

Catalytic Treatment of Dye Bearing Wastewater

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Abstract
Zeolite catalyst was synthesized from the fly ash, and it was used for thermal treatment and catalytic wet oxidation (CWO) of congo red dye bearing wastewater. Effects of various operating parameters like temperature, pH, H_2O_2 concentration and catalyst loading was observed on chemical oxygen demand (COD) and color removal at pH 2 and temperature 70°C with 4 ml dm^{-3} H_2O_2 and 4 gm dm^{-3} catalyst. Maximum 99.52% dye and 88% COD removal was obtained. Between CWO and catalytic thermolysis, the CWO was found to give better result.
Keywords: dye wastewater, congo red, thermolysis, wet oxidation

1. INTRODUCTION
A dye is a substance that provides color to the substrate to which it is being applied. Large number of dyes and other additives are added during the coloring process (Wang et al., 2007). Varieties of functional groups and inorganic metals are contained in different dyes and have diverse properties which are responsible for color. Food processing, textile and dye industries are the main consumption of dyes. Effluents generated from dye processing plant are usually very complex and very harmful for life. It's contain in wastewater stream reduces the air diffusion and sunlight penetration. Due to this, photosynthesis process hindered and life of water plants and animals died. Therefore, necessary treatment is required earlier to discharge in water receiving bodies. The incapability of conventional methods to efficiently remove many organic pollutants has made to need of new, compact and more efficient system (Levec and pinterl, 2007; Kondru et al., 2009; Hua et al., 2013). Various process viz: thermolysis and coagulation (Gao et al., 2007; Kumar et al., 2008), wet oxidation (Kondru et al., 2009; Hua et al., 2013) and adsorption (Wang et al, 2005) have been reported for removal of various dyes. Some of these methods are usually non-destructive, inefficient and costly. The results are shown in the production of secondary waste products, which need further treatment earlier to disposal. Catalytic and non-catalytic thermal treatment have been proved to efficient process for treatment of various organic effluents (Belkacemi et al., 2000; Garg et al.,2005; Kumar et al.,2008; Verma et al., 2011). Very little work have been reported on thermal treatment of dye bearing wastewater while no work has been found in open literature on catalytic treatment of Congo red dye, therefore, this problem has been taken in present studies.

2. MATERIAL AND METHODS
2.1. Materials
Sodium hydroxide pellets Sulphuric acid, hydrogen peroxide (30% analytical grade) and COD reagent A and B were procured from Merck India Ltd, Mumbai. Fly ash was arranged from SKS Ispat & Power Limited Siltara, Raipur, India. Congo red dye was arranged from local suppliers,

2.2. Methods
2.2.1. Zeolite Synthesis and Its Characterization
Synthesis: Fly ash was initially screened through 355 micron mesh and the particle that passes the screen was taken to prepare catalyst. Screened fly ash was calcined at 800±10°C to eliminate unburnt carbon and volatile matters. NaOH in form of pellets was grinded to fine powder and its 24 g was thoroughly mixed with 20 g of calcined fly ash. The mixture was then taken into a crucible and fused at 550 °C in a furnace. The fused mixture was then cooled, grinded and aged for 10 hours at room temperature. The sodium aluminate slurry obtained after aging was subjected to microwave heating for a period of 15-20 minutes and then kept for crystallization in an oven at temp for 10-12 hours at static state. After hydro thermal crystallization the upper layers of slurry were collected, cooled, washed thoroughly with deionized water followed by filtration and drying at 100-110°C for 4 hours. The zeolite thus formed is in powdered form and stored in a dry place.

2.2.2. Treatment Process and Analysis
The experimental studies were carried out in a 0.5 dm^3 three-necked glass reactor equipped with condenser and magnetic stirrer with heater (Figure 1). The process was performed at total reflux condition. 250 ml water containing Congo red (1 gm dm^{-3} water) was transferred to the three-necked glass reactor. Thereafter, catalyst and hydrogen peroxide (H_2O_2) was added to the solution at desired temperature. The raising of the temperature of the reaction mixture from ambient took about 15-30 min. The total reflux was used to prevent any loss of vapor and magnetic stirrer was used to agitate the mixture. The runs were conducted at desired temperature for 3 hours and the samples were taken at periodic intervals. After the completion of the run, the collected samples were allowed to cool and settled overnight. Finally the collected samples were tested for COD and percentage color removal.

The COD estimation was done using closed reflux method (APHA, 2013). The digested sample's UV spectrum (adsorption) was taken at 605 nm wavelengths for COD estimation and at 497 nm for color estimation. UV-1800, Shimadzu made spectrophotometer was used for this. The images and composition of catalyst was taken by Scanning Electron Microscope (SEM)/EDX, (ZEISS, model EV018, England). Crystalinity of the catalyst was estimated using X-ray diffractometer (PAN analytical, XPERT-PRO diffractometer) by using Cu Kα as a source and Ni as a filter media.

3. RESULTS AND DISCUSSION

3.1. Characterization of Catalyst

SEM/EDX analysis of synthetic zeolite catalyst is presented in Figure 2a. It shows the amorphous nature of catalyst. The presence of Si, Al, Fe, Na, Mg, Ca and Ti was seen. Components Al, Si and Fe are in large amounts in synthesis catalyst are due to its presence in fly ash. A small amount of Ca, Mg and Ti are also present in it. Na appeared in catalyst is due to use of NaOH for catalyst preparation. X ray analysis shows a sharp peak at $2\Theta = 26^0$ (Figure. 2b). However detailed analysis could not be explained at presently.

3.2 Effect of pH on Dye and COD Removal by Oxidation Process

Influence of pH on dye and COD removal was studied at Temp 70 ºC, catalyst loading 4 g dm^{-3} and oxidant H_2O_2 amount 4 ml dm^{-3} with initial dye concentration 1 g dm^{-3}. The initial pH was varied to 2, 3, 4, 6, 7, and 8. The percentage dye removal is presented in Figure 3a. For treatment at pH 2, 3, and 4 in 15 min dye removal was 84.81%, 36.54% &, and 23.97% respectively, which further increased to 99.52%, 63.94%, and 50.11% on 3h treatment. Also, for pH 6, 7, and 8 in 15 min dye removed was 21.12%, 19.17%, and 10.55% respectively, which increased to 40.41%, 32.01%, and 30.99% in 3 h treatment.

The COD reduction at different pH is presented in Figure 3b. At pH 2,3,4,6,7 and 8 respectively, the initial COD value of 190 mg dm^{-3} reduced to 20.32, 38.48, 47.21, 58.24, 60.42 and 78.45 mg dm^{-3} which increases to 89.31%, 80,75%, 15%, 69.35%, 69.2%, and 58.71% COD reductions. It was also seen that COD reduced at a faster rate in first 60 min after that its rate became slow. These dye and COD removal data show low pH to favorable for treatment. At low pH, a large amount of settled mass was seen after settling, which is one of the reasons of dye removal. Formation of solid mass may be due to reaction between functional groups present in the dye which forms heavy mass and settled down. The metals present in catalyst also make completion with NH_2 group present in dye as per Figure 4 and settled down. Lone pair of electrons contains in functional group nitrogen (NH_2) and oxygen (SO_3H). These are electron donor group and due to this, congo red has net negative charge. Apart from this oxidation of dissolved organics by H_2O_2 is responsible for dye and color removal. In oxidation, benzene ring is oxidized to lower carboxylic acids like acetic acid and oxalic acid which further oxidized to CO_2 and H_2O. (Hua et al., 2013). The oxidation and complex formation is strongly dependent on solution pH (Chaudhari et al., 2010).

3.3. Dye and COD Removal by Thermolysis and Oxidation Process

Treatment of dye wastewater by heating was performed at 70ºC and optimum pH 2 in presence of oxidant H_2O_2 (wet oxidation) and in absence of oxidant (thermolysis) using catalyst. H_2O_2 concentration was 4 ml dm^{-3} and catalyst mass loading was 4 g dm^{-3}. The results are presented in Figure 5a. At pH 2, in the presence of H_2O_2 and absence of catalyst (non CWO) the dye removal was 90.68% in 3 h, while in presence of H_2O_2 and catalyst (CWO) the dye removal was 99.52% in same time. Similar process in absence of H_2O_2 and presence of catalyst (catalytic thermolysis) gave 70.01% dye removal. COD values were also evaluated at these conditions and results are presented in Figure 5b. COD 190 mg dm^{-3} reduced to 133.66, 84.92 and 20.32 mg/l in thermolysis, non CWO and CWO respectively. Results reflect CWO process to best among all the three treatment. At the end of wet oxidation the solid residues were also noted at bottom of reactor, thus, COD reductions in wet oxidation is due to solid formation and oxidation of dye, while, in thermolysis COD reductions are by formation of solid residues. (Belacacemi et al., 2000) also found more reductions in CWO as compared to thermolysis for treatment of distilled effluent.

3.4. Effect of Temperature on CWO

Effect of temperature on dye and COD removal at pH 2 and temperature range 60-90 °C were investigated. It was seen that dye removal was increased when temperature was increased from 60°C to 70°C and decreased when the temperature was further increased to 80°C and 90°C. The results obtained are presented in Figure 6. 71.11%, 99.52%, 90.38% and 83.85% dye removal were achieved at temp 60°C, 70°C, 80°C and 90°C respectively in 3h treatment. The COD reduced to 74.11, 20.32, 46.42 and 54.18 mg dm^{-3}. At this temperature less reduction in dye at 80°C and 90°C as comparison to 70°C may be due to the degradation of settled solid mass which further appeared in the solution. In the thermal treatment of pulp and paper mill effluent, highest COD removal was at 60 ^{0}C for studies in temperature range 40-90 ºC (Garg et al.,2005).

3.5 Effect of H_2O_2 Concentration

The effect of amount of H_2O_2 on percentage dye removal was studied at temperature 90°C, pH 2 and catalyst load 4 g dm^{-3} results are presented in Figure 7. In 15 min of CWO, dye removal were 79.30%, 81.77%, 82.40% and 83.10% respectively with 2, 4, 8 and 16 ml of H_2O_2 per dm^3 of dye solution. The reductions increased to 95.87%, 96.72%, 97.99% and 99.00% in 3 h. Higher dye removal at higher concentration of H_2O_2 is due to availability of more oxidants.

4. CONCLUSIONS

Fly ash based sodium zeolite catalyst was found very effective to treat cango red bearing wastewater. COD and color removal depended on pH. Highest 99.52% dye removal and 88% COD removal found at pH 2, 70 ^{0}C, 4 g catalyst and 4 ml H_2O_2 dm^{-3} dye solution.

Among the catalytic wet oxidation, catalytic thermolysis and wet oxidation, the catalytic wet oxidation was found to most effective. For catalytic wet oxidation in the temperature range 60 to 90^{o}C, 70^{o}C was found to most effective. The dye removal was found to increase with increase in H_2O_2 concentration.

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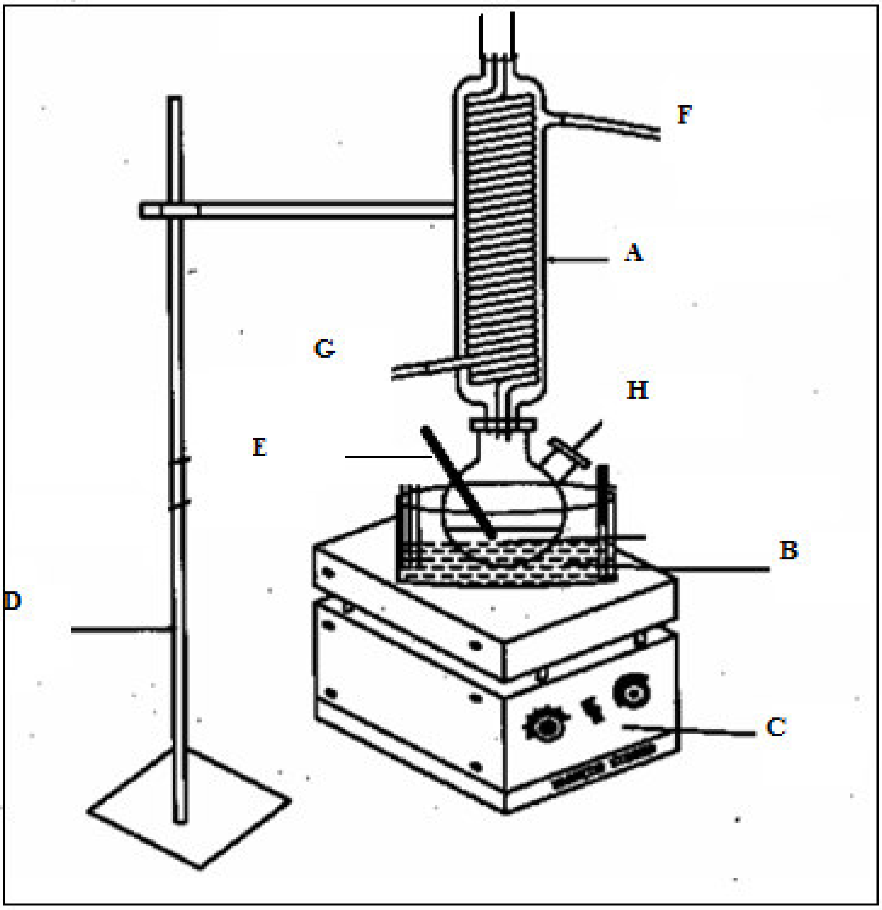
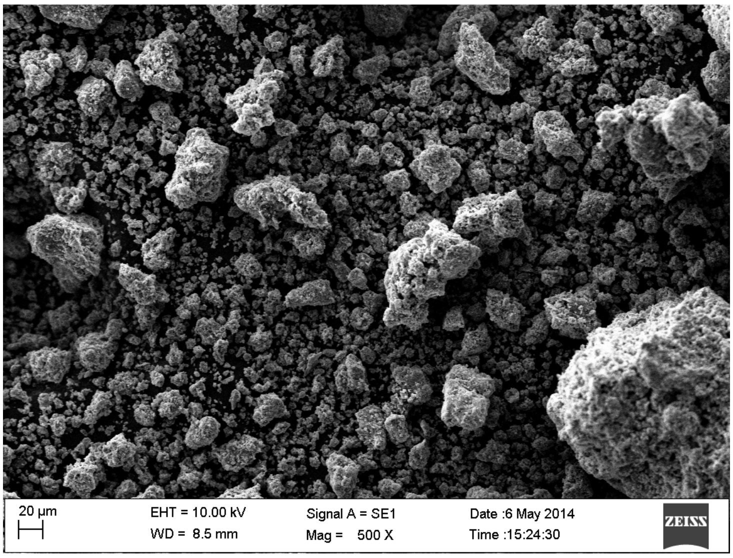


Figure 1: Experimental setup

(a)



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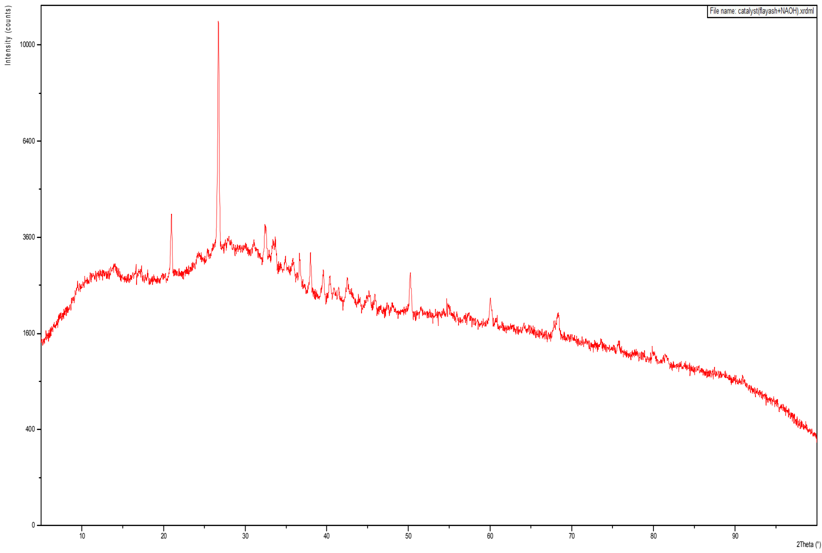
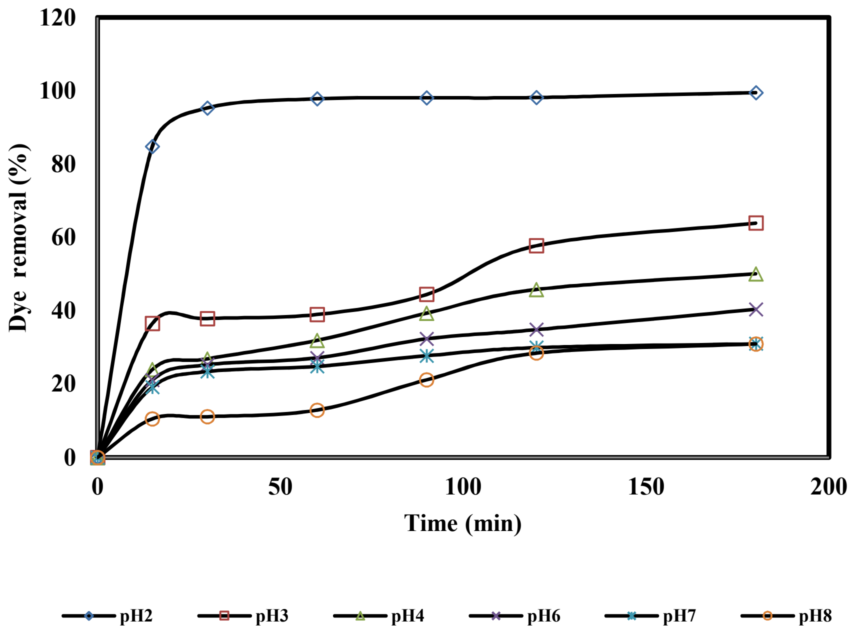


Figure 2 (a) SEM/EDX **(b)** XRD analysis of synthesized zeolite catalyst

(a)



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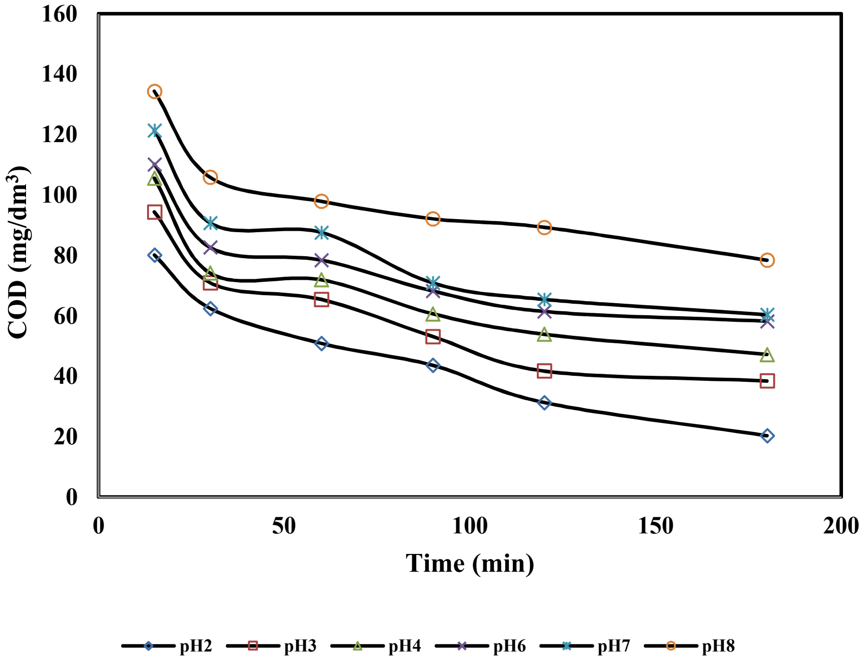


Figure 3: Effect of pH on (a) dye removal (b) COD removal. Temp 70ºC, dye 1 g dm^{-3}, catalyst 4 g dm^{-3}, H_2O_2 4 ml dm^{-3} dye solution.

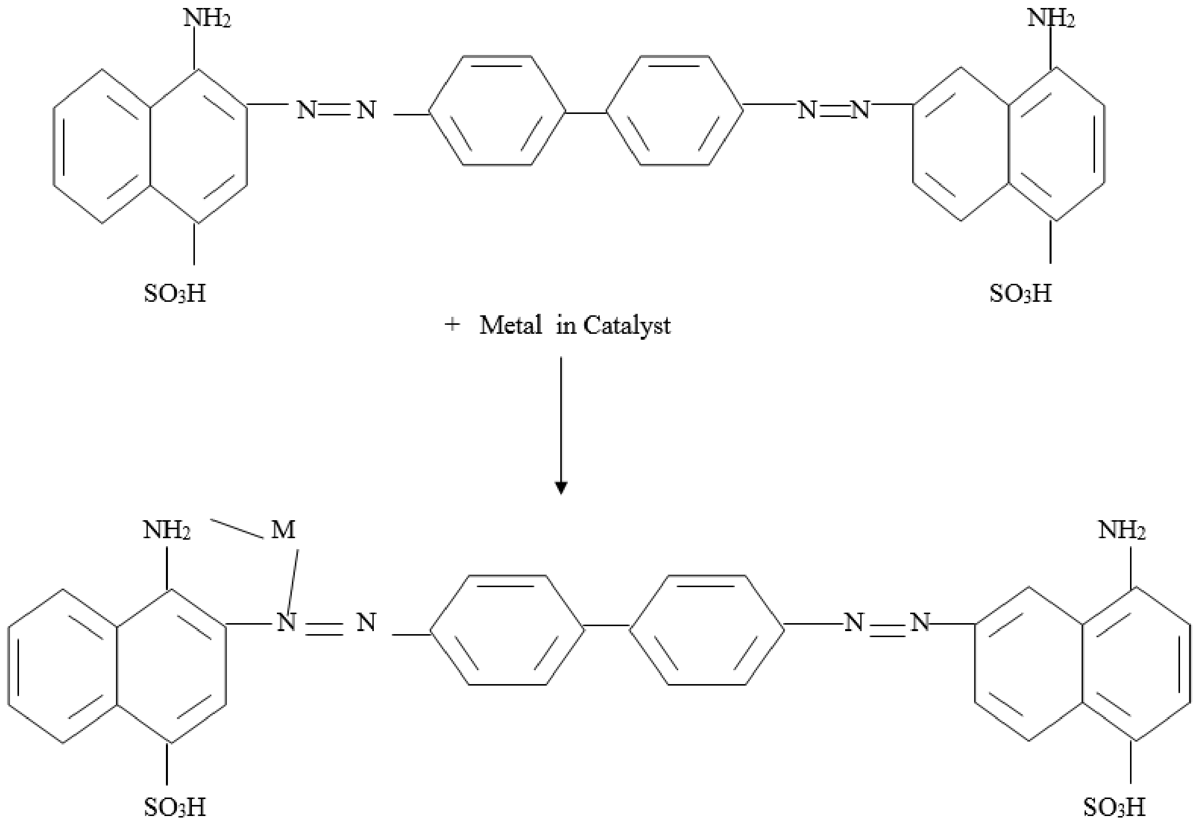
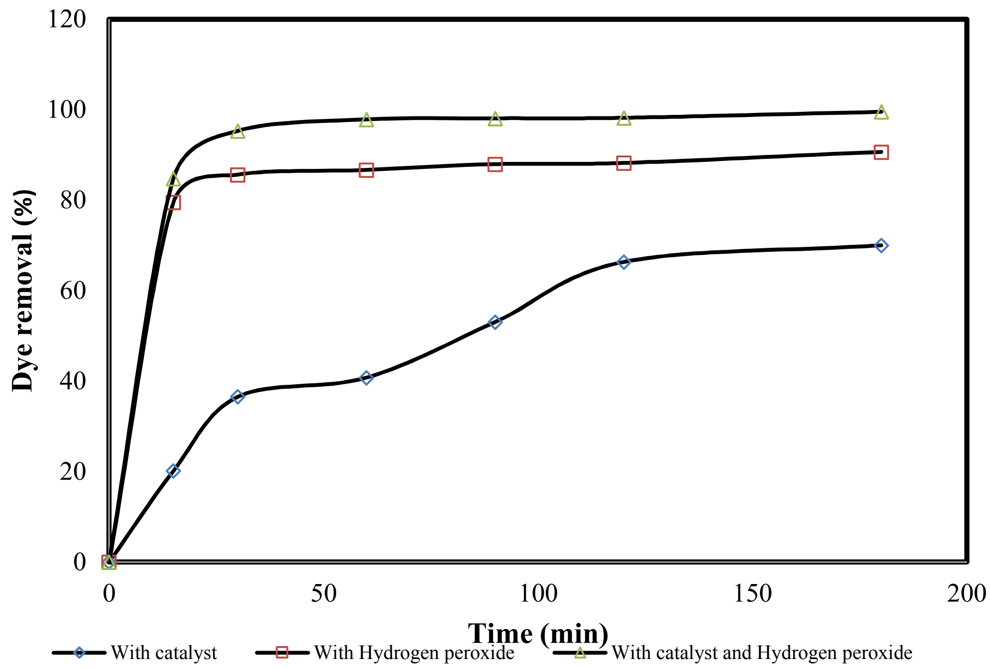


Figure 4: Structure of Congo red dye and complex with Metal

(a)



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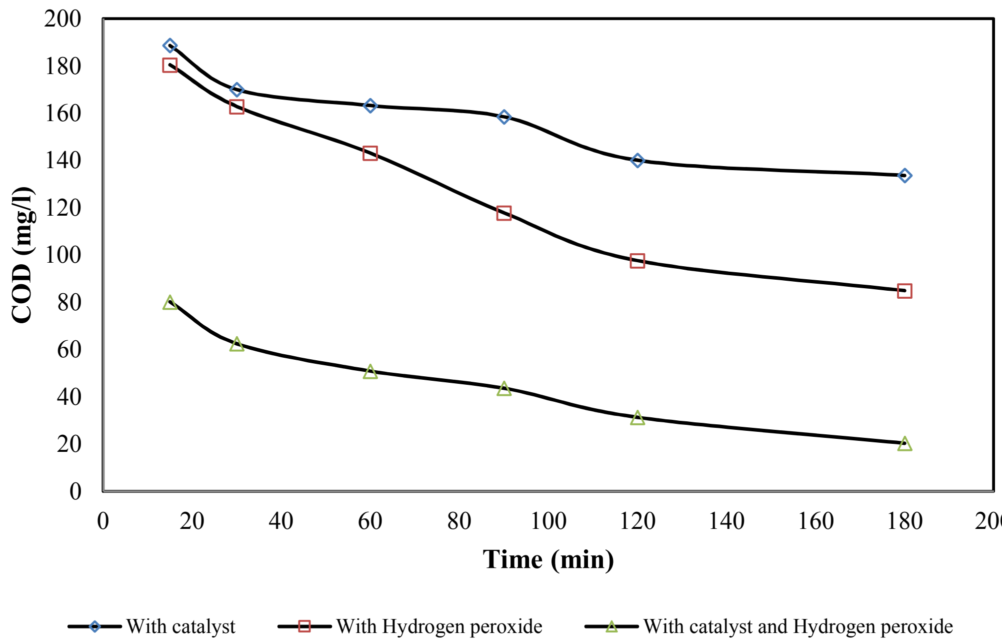
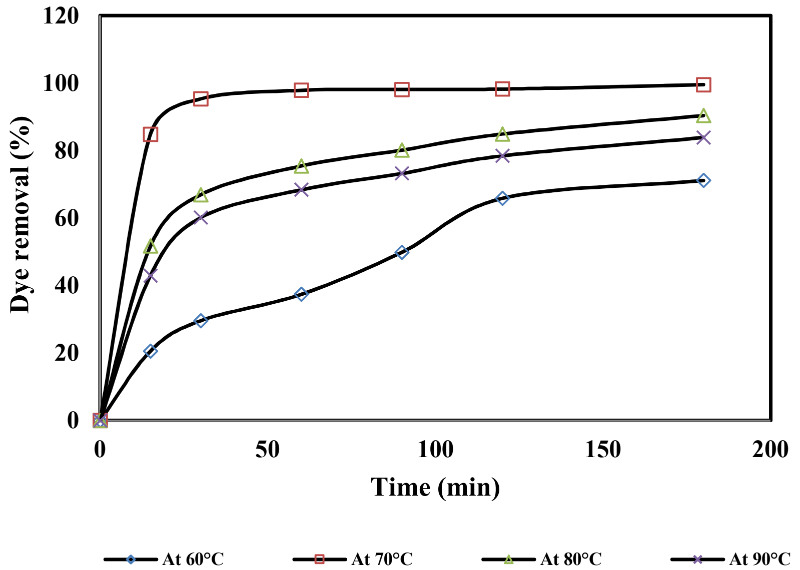


Figure 5: Treatment using catalyst, catalyst and H_2O_2 and H_2O_2 (a) dye removal (b) COD reduction. pH 2 , temp 70°C

(a)



(b)

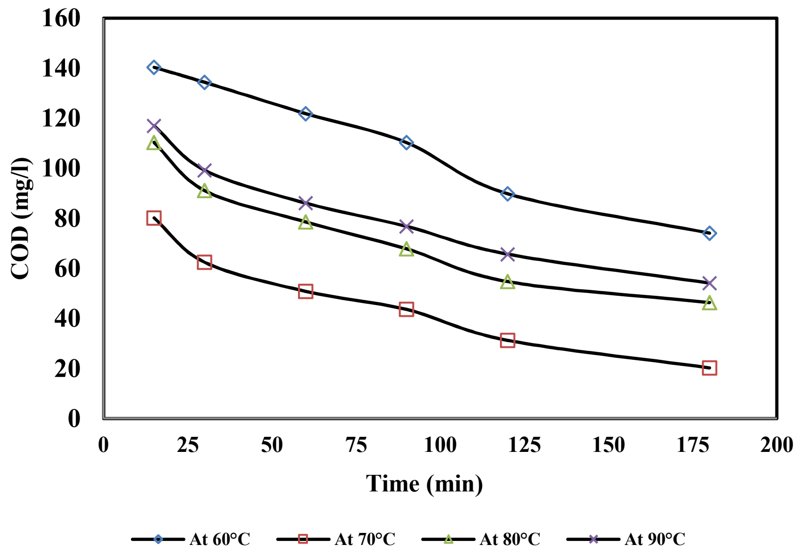


Figure 6: Effect of temperature on (a) dye removal (b) COD removal. Catalyst loading 4 g dm^{-3}, pH2

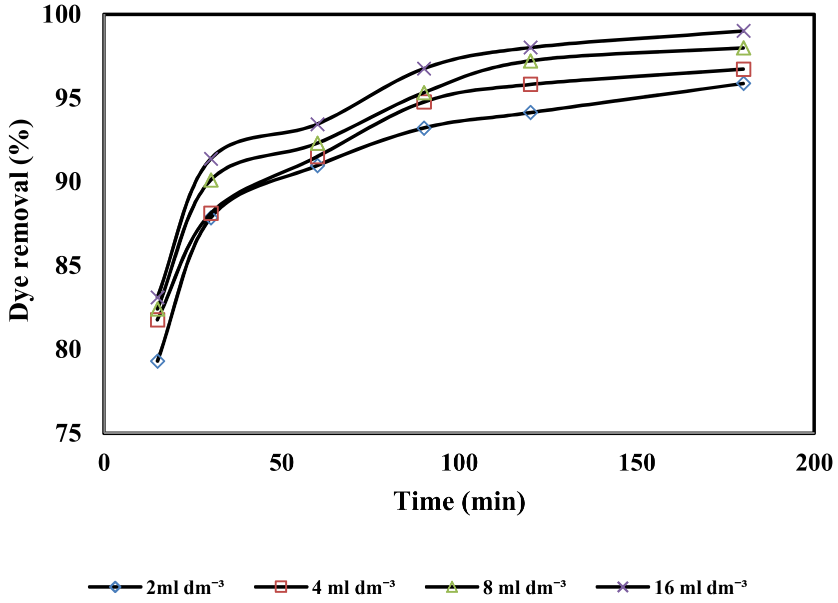


Figure 7: Effect of H_2O_2 concentration on percentage dye removal at pH 2 and 90°C.