

REMOVAL OF ORANGE II DYE FROM WATER USING ZnO AND ITS ACID TREATED FORMS

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Abstract: Catalytic wet air oxidation is one of the major alternatives for the degradation of waste water. In the present work, ZnO treated with 0.5, 0.75, 1.0N H₂SO₄ for 5 h was used as the catalyst for wet oxidation of Orange II dye in water. The catalysts were characterized by FT-IR and BET adsorption isotherm method. The oxidation was carried out at room temperature under various reaction parameters like dye concentration, catalyst loading, initial pH and temperature. The results show that the acid treated ZnO could be an effective catalyst for wet oxidation of Orange II (1.0 mg/L). The final products found were less harmful for the environment.

Keywords: ZnO; wet oxidation; Orange II; acid treatment

1. Introduction:

Textile industries release a large quantities of azo dyes into the environment [1,2]. The effluents release from these industries are usually strongly colored, and the direct discharge of the wastewater into receiving water body causes damage to both aquatic life and human beings due to their toxic, carcinogenic and mutagenic effects.[3] Color is usually the first contaminant to be recognized in wastewater. Azo, anthraquinone and indigo are the major chromophores found in commercial dyes.[4] These wastewater containing commercial dyes are danger for water body and should be remove from the same to protect aquatic life. Conventional dye wastewater treatment methods are gradually becoming inadequate to meet the requirements of a higher environmental quality. In recent years, various advanced oxidation processes such as ozonation,[5] wet air oxidation,[6] supercritical water oxidation,[7] photocatalytic oxidation,[8] electrochemical oxidation[9] and other integrated techniques[10,11] have been proposed as substitutes for the conventional treatment techniques. Nowadays, wet air oxidation method is a well-established technique of importance for wastewater treatment In catalytic wet oxidation the reaction conditions are milder than in uncatalysed wet oxidation, but high temperature (over 150°C) and high pressure (1–5 MPa) are still required.[12] Noble metal catalysts such as Ru, Pt and Rh were also proved to be reactive toward the wet oxidation of phenols and other model compounds. Mixed copper, zinc and cobalt oxide catalysts were used for the catalytic oxidation of phenol and substituted phenols, and the FeOx-MoO₃-P₂O₅ catalyst was proved to be effective for the oxidation.[13]

Metal oxides and their modified forms are one of the most important groups of catalysts for the oxidation of organic dyes. Wang et al. (2008) observed the degradation of Orange II with Au-loaded TiO₂ (Au/TiO₂) in sonocatalytic reaction and got successful degradation of color by 80 % removal of total organic carbon.[14] Li et al. (2013) degraded Methyl Orange under UV light irradiation with TiO₂ and ZnO as photocatalysts. They observed 95% conversion with TiO₂ and 96 % with ZnO.[15] Sun et al. (2014) used graphene oxide (rGO) to prepare various composites of rGO/photocatalyst of G/TiO₂, G/ZnO and G-Ta₂O₅ for the degradation of Methylene Blue.[16]

In the present work, we have used ZnO and its acid treated form as a catalyst for the wet oxidation of Orange II dye in water using different variables such as reaction time, dye concentration, catalyst load, pH of the medium and temperature. The degradation products found were less harmful than the original dye.

2. Materials and methods:

2.1. Chemicals:

The chemical used were ZnO (Merck Mumbai), H₂SO₄ (Merck Mumbai), Orange II (Merck Mumbai). All chemicals were analytical grade and used without further purification.

2.2. Preparation of catalysts:

The catalysts were prepared by treating the metal oxide with 0.5 N, 0.75 N and 1.0 N H_2SO_4 . ZnO was taken in a 500 mL conical flask and was treated with 250 mL of 0.5, 0.75, 1.0N H_2SO_4 acid for 4 h at room temperature in a batch reactor, followed by washing with distilled water till the washings become neutral. The material was dried at 373 K in an air oven for 5 h and preserved. In all, four catalysts were obtained viz., untreated ZnO (C1), 0.5 N acid treated ZnO (C2), 0.75 N acid treated ZnO (C3), 1.0 N acid treated ZnO (C4).

2.3. Preparation of stock dye solutions:

Synthetic dye solution of Orange II was used in this study without further purification. The dye used was purchased from Merck Mumbai. Standard dye solutions of 1000 mg/L were prepared as stock solution and subsequently diluted when necessary reactions were done.

2.3. Characterization of the catalysts:

The catalysts were characterized by FT-IR measurements (Perkin-Elmer Spectrum RXI, range 4000–450 cm^{-1}) using KBr self-supported pellet technique. The surface areas of the catalysts were determined by BET Adsorption isotherm method (Micromeritics Tristar Surface area and Porosity Analyzer).

3. Results and discussion:

3.1. Characterization of the catalysts:

3.1.1. FT-IR study:

Samples of untreated ZnO and that of 0.5, 0.75, 1.0N acid treated ZnO showed a characteristic FT-IR bending bands at 516, 514, 512 and 510 cm^{-1} and stretching bands at 708, 706, 706 and 704 cm^{-1} respectively (Fig. 1). These bands may be due to the bending modes of vibrations of M-O bonds.[17] By carefully examining this band, it is seen that there was a little shift of bands towards left after acid treatment. But the intensities go higher after acid treatment. There were also a broad absorption band between 3410 and 3300 cm^{-1} (3402 cm^{-1} for untreated ZnO and 3402, 3390, 3340 cm^{-1} in case of 0.5, 0.75, 1.0 N acid treated ZnO) may be attributed to O-H stretching. These O-H bonds may be due to the presence of co-ordinated/ entrapped water. Similar types of results were obtained in Muthukumaran et al. (2012) for ZnO stretching and bending frequencies.[18]

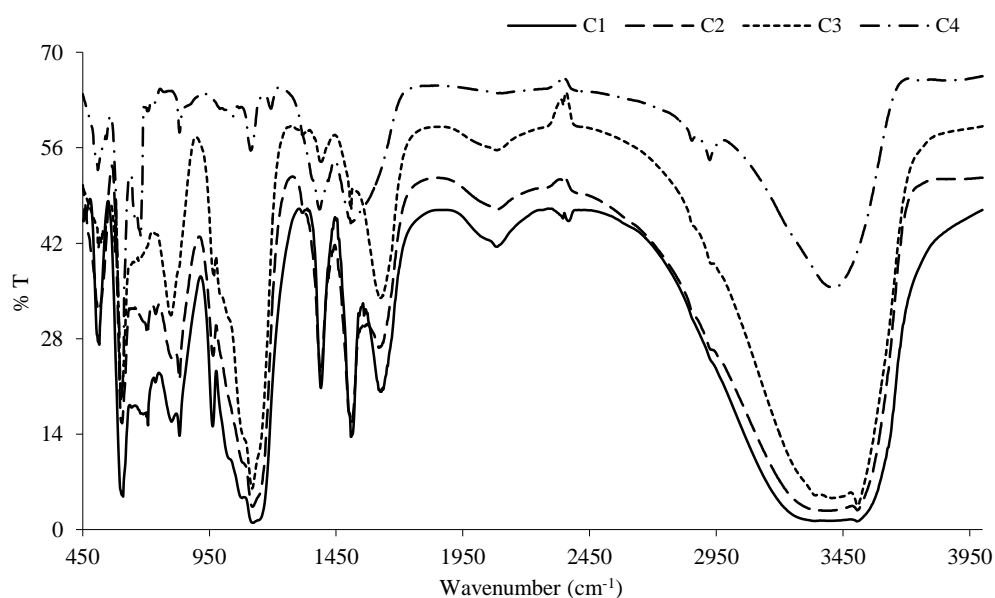


Figure 1: FT-IR bands of untreated and acid treated ZnO (C1, C2, C3 and C4).

3.1.2. BET surface area study:

The surface areas of the catalysts were determined by BET adsorption isotherm method. For the determination of the surface area of the oxides, the samples were first degassed under vacuum at 300°C for 4hr. N₂ was used as the absorption gas. After cooling the sample, the surface areas were determined. The surface areas found were 8.57, 10.01, 11.59 and 17.02 m²g⁻¹ for C1, C2, C3 and C4 catalysts. The surface areas of the catalysts were found to increase after acid treatment. The increase in surface area of the catalyst after acid treatment indicated the increase in catalytic activity of the same.

3.2. Wet Oxidation of Orange II:

3.2.1. Blank Experiment:

Before we investigated the effectiveness of ZnO and its acid treated forms as catalysts for wet oxidation of Orange II, in water (1 mg/L each), a set of blank experiments (i.e. without any catalysts) were carried out under the same conditions of temperature (room temperature), atmospheric pressure, and time interval (5 h). No measurable conversion could be observed in this case.

3.2.2. Effect of reaction time:

The wet oxidation of Orange II was first done using untreated ZnO as a catalyst, after that the oxidation was done using 0.5, 0.75, 1.0N acid treated ZnO as catalysts. The reaction were carried out in batch reactor at room temperature, atmospheric pressure, Orange II concentration of 1mg/L and catalysts load of 5.0g/L at as prepared pH for 5h. The samples were taken out at different interval of time within 15 to 300 min. It was found that the catalytic degradation of Orange II increases as time passed and after 4h the reaction become constant. The % degradation of Orange II with C1 catalyst was 68.7% while that with C2, C3 and C4 catalysts were 76.9, 78.7 and 79.5%. All of the degradation of dye with time was shown in Fig. 2.

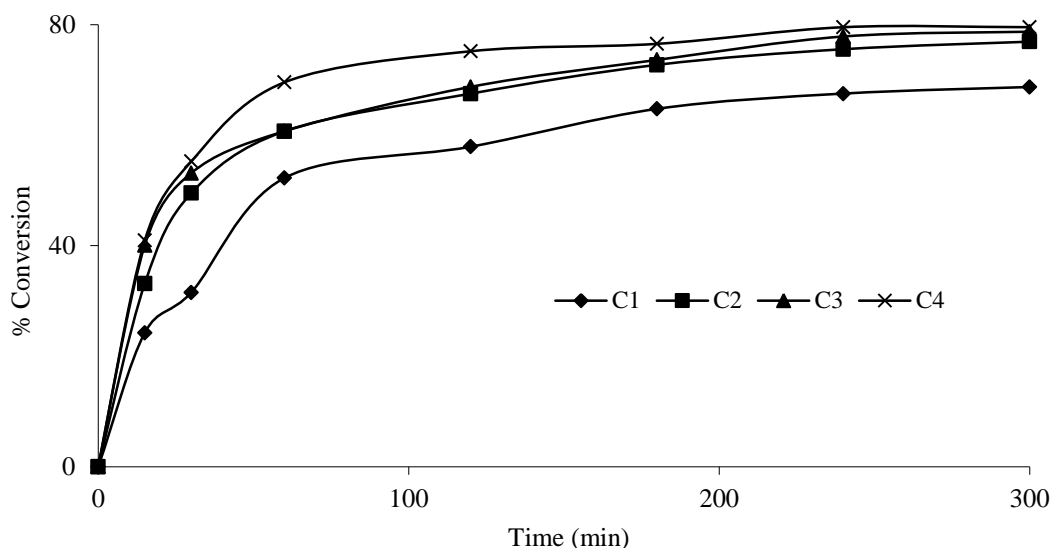


Figure 2: Effect of % Conversion with time for C1, C2, C3 and C4 catalysts.

3.2.3. Effect of reactant concentration:

The conversion at a constant catalyst load of 5.0 g/L for increasing concentrations of the Orange II had shown a decline (Fig. 3). The concentration of Orange II taken were 1, 10, 50, 100mg/L and it was found that when concentration increased from 1-100mg/L, the conversion decreased from 68.7- 12.6 % for C1 catalyst. Similarly for C2, C3 and C4 catalysts, the conversions were, 76.9- 24.7 %, 78.7- 26.7 % and 79.5- 28.0 %. Thus, when the

concentration of Orange II was increased from 1 to 10, 50, 100 mg/L in the reaction, Orange II conversion decreased. The reason may be due to as dye molecule increased there would be more competition among them for the attachment to the active site of the catalysts, resulted the decrease of dye degradation.[19]

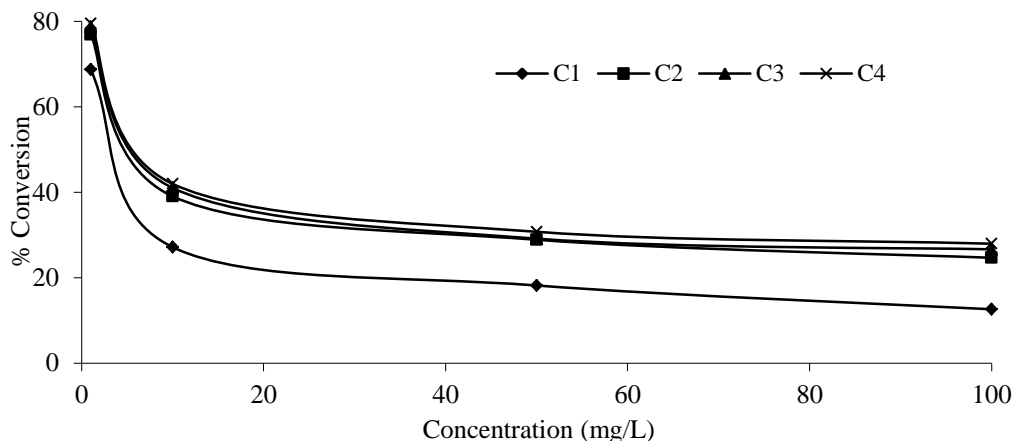


Figure 3: Effect of % Conversion with dye concentration for C1, C2, C3 and C4 catalysts

3.2.4. Effect of catalysts load:

Four different catalyst loadings of 0.5, 2.5, 5 and 7.5 g/L were used to carry out the oxidation reactions at constant reaction time of 300 min. The results were shown in Fig. 4. The catalyst load did not have much influence on the conversions. As the load increases from 0.5 to 5.0g/L the conversion gradually increases, after that the conversion remains almost same. Thus, Orange II oxidation with untreated ZnO (C1) catalyst was increased from 60.2% (with 0.5g/L) to 68.7% (with 5g/L). Similar trends were found with C2, C3 and C4 catalysts. The increase in conversion for catalyst load of 0.5-5 g/L with C2, C3 and C4 catalysts were 69.7-76.9%, 70.6-78.7% and 71.0-79.5%.

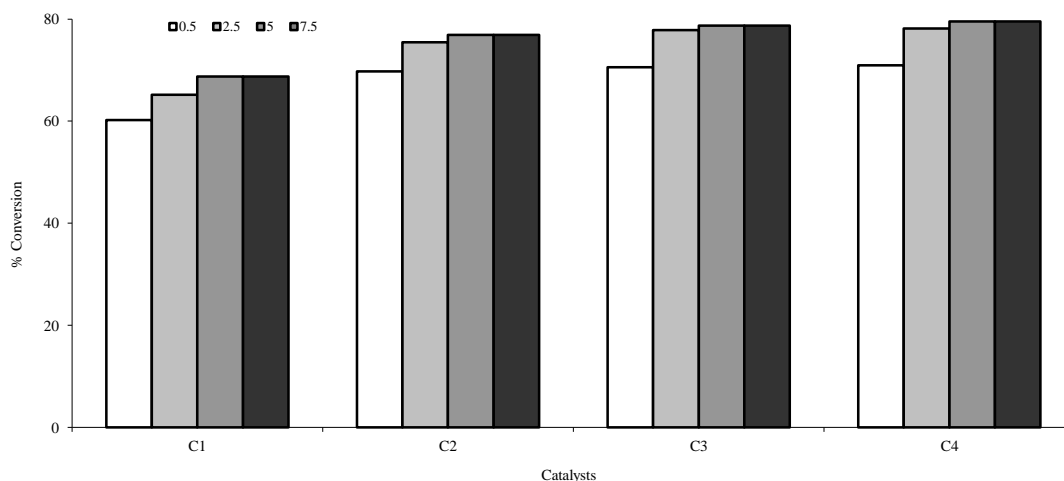


Figure 4: Effect of % Conversion with different catalyst load of C1, C2, C3 and C4 catalysts

3.2.5. Effect of pH:

The pH of the medium has important influences on the wet oxidative destruction of the Orange II. In this study the effect of pH was examined by adjusting the initial pH of the reaction mixture in the range of 2.0–8.0 (initial concentration 10mg/L, catalyst amount 5g/L). The pH of the medium was adjusted by using 0.1N HNO₃ and 0.1N NaOH. The %degradation of dye was found maximum at pH 2. When the pH of the solution was increased, the %degradation decreased and it found minimum in the basic medium i.e. at pH 8. The effect of pH

was compared with untreated ZnO and 1.0N acid treated ZnO. In both the cases the oxidation followed the same trend. The %degradation was more in the later reaction than that of former reaction. The % degradation was 42.6 - 17.8 % for untreated ZnO (C1) and 62.8 - 26.4 % for 1.0N acid treated ZnO (C4) in the pH range of 2.0 to 8.0 as shown in Fig. 5. The reason of more oxidation in acidic medium may be attributed to the presence of a large number of H⁺ ions in the acidic medium that would facilitate the transport of Orange II anions to the catalyst surface for undergoing transformation. The removal of dye was thus most effective in acidic medium and was of uncertain nature in alkaline medium. Deng et al. (2008) also found that a pH range of 3-8 is the most effective in bringing about degradation of the dye, Orange II with FeVO₄, a Fenton-like catalyst.[20]

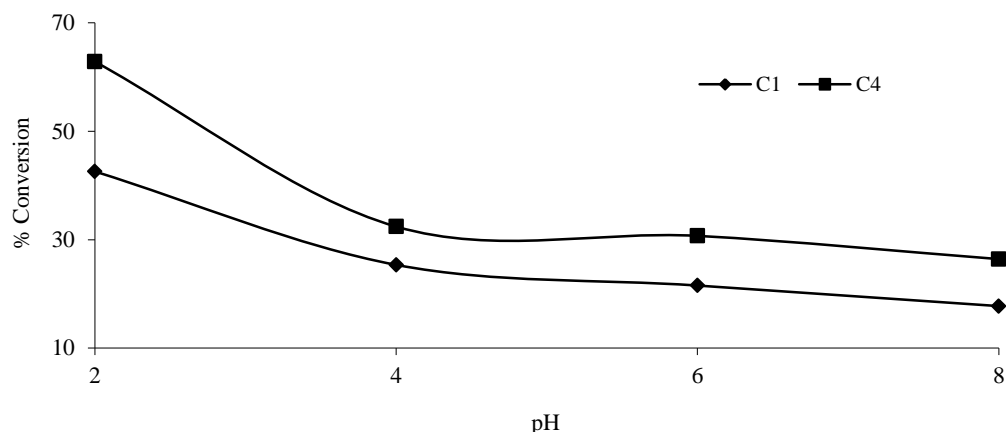


Figure 5: Effect of % Conversion with different pH of the medium for C1 and C4 catalysts

3.2.6. Effect of temperature:

All the reactions were carried out at room temperature. But, the effect of temperature was also studied by changing the temperature from 298- 313 K. Increase in temperature have shown a positive effect on the % degradation (Fig. 6). The reason may be due to increase in mobility of the dye molecule with increase in temperature.

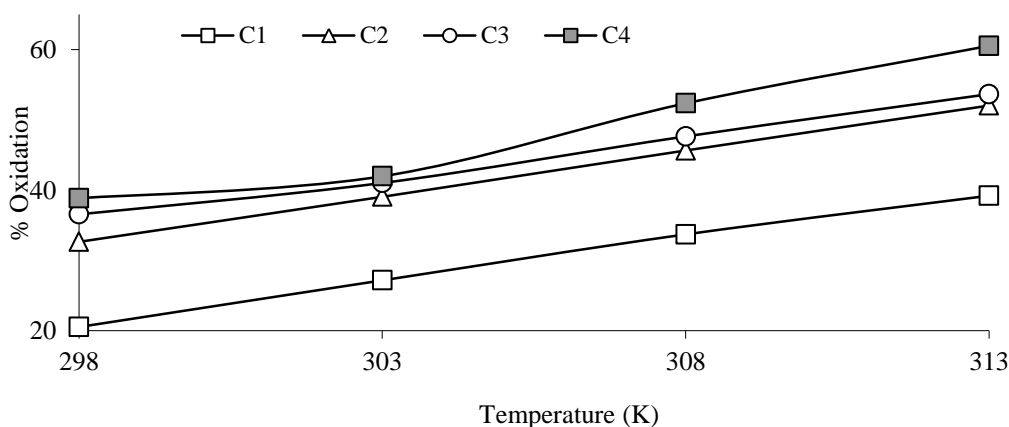


Figure 6: Oxidation of Orange II (10.0 mg/L) with ZnO (5.0 g/L of C1, C2, C3 and C4) catalysts at different temperatures (pressure 1 atm, time 5 h)

3.3. Reaction Study:

The products of the reaction were studied by GC-MS analysis (Perkin Elmer Precisely Clarus 600 C Mass Spectrometer). The products found were low molecular weight organic acids which are less harmful than the original dye, which could further be converted to CO₂ and H₂O.

4. Conclusions:

From the above discussion, it was concluded that acid treated ZnO was act as a good catalyst than that of untreated ZnO. 1.0N acid treated ZnO is more active than other catalysts. As the oxidation of the dye showed a high degradation, so this is very useful study for removal of dye in aqueous medium and the final products found were less harmful than the original one. So, ZnO act as an active catalyst for removal of Orange II dye at room temperature.

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