Heterogeneous photo-Fenton like degradation of rhodamine B using copper loaded bentonite and H₂O₂

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Photo-Fenton like degradation of rhodamine B using copper loaded bentonite and hydrogen peroxide is reported. The catalyst has been prepared by loading copper ions on bentonite by wet impregnation method using Na₂CO₃, Cu(NO₃)₂·3H₂O and bentonite clay. On photo-Fenton treatment, the dye mineralizes into smaller ions like CO₃²⁻, NO₃⁻, NO₂⁻ etc. The photodegradation efficiency of the catalyst for the rhodamine B dye is found to be 67.92%. Under optimal conditions, the rate constant k is 3.72 × 10⁻³ s⁻¹. A tentative mechanism involving ‘OH radical as an oxidant in degradation process is proposed. Involvement of ‘OH radicals as an active oxidizing agent is confirmed by the drastic reduction in rate of reaction in presence of isopropanol and butylated hydroxy toluene as radical scavengers. The reduction in reaction rate is higher with butylated hydroxy toluene as compared with isopropanol as the radical scavengers.

Keywords: Degradation, Photodegradation, Photo-fenton reaction, Photo catalyst, Dye degradation, Rhodamine B, Bentonite

Effluents from various industries like textile, pulp, paper, dyeing and printing industries contain pollutants like acids, detergents, soaps, chemicals, pesticides, dyes etc. and are the major sources of water pollution.¹² Dyestuffs from the textile industries make water coloured, toxic and unfit for any use. Various methods such as flocculation, coagulation, reverse osmosis, ozonation³, activated carbon adsorption⁴, etc., have been used for removing colour from water. However, these conventional processes generate a large amount of sludge leading to disposal problem which is a major drawback. To overcome this drawback, Advanced Oxidation Processes (AOP) have been used in recent years. AOPs are based on the generation of highly reactive radicals, especially hydroxyl (‘OH) radicals, which possess high reactivity and low selectivity.

In Fenton process, generation of hydroxyl radicals take place which are responsible for oxidative decomposition of pollutants.¹⁰⁻¹³ It has been observed that irradiation of Fenton reaction with UV or visible light makes the process cyclic and less expensive than Fenton reactions.¹⁴⁻¹⁹ However, iron ions which act as catalyst get dissolved in water in the homogeneous Fenton process.¹⁸ Due to this, the iron ions in the treated water normally exceed 10 mg/L and need to be removed. However there are several drawbacks associated with this process. To overcome drawbacks associated with homogeneous photo-Fenton process, heterogeneous photo-Fenton catalysts have been widely employed for the oxidation of organic pollutants.²⁰⁻²⁴ The major advantage of the use of heterogeneous catalytic materials is their easy recovery after the completion of treatment.

Bentonite clay is used as adsorbent in removal of dyes from water. Arora et al.²⁵ observed photo-Fenton degradation of rose Bengal using hydroxyl-Fe-pillared bentonite. Zhang et al.²⁶ studied degradation of dye wastewater by nano-ferrous modified bentonite as the heterogeneous catalyst for Fenton like oxidation. Chen and Zhu²⁷ proposed oxalate enhanced mechanism for the degradation of orange II by UV-Fenton process using hydroxyl-Fe-pillared bentonite. Synthesis, characterization, and visible-light photo-Fenton catalytic activity of hydroxyl Fe/Al-intercalated montmorillonite was studied by Li et al.²⁸ Chen and Zhu²⁹ observed the heterogeneous UV-Fenton catalytic degradation of dyestuff in water with hydroxyl-Fe pillared bentonite.

In the present work, a novel visible light sensitive photo-Fenton like catalyst has been prepared by loading copper ions in bentonite clay by a simple wet impregnation method. It has been used for the degradation of rhodamine B dye in presence of H₂O₂/visible light.

Experimental

The catalyst was prepared by loading copper ions in bentonite clay by wet impregnation method. Powdered Na₂CO₃, was added slowly into the solution of Cu(NO₃)₂·3H₂O (Himedia) under magnetic stirring, until the ratio of [Na⁺]/[Cu²⁺] was 1:1. This solution was kept in an oven at 60 °C for one day and then added to the clay suspension under stirring. The final [Cu²⁺]/[clay] ratio was equal to 0.5 mol/kg of dry clay. The catalyst was then filtered, washed with deionized water several times and finally dried overnight at 105 °C in an oven.
The prepared catalyst was used for the degradation of rhodamine B dye. For this purpose, stock solution of rhodamine B (10^{-3}M, Himedia) was prepared. Degradation of dye was observed by taking 40.0 mL of a mixture of 0.75×10^{-5} M dye solution, 0.25 mL H_{2}O_{2} (CBH, 30 % vol.) and 0.020 g Cu-loaded bentonite. The reaction mixture was irradiated with a 200 W tungsten lamp (Philips). The intensity of light at various distances from the lamp was measured using a Solarimeter (SM CEL 201). A water filter was used to cut off thermal radiations. A digital pH meter (model 232) was used to measure the pH of the reaction mixture. The pH of the solution was adjusted by the addition of previously standardized 0.1 N sulphuric acid and 0.1 N sodium hydroxide solution.

The progress of degradation was monitored by measuring the absorbance of the reaction mixture at regular time intervals using a UV visible spectrophotometer (Systronics model 106). Scanning electron microscope (model Leo 430 Cambridge) was used to observe the SEM images of catalyst. XRD patterns of the samples were recorded on a powder X-ray diffractometer (Bruker D8 Advance X-ray diffractometer) using Cu K_{α} radiation. Diffraction patterns were recorded in the 2θ range from 5° to 90° with a step size of 0.02°. Stability of the catalyst was checked by atomic absorption spectroscopy (model ECTL 4129A).

Quality parameters for water, i.e., COD, DO, conductivity, salinity, TDS and pH have been determined before and after photo-Fenton degradation of dye using a water analyser (Systronics model 371).

Loading of copper ions led to the formation of smaller particles of the catalyst, which increased the surface area of the catalyst as well as the rate of degradation. The SEM photographs of unloaded and loaded bentonite are shown in Fig. 1. The average particle sizes of Cu–loaded bentonite and naive bentonite were found to be 5.0 µm and 35.0 µm, respectively.

The indexed XRD patterns of the pure bentonite and copper loaded bentonite are shown in Fig. 2. All the Bragg reflections could be indexed to the rhombohedral structure. The cell parameters obtained for pure bentonite are as follows: \(a = 5.096 \, \text{Å}, \quad b = 8.937 \, \text{Å}, \quad c = 9.871 \, \text{Å}; \quad \text{cell volume} = 444.37\, \text{Å}^{3}\). Relative changes in the peak positions and peak intensities in the Cu loaded sample clearly indicate that the Cu atoms are well incorporated in the clay matrix. The cell parameters obtained for Cu loaded bentonite are \(a = 5.1732 \, \text{Å}, \quad b = 8.9470 \, \text{Å} \quad \text{and} \quad c = 9.9346 \, \text{Å}; \quad \text{cell volume} = 453.52 \, \text{Å}^{3}\). Thus, Cu loading in bentonite leads to small increase in the unit cell volume.

From atomic absorption spectroscopy it was observed that even after one month, leaching of copper ions from the catalyst was nil. Thus, the catalyst was found to posses good stability for its use as photo-Fenton like reagent under visible range.

**Results & discussion**

The absorbance of the reaction mixture at 560 nm was found to decrease with increasing time intervals, which indicates that the concentration of rhodamine B decreases with increasing time of exposure. A plot of \(2+\log A\) against time was linear and follows pseudo-first order kinetics.

An increase in pH, increased the rate of reaction and after attaining the maximum value at pH 8.0, the rate decreased with increase in pH. A decrease in the degradation from pH 8.0 to 6.0 may be explained by the fact that relative concentration of \(\cdot \text{OH}\) ions

![Fig. 1 — SEM image of (a) bentonite, and, (b) copper loaded bentonite.](image-url)
decreases as the pH decreased from 8.0 to 6.0, resulting in the generation of fewer •OH radicals by the reaction of Cu$^2+$ with •OH.

$$\text{Cu}^{2+} + \cdot \text{OH} \rightarrow \text{Cu}^+ + \cdot \text{OH} \quad \ldots (1)$$

In addition, in acidic medium, the surface of the catalyst gets covered with $\text{H}^+$ ions. Hence, there is a coloumbic repulsion between positively charged catalyst surface and cationic dye. Both these factors are probably responsible for the decrease in rate of degradation on moving from $\text{pH}$ 8.0 to 6.0.

However, a decrease in rate of degradation was observed beyond 8.0, which may be due to the fact that dye does not remain in its cationic form, since •OH ions surround the dye molecules at much higher $\text{pH}$. Hence, there is repulsion between the dye molecules and the negatively charged catalyst surface (due to adsorption of •OH ions), and approach of dye molecules towards catalyst surface is retarded. As a result, the rate of degradation also decreases.

The effect of variation in concentration of dye on rate of degradation was studied in the range from 0.25×10$^{-5}$ $M$–1.75×10$^{-5}$ $M$. It has been observed that the rate of degradation increased with increasing concentration of dye up to 0.75×10$^{-5}$ $M$. Further increase in concentration beyond 0.75×10$^{-5}$ $M$ decreases the rate of degradation. Initially, on increasing the concentration of dye, the reaction rate increases as more molecules of dye are available for degradation. However, further increase in concentration beyond 0.75×10$^{-5}$ $M$ causes retardation of reaction due to increase in number of collisions between dye molecules, while the collisions between dye and •OH radicals decrease. As a consequence, rate of reaction is retarded.

The effect of varying amounts of catalyst on the rate of dye degradation was observed in the range of 0.010–0.045 g. With increase in the amount of catalyst, the rate of degradation increased up to a certain amount of catalyst (0.020 g), which may be regarded as a saturation point. Beyond this point, the rate of reaction decreased with increase in amount of catalyst. With increase in the amount of catalyst, the surface area of catalyst increases leading to rise in the rate of reaction. Further increase in the amount of catalyst, also increases the number of copper ions, which leads to a possibility of short circuiting of cuprous and cupric ions, in which a cyclic process involving a change from Cu$^2+$ to Cu$^+$ ions and vice versa takes place. Due to this, generation of •OH radicals is decreased.\textsuperscript{30} As a result, fewer of hydroxyl radicals are formed and reaction rate is retarded.

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The effect of variation of amount of H$_2$O$_2$ on the dye degradation was investigated in the range from 0.05 mL to 0.35 mL. On increasing the amount of H$_2$O$_2$ from 0.05 mL to 0.25 mL, the •OH radical concentration increases and hence rate of degradation of dye also increases. At high H$_2$O$_2$ concentration, i.e., beyond 0.25 mL, scavenging of hydroxyl radical also takes place due to the H$_2$O$_2$ generating perhydroxyl radical (Eq. 2). Perhydroxyl radical is a weaker oxidant as compared to the hydroxyl radical. Therefore, the rate of degradation of dye decreases when amount of H$_2$O$_2$ is increased beyond 0.25 mL.

$$\text{H}_2\text{O}_2 + \cdot \text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2^* \quad \ldots (2)$$

It was observed that with increase of light intensity, the rate of reaction increased with the maximum rate observed at 70.0 mW cm$^{-2}$. When light intensity was increased, the number of photons striking per unit
area also increased, resulting in a higher rate of degradation. Further increase in the light intensity beyond 70.0 mW cm\(^{-2}\) results in a decrease in the rate of reaction which may probably be due to thermal side reactions.

On the basis of experimental observations and the existing literature, a tentative mechanism has been proposed for the degradation of rhodamine B by heterogeneous photo-Fenton like reagent. Initially, cupric ions from catalyst react with water in the presence of light and are reduced to the cuprous state along with the formation of hydroxyl radicals. The cuprous ions so formed react with hydrogen peroxide without the requirement of photons generating cupric ions and \(^{\cdot}\)OH radicals. The cupric state is again converted into cuprous state with the aid of photons in the aqueous medium (Scheme 1).

\[
\text{Cu}^{2+} + \text{H}_2\text{O} \xrightarrow{ hu} \text{Cu}^{+} + \text{^{\cdot}\text{OH}} + \text{H}^+ \\
\text{Cu}^{+} + \text{H}_2\text{O}_2 \rightarrow \text{Cu}^{2+} + \text{^{\cdot}\text{OH}} + \text{^{\cdot}\cdot}\text{OH}
\]

**Scheme 1**

The \(^{\cdot}\)OH radical is non-selective and a strong oxidizing agent with a oxidation potential, which is relatively high as compared to common oxidizing agents like \(\text{H}_2\text{O}_2\), \(\text{O}_3\), \(\text{O}_3\), etc. These \(^{\cdot}\)OH radicals react with the triplet state of dye molecule and degrade it into smaller gaseous products like \(\text{CO}_3^{2-}\), \(\text{NO}_3^{-}\), \(\text{SO}_4^{2-}\), etc. These products have been identified by usual chemical tests (Scheme 2).

\[\text{1[Dye]} \xrightarrow{ h\nu} \text{1[Dye]*}\]
\[\text{1[Dye]*} \xrightarrow{\text{isc}} \text{3[Dye]*}\]
\[\text{3[Dye]*} + \text{^{\cdot}\text{OH}} \rightarrow \text{Smaller products}\]

**Scheme 2**

The involvement of \(^{\cdot}\)OH radicals in the reaction has been confirmed by carrying out the reaction in presence of \(^{\cdot}\)OH radical scavenger, e.g. 2-propanol and butylatedhydroxy toluene (BHT). In the presence of 2-propanol and BHT, the reaction rate is drastically reduced. The involvement of triplet state of dye has been confirmed by conducting the reaction in the presence of a small amount of potassium ferrocyanide as triplet state quencher.\(^{31}\) The rate of reaction was found to be considerably reduced.

Chemical oxygen demand of dye solution before and after illumination was calculated by redox method. COD of dye solution before and after exposure was found 66.4 mg/L and 21.3 mg/L, respectively. The photodegradation efficiency after 2 hours of illumination was 67.99%.

Increase in the value of dissolved oxygen after photo-Fenton degradation (from 8.0 ppm to 11.1 ppm) indicates mineralization of dye. Conductivity as a summation parameter is a measure of the level of ion concentration of a solution. Conductivity increased after the photo-Fenton degradation (from 92.3 to 140 µs) since the dye had been mineralized into ions like \(\text{CO}_3^{2-}\), \(\text{NO}_3^{-}\), \(\text{SO}_4^{2-}\), etc. Also, total dissolved solids (TDS) and salinity of the dye solution increased after photo-Fenton degradation of dye (45.8 ppm and 0.42 respectively) as compared to the values prior to the degradation (24.06 ppm and 0.27 respectively).

Due to mineralization of the dye during the degradation, pH of the reaction mixture becomes neutral from the initial basic pH of 6.69.

The present study shows that Cu–loaded bentonite catalyst has been prepared by wet impregnation method using bentonite and copper nitrate. The amount of catalyst required (typically around 0.020 g in 40 mL) is much less than usually used\(^{30,32,33}\). At optimal conditions (\(\text{pH}= 8\), [rhodamine B] = 0.75×10\(^{-3}\) \(\text{M}\), amount of catalyst = 0.020 g, amount of \(\text{H}_2\text{O}_2\) = 0.25 mL, light intensity = 70 mW cm\(^{-2}\)), the rate of degradation of rhodamine B was 3.72×10\(^{4}\) s\(^{-1}\). During the heterogeneous photo-Fenton like process, \(^{\cdot}\)OH radicals react with dye and degrade them into smaller products like \(\text{H}_2\text{O}\), \(\text{CO}_3^{2-}\), \(\text{NO}_3^{-}\), etc.

**Supplementary Data**

Supplementary data associated with this article i.e., Tables S1-S5, and Figs S1-S5, are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_52A(11)1416-1420_SupplData.pdf.

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**References**