



Photodegradation of Congo Red Dye Via Simple and Effective Air Oxidation Using Copper(II) Chloride and Sunlight

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ABSTRACT

This paper reports the study of photodegradation of Congo red dye which is a major pollutant in dyeing industry using copper(II) chloride dihydrate as a catalyst. The rate of degradation is improved by direct supply of air instead of using other strong oxidants. The effects of other parameters such as pH, catalyst dosage, initial dye concentration and irradiation time were studied. It was found that over 100% of the dye removal can be effectively achieved within 90 minutes of air oxidation at pH 11 and a catalyst dosage of 0.4g/L. The kinetics on the rate of degradation of the dye has also been examined by using UV-Visible spectroscopic technique. Air oxidation of Congo red dye using $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was found to obey pseudo-first-order kinetics with respect to the substrate concentration. The study suggests the use of homogeneous $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ catalyst for the photodegradation of dyes of reactive azo dye category. Future studies on the use of catalytic activity of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ for industrial effluents containing azo dyes as a major pollutant can be affected.

INTRODUCTION

Effluents from the textile, paper, leather, food and other industries increase the level of pollutants in our water bodies. More predominantly, the wastewater let out from the textile industries contains the chemicals associated with the dyeing process. Also, the wastewater generated by the textile industries contains an excess amount of non-fixed dyes especially the azo dyes (Riga et al. 2007, Mittal et al. 2013). Congo red dye is frequently used in the industries as an anionic dye, because of its complex structure and various di-azo aromatic groups present. Congo red dyes are banned in many countries due to serious health concerns. Its structural stability makes it highly resistant to biodegradation and its bright colour and toxic nature are undesirable to the environment (Lachheb et al. 2002, Bark et al. 2010, Abo-Farha 2010). The structure of Congo red dye is shown in Fig. 1.

Due to the toxicity, mutagenic and carcinogenic characteristic of these dyes, their removal from the water bodies has become a serious concern. The advanced oxidation processes (AOPs) are the most recently employed wastewater treatment technologies, among which the catalytic air oxidation is a technique that uses a catalyst for the degradation of effluents, which require high chemical oxygen demands (Rivas et al. 2005A, Rivas et al. 2005B, Li et al. 2008). Copper(II) halides are moderate oxidizing agents (Allen et al. 2013, Bhargava et al. 2007). Air containing oxygen

(21%) is highly atom-economical, environmentally benign, and abundant oxidant, which makes it ideal in many ways. The high activation energies in the reactions of oxygen require the use of catalyst. In combination with air oxidation, the chemistry of copper catalysis increases because the oxygen used here can act as a sink for electrons (Kyoung-Hum Kim et al. 2011, Cuauhtémoc et al. 2008, Guolin Jing et al. 2013). With these considerations in mind, we have developed an affordable, readily available and eco-friendly catalyst for the photocatalytic-oxidation of organic azo dyes. The main objective of the study is to evaluate the degradation efficiency of Congo red dye by using copper(II) chloride dihydrate as a catalyst. The kinetic studies were performed for the degradation process of Congo red dye.

EXPERIMENTAL

Materials and Methods

All the chemicals used in this experiment were of analytical grade. The $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was purchased from Qualigens Fine Chemicals (purity 98%). The air pump used for the experiment was purchased from RS Electricals, the air supplied is 2.5L/min. The pH of the solution was measured using Elico Digital pH meter. The Dye used for representing organic dyes is Congo red because it is readily soluble in water. Thus, it is prepared using distilled water and used for all the experiments. The instrument UV-Visible spectropho-

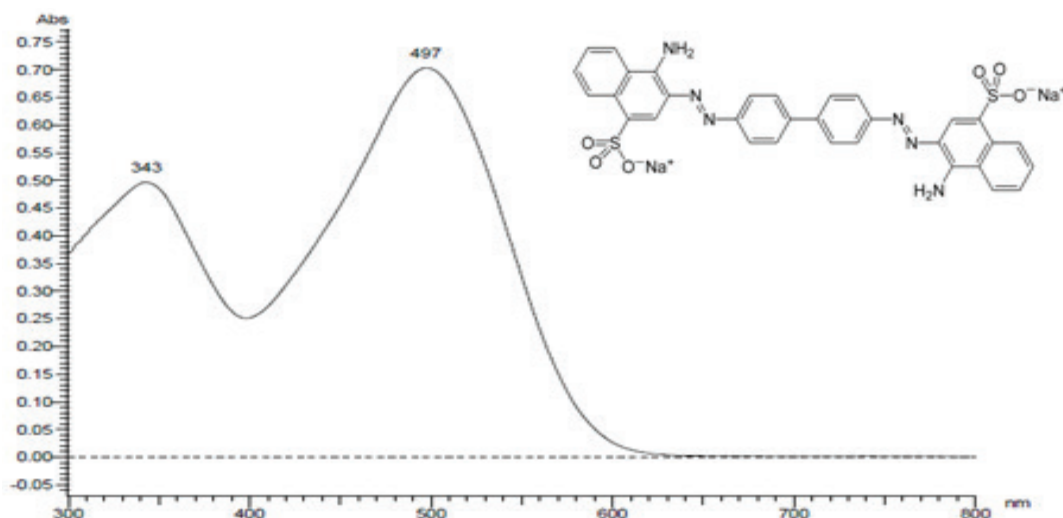


Fig. 1: UV-Visible spectrum and chemical structure of Congo red dye.

tometer (Hitachi U2910) was used to monitor the decolourization of Congo red dye for all the parameters optimized.

Photocatalytic Degradation Experiments

All the photocatalytic experiments were carried out on sunny days between 11 a.m. to 2 p.m. The sunlight intensity was measured by LT Lutron LX-10/A digital Lux meter. The intensity was nearly constant during the experiments. The average sunlight intensity was measured to be $(1250 \times 100) \pm 100$ Lx. About 0.01 g/L Congo red dye was prepared as the stock solution, from which 50 mL was withdrawn for each experiment. Before exposing the dye solution to sunlight irradiation, the initial absorption peak was recorded. To evaluate the effect of initial dye concentration, the concentration of the dye was varied from 0.01 to 0.05 g/L and the percentage decolourization was calculated using the formula $(C_0 - C_t)/C_0 \times 100$, where C_0 is the initial concentration of the dye solution and C_t is the concentration of the dye solution at time t . The experiment was continued for 3 hours, by withdrawing 1 mL of the dye solution for every 30 minutes of irradiation. The effect of pH was studied by adjusting the solution using 0.1 N NaOH and 0.1 N HCl. The amount of the catalyst was varied from 10 mg to 50 mg for 0.01 g/L of Congo red dye solution and the sufficient amount of catalyst for decolourization was optimized. The blank experiments were performed in the dark at room temperature following the above procedure.

RESULTS AND DISCUSSION

To determine the degradation efficiency of the copper(II) chloride catalyst, the experiments were carried out under

solar light irradiation on sunny days during 11:00 a.m. to 2:00 p.m. and also in the dark conditions at room temperature. The initial absorption of the Congo red dye using UV-visible spectrophotometer showed an intense peak at 498 nm which is the characteristic peak for Congo red dye. A decrease in the intensity of absorption was observed during the course of the reaction. When 0.01 g/L of the dye solution was stirred in the dark along with the copper(II) chloride salt, the calculated percentage decolourization was found to be only 31% within 90 minutes whereas the dye solution stirred under the sunlight radiation showed 85% decolourization. To improve the rate of degradation, along with copper chloride salt, air was pumped through the dye solution, which led to complete decolourization of Congo red dye as shown in Fig. 2.

Effect of Initial Dye Concentration

The effect of initial dye concentration was studied by varying the concentration of the dye from 0.01 g/L to 0.05 g/L keeping the amount of the catalyst 0.4 g/L as fixed. When the dye concentration was 0.01 g/L, complete decolourization of the dye solution is achieved, whereas it has drastically reduced to 46% at 0.05 g/L as shown in Fig. 3. The degradation efficiency of the dye was found to decrease with an increase in the initial concentration of the dye solution. The intensity of the solution gets increased by increasing the concentration of the dye and thereby the path length of the photons entering into the solution gets decreased. Hence, the generation of hydroxyl and superoxide radical is limited. On further increasing the concentration of the dye solution, the length of penetration of light is further reduced and the photodegradation becomes negligible (Dafare et al.

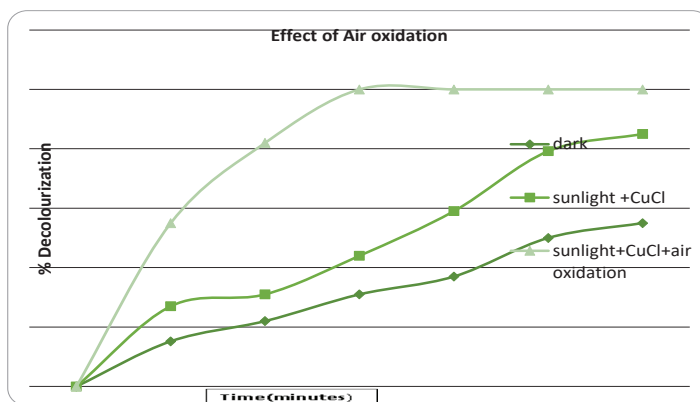


Fig. 2: Decolourization efficiency for (0.01g/L) of Congo red dye solution with 20mg of copper chloride as catalyst with pH 11 under varying conditions.

2013, Movahedi et al. 2009).

Effect of Catalyst Loading

Experiments were carried out by varying the amount of the copper(II) chloride catalyst for 0.01g/L of the dye solution shown in Fig. 4.

The maximum degradation efficiency was obtained for 20mg of the catalyst, beyond which an increase in the amount of catalyst led to the decrease in dye degradation, which may be due to the fact that, when the catalyst loading was high, there is an increase in turbidity of the suspension and shrinking of the effective photoactivated volume of suspension takes place, and thus, the photocatalytic performance of the copper catalyst gets decreased (Hatwar et al.

2016). Hence, catalyst loading was optimized to 0.4 g.L⁻¹ for further study.

Effect of pH

The pH of the dye solution in the present study was varied by adding solutions of NaOH and HCl. At 60 minutes, about 82% of the dye was removed at pH 11 as shown in Fig. 5. However, in the acidic pH, a change in colour from Congo red to violet took place which continued on decreasing the pH from 5 to 3 and increasing the time of sunlight irradiation. This may be due to:

- i. The metachromatic property of the dye in strongly acidic solutions.
- ii. Aggregation phenomenon of the dye molecules.

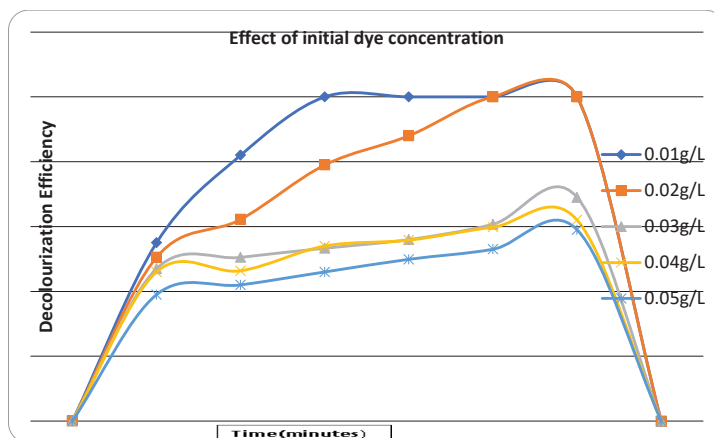


Fig. 3: Decolourization efficiency for varied concentration of congo red dye Solution (0.01g/L to 0.05g/L) with 20mg of copper chloride as catalyst with varying pH range from 3-12.

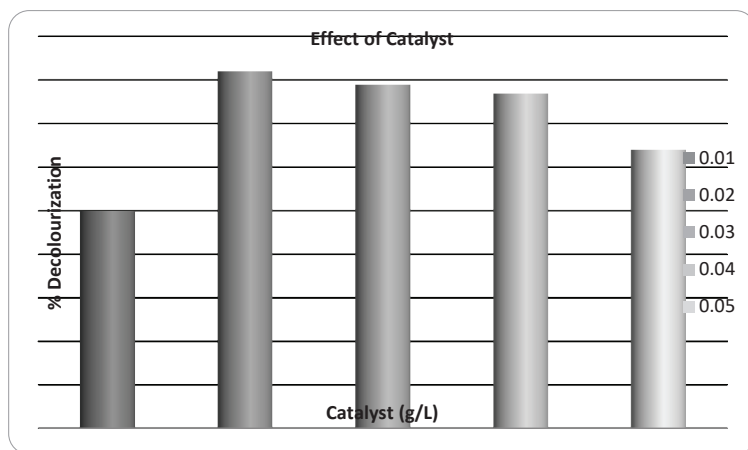


Fig. 4: Decolourization efficiency for 50mL (0.01g/L) of Congo red dye solution with varying amount (10mg to 50mg) of copper chloride as catalyst at pH range 11.

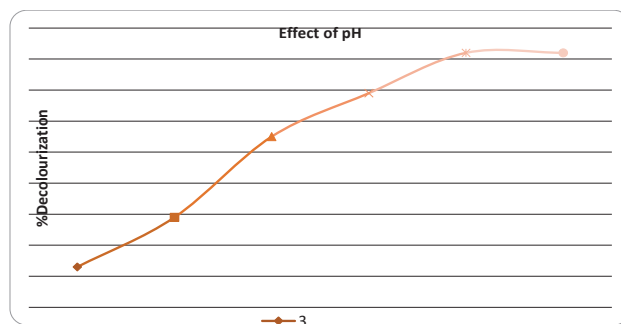


Fig. 5: Decolourization efficiency for 50mL (0.01g/L) of congo red dye solution with 20mg of copper chloride as catalyst with varying pH range from 3-12.

At alkaline pH, the more availability of hydroxyl radicals led to the dye degradation (Movahedi et al. 2009, Hatwar et al. 2016, Elaziouti et al. 2001).

Kinetic Studies

Studies from the previous research work show that most of the catalytic air oxidation (CAO) processes follow pseudo-first-order kinetics with respect to pollutant concentration (Eftaxias et al. 2001, Bhargava et al. 2016, Garg et al. 2010, Santos et al. 2004)). The first-order rate expression can be written as:

$$\ln C_0/C_t = k.t$$

Where, C_0 is the initial dye concentration, C_t is concentration of the dye at time t , k is the reaction rate constant. Fig. 6 shows the plot of $\ln C_0/C_t$ versus t giving a straight line for 0.01g/L of the Congo red dye solution with 20mg of the copper chloride dihydrate salt as the catalyst, the rate constant value is 0.0092 and the R^2 value is 0.9693. All the

data points are positioned well on a straight line and validate the assumption.

Removal of Homogeneous Copper Ions After the Catalytic Reaction

The major drawback of using a metal ion as a catalyst in degradation of the organic pollutant is that the recovery of the metal ion from the solution is a tedious process. In the present work, the copper ions used, are considered to be toxic for microorganisms and aquatic life if present in excessive concentrations. Hence, copper needs to be eliminated from the treated water before subjecting to post bio-treatment or final disposal in a water body. Studies from the previous research work have shown that pH adjustment in a range of 6.0-8.0 gives the maximum precipitation of copper in the form of insoluble copper hydroxide (Garg et al. 2005). At higher pH values (>8.0), the formed metal hydroxide species were dissolved again in the solution. However, in the

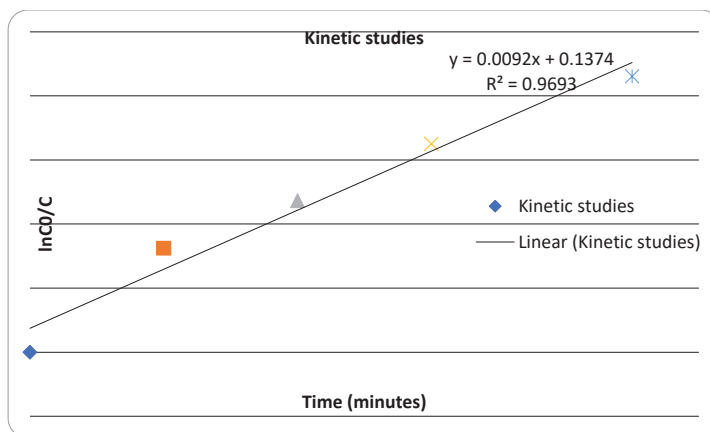


Fig. 6: The plot of $\ln C_0/C$ Vs time for 0.01g/L of Congo red dye solution.

present study, the amount of copper chloride catalyst used is well below the permissible standards (0.4g of copper salt for 0.02g/L of the dye solution) for discharge in inland surface water given by the Central Pollution Control Board, New Delhi, India (CPCB 2012).

CONCLUSIONS

The use of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ as a homogeneous catalyst in the degradation of Congo red dye was shown to be remarkably greater and the air oxidation implemented along with the copper(II) chloride catalyst in the degradation of Congo red dye enhanced the photo-degradation process. Treatment of Congo red dye under direct sunlight showed 100% decolourization within 90 minutes of reaction time and only 31% degradation took place under dark condition. Control experiments demonstrated that both sunlight, copper chloride catalyst as well as air oxidation were needed for the effective destruction of dye. The highest percentage decolourization of Congo red dye is obtained under the alkaline pH. The observations of these investigations clearly demonstrate the importance of choosing the optimum degradation parameters to obtain high degradation rate, which is essential for any practical application of photocatalytic oxidation processes. The photocatalytic degradation of Congo red dye in the solution follows pseudo-first order reaction kinetics. As a whole, copper(II) chloride salt used as a catalyst for the decolourization of Congo red dye was nontoxic, economically viable and environmentally benign under the present reaction conditions. Future work may be extended for decolourization of the textile effluents containing dyes as major pollutants.

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