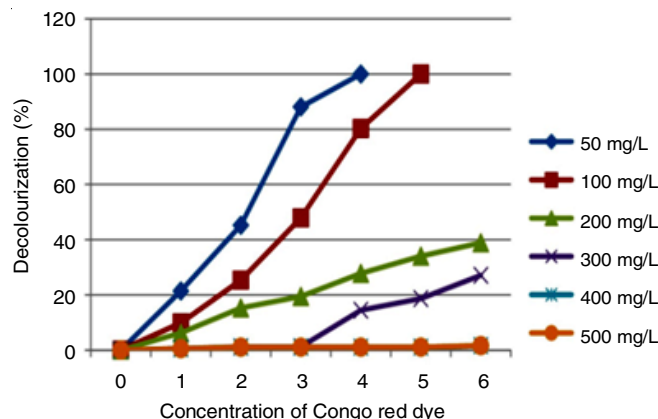


Fig. 4. Effect of dye concentration on decolorization of Congo red dye (Reaction conditions: pH = 2, [Dye] = 50-500 mg/L and [H<sub>2</sub>O<sub>2</sub>] = 1000 mM)

Both dye and H<sub>2</sub>O<sub>2</sub> absorb solar radiation in the same range. But, increase in dye concentration increases internal absorbance and the solution becomes more and more impermeable to solar radiation [4]. But H<sub>2</sub>O<sub>2</sub> in the reaction mixture can be irradiated only by a smaller portion of solar light and it forms lower concentration of hydroxyl radicals. Also the concentration of intermediate compounds formed increases which are highly reactive free radicals. There arises competition between dye and intermediate compounds for reaction with hydroxyl radicals, which reduces the bleaching effect of H<sub>2</sub>O<sub>2</sub>. Hence even at optimum concentration of H<sub>2</sub>O<sub>2</sub>, increase in dye concentration leads to lesser extent of decolorization [4,15].

### Kinetic studies

**Effect of H<sub>2</sub>O<sub>2</sub> concentration on the kinetics of Congo red decolorization:** To optimize the H<sub>2</sub>O<sub>2</sub> concentration, the kinetics study was performed by varying the concentrations of H<sub>2</sub>O<sub>2</sub> and study its effect in decolorization of Congo red. The order of the reaction was found to be pseudo-first order with respect to the dye concentration.

By plotting  $\ln(A_t/A_0)$  vs. time of decolorization of dye, values obtained shows that the maximum 100% decolorization at 1000 mM of H<sub>2</sub>O<sub>2</sub> was occurred within the shortest period of 5 h. Rate constants can be calculated by linear regression method [8]. Fig. 5 shows that plotting rate constants against different concentrations of H<sub>2</sub>O<sub>2</sub>, the optimum concentration of H<sub>2</sub>O<sub>2</sub> can be obtained. The rate of decolorization increases on increasing concentrations of H<sub>2</sub>O<sub>2</sub> up to 1000 mM and then decreases. Hence, 1000 mM was considered as the optimum concentration of H<sub>2</sub>O<sub>2</sub> [12].

**Effect of solar light intensity:** The effect of solar light intensity in decolorization of Congo red dye was studied by



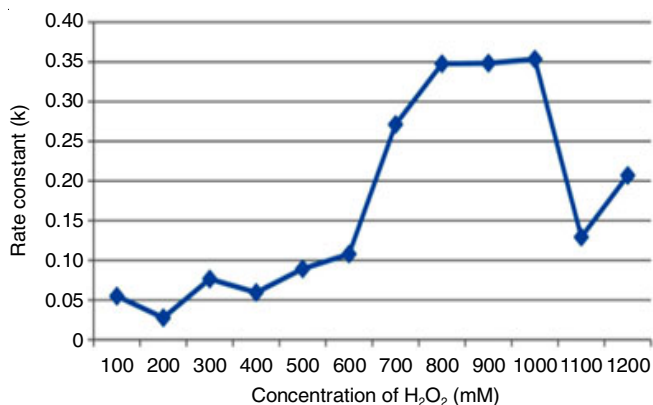


Fig. 5. Plot of concentration of H<sub>2</sub>O<sub>2</sub> vs. rate constants

comparing the increase in the percentage of decolourization per hour in highest and lowest solar light intensities. Fig. 6 shows the effect of solar light intensity on decolourization of Congo red dye. It was found that when the solar light intensity increased from 20,000 lux to 62,000 lux, then decolourization was also increased from 9 to 25% with 16% increase in the decolourization in second hour. When, again the solar light intensity was increased from 62,000 to 75,000 lux, a further increase in the decolourization was 48% in the third hour and upto 80% in the fourth hour was observed. However, when the solar light intensity was decreased from the range of 75,000 lux to 40,000 lux, there was a also decrease in the percentage of decolourization from 32 to 16% in the fifth hour. Since, the solar light intensity cannot be controlled and its effect can be studied when its intensity is high in noon and low in the morning and evening. Thus, in the solar/H<sub>2</sub>O<sub>2</sub> process, the photolysis of H<sub>2</sub>O<sub>2</sub> directly depends on incident solar light intensity [9]. Therefore, more number of hydroxyl radicals are produced by photolysis of H<sub>2</sub>O<sub>2</sub> in high solar light intensity, which leads to more decolourization of the dye by the attack of hydroxyl radicals.

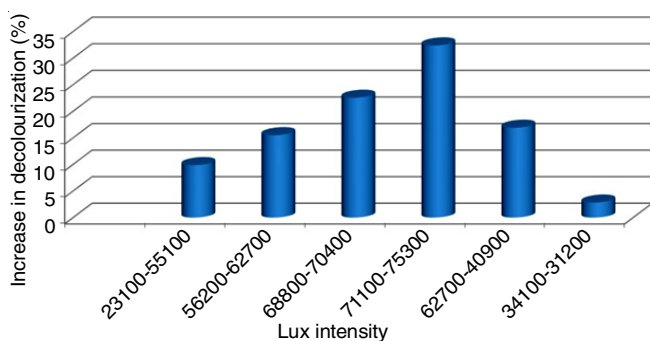


Fig. 6. Effect of solar light intensity on decolourization of Congo red dye (Reaction conditions: pH = 2, [Dye] = 100 mg/L and [H<sub>2</sub>O<sub>2</sub>] = 1000 mM)

**Effect of additives:** Effect of two ions like H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and Cl<sup>-</sup> of concentration 1 M was investigated on the photolytic decolourization of Congo red dye in the acidic medium. The obtained results have clearly shown that the ions have produced an inhibitory effect on decolourization. By adding H<sub>2</sub>PO<sub>4</sub><sup>-</sup> to the dye solution, decolourization was lowered to 74.64% (Fig. 7). Similarly, on adding Cl<sup>-</sup> ions to the dye solution, decolourization was lowered to 97.14%. This inhibitory effect occurred

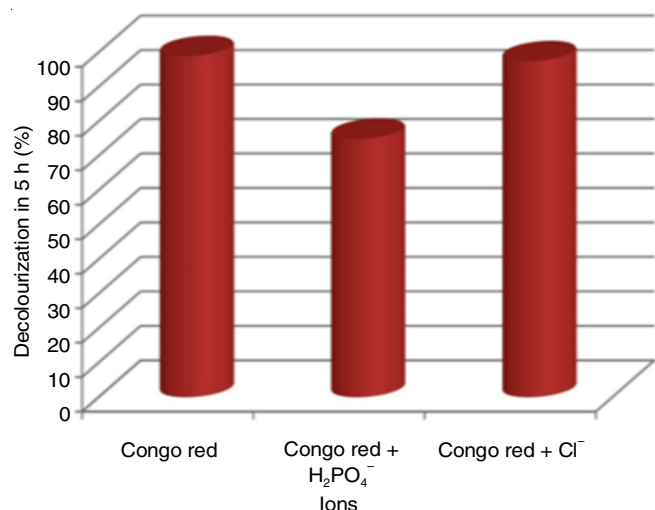


Fig. 7. Effect of additives on decolourization of Congo red dye (Reaction conditions: pH = 2, [Dye] = 100 mg/L, [H<sub>2</sub>O<sub>2</sub>] = 1000 mM, [Cl<sup>-</sup>] = 1 M, [H<sub>2</sub>PO<sub>4</sub><sup>-</sup>] = 1 M)

since both H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and Cl<sup>-</sup> were acted as scavengers on the hydroxyl radicals [5,10]. Both the anions reacted with hydroxyl radicals, which form inorganic radical ions (ClOH<sup>•-</sup>) & and (HPO<sub>4</sub><sup>•-</sup>) and show lower reactivity than hydroxyl radicals. But the inhibitory effect was less pronounced on adding Cl<sup>-</sup> ions [16]. It was due to the following reasons:



In 1 M of Cl<sup>-</sup>, the formed intermediate radical ion ClOH<sup>•-</sup> dissociates to form Cl<sup>-</sup> ion and hydroxyl radical which was not found in H<sub>2</sub>PO<sub>4</sub><sup>-</sup> ion. Therefore, competition takes place between scavenging effect by Cl<sup>-</sup> and formation of hydroxyl radicals. But results obtained showed that there was a slight inhibitory effect produced in decolourization of Congo red dye of 2.86%. Thus, it is concluded that scavenging effect by Cl<sup>-</sup> dominates the attack of formed hydroxyl radicals on dye [17].

**COD analysis:** The values of chemical oxygen demand (COD) represent the amount of oxygen needed for complete oxidation of a substance in a specific volume of an aqueous sample. The values of COD depend on the initial concentration of dye, its chemical structure and the time taken for complete decolourization. The COD value of Congo red dye before degradation was 10,755 mg/L and after degradation, it was reduced to 1800 mg/L. Thus, the COD removal % was found to be 83.26%. Hence, it was observed that oxidation of organic substances was done effectively.

**TOC analysis:** Total organic carbon (TOC) is a measure of the quantity of organically bound carbon that can be oxidized to CO<sub>2</sub>. TOC value of Congo red dye before degradation was 17.57 mg/L and after degradation it was reduced to 16.66 mg/L. TOC removal % was found to be 5.18%. Hence, it was observed that new organic substances were formed during decolourization and mineralization, which were unidentified.

## Conclusion

The solar-assisted H<sub>2</sub>O<sub>2</sub> photodegradation process was found to be an effective method for complete degradation of Congo red dye at the optimum conditions of pH 2 and the H<sub>2</sub>O<sub>2</sub> concentration of 1000 mM. The decolourization occurred within 5 h for the dye concentration of 100 mg/L. The COD and TOC removal percentage by this method was found to be 83.26% and 5.18%, respectively.

## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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