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Catalytic wet Oxidation of 2,4,6-trichlorophenol with Fe(III) supported ZSM5

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Abstract

The common practice of microbiological oxidation of organic pollutants in the effluents of organochemical and petroleum-based industries is not effective in mineralizing chlorinated phenols, which are persistent and toxic to organisms even at low concentrations. Effluents containing these recalcitrant organics require tertiary treatment and catalytic wet oxidation has shown tremendous promise in this regard. The use of hydrogen peroxide as the oxidizing agent in the presence of a catalyst (Catalytic Wet Peroxide Oxidation, CWPO) has emerged as a clean and effective alternative among other catalytic oxidation processes. In the present work, HZSM5 was first synthesized by hydrothermal method and was impregnated with Fe(III). The material was used as a catalyst for oxidation of 2,4,6-trichlorophenol (2,4,6-TCP) in water with or without the presence of H₂O₂. The catalyst was prepared by refluxing HZSM5 with aqueous 1M Fe(NO₃)₃ .6H₂O for 6 h. The structural features of the catalyst were determined with XRD and FTIR measurements and the amount of Fe(III) entering into ZSM5 matrix was estimated with atomic absorption spectrometry. The material was calcined at 873 K before using as a catalyst. The oxidation was carried out in a high-pressure stirred reactor at different temperatures and other process variables. As much as 69.7 % conversion could be achieved. Results showed that with increasing temperature, catalyst load and mole ratio of H₂O₂ in the feed, the oxidative conversion could be further improved both in presence of the chemical oxidant and without it. Effects of various reaction conditions, kinetics of the catalytic process and the probable mechanism of oxidation have been discussed.

Keywords: 2,4,6-TCP; catalytic wet oxidation; Fe(III)-ZSM5

1. Introduction

Phenols and their chlorinated derivatives represent one of the most abundant families of industrial toxic compounds which are resistant to biodegradation and persist in the environment for long periods.[1] The main sources of these pollutants are Petroleum and Petrochemical Industries, Chemical industries, Kraft Mills, Olive oil production etc. These pollutants have extreme toxicity to aquatic life even at concentration levels of 1 ppm or less. Due to their high toxicity and carcinogenic properties, much attention has been focused on their removal from the environment and transforming them into harmless species. [2, 3]

Microbiological oxidation as is the common effluent treatment practice in organochemical and petroleum-based industries is not effective in mineralizing chlorinated phenols, which are persistent and toxic to organisms as well as humans even at low concentrations. Effluents containing these recalcitrant organics require tertiary treatment and catalytic wet oxidation has shown tremendous promise in this regard. [3, 4]

Catalytic Wet Air Oxidation (CWAO) is a process of converting organic compounds in water to less persistent and less harmful products and ultimately to CO₂ and H₂O. Air serves as the oxidizing agent in these reactions in presence of

water. CWAO is particularly cost-effective for effluents that are highly concentrated or which contain components that are not readily biodegradable or are toxic to biological treatment systems. [4,5]

Catalytic wet peroxide oxidation (CWPO) is a liquid phase catalytic oxidation with H_2O_2 , which does not form any harmful byproduct. H_2O_2 is an eco-friendly oxidizing reagent. CPWO is suitable for low concentration wastewaters. [6,7]

Inclusion of catalysts in wet oxidation systems increases complete destruction of organic compounds and reduces the severity of the operation conditions, resulting in a substantial decrease in processing cost. [8]

The technical goal for the catalyst proposed in this work will be to achieve high oxidation activity and stability under relevant conditions with minimal leaching.

2. Materials and Method

2.1. Chemicals used

The following commercially available chemicals were used without further purification:

- (i) Sodium Silicate (Sigma)
- (ii) $Al_2(SO_4)_3 \cdot 16H_2O$ (E. Merck)
- (iii) Sulphuric acid (98% , BDH Analytical Grade)
- (iv) Tetrapropylammoniumbromide (TPABr) (HIMEDIA reagent)
- (v) $Fe(NO_3)_3 \cdot 6H_2O$ (E. Merck, Mumbai, India)
- (vi) 2,4,6-Trichlorophenol (TCP) (Merck)
- (vii) Hydrogen Peroxide (H_2O_2) (E Merck)

2.2. Synthesis of Fe(III)-ZSM5

Aluminiumsulphate (1.563g) and sulphuric acid (4.16g) were dissolved in water (58 ml) to yield solution A. 5.84 g of TPABr was added to solution of sodium silicate (46.56 g + 59 ml water) to yield solution B. The two solutions, A & B were then transferred into a Teflon-lined beaker and were stirred continuously to form a free flowing gel which had a composition of $4.37 (TPA)_2O \cdot 29Na_2O \cdot Al_2O_3 \cdot 88.80 SiO_2 \cdot 3526 H_2O$. The gel was transferred into an autoclave and was kept in an oven at 443 K under static condition. It was held at this temperature under autogenous pressure for 36h. Crystal formation was observed after this time and then the mixture was cooled to room temperature. The contents were filtered and washed with distilled water till free from anions. The residue was dried in an oven and calcined at 773 K in a muffle furnace. The samples (NaZSM5) were then preserved in a desiccator. The sodium form was treated with 1 M $(NH_4)_2NO_3$ to produce NH_4ZSM5 , which was calcined at 873K in a muffle furnace to obtain HZSM5. Fe is incorporated by refluxing HZSM5 With 1M $Fe(NO_3)_3 \cdot 9H_2O$ for 6 h, filtered, washed and dried in an oven. The material was calcined at 873 K before using as a catalyst.

2.3. Characterization

Fe(III)-ZSM5 synthesis was characterized by FT-IR measurements (Perkin-Elmer Spectrum RXI, range 4400–440 cm^{-1}) using KBr self-supported pellet technique. The percentage of Fe(III) entering into ZSM5 was determined with atomic absorption spectrophotometer (Agilent SpectraAA 240). The catalysts were further characterized by XRD

measurements (Philips Analytical, PW 1710, Cu K_α radiation) and comparing the same with known XRD patterns of ZSM5.

2.4. Wet Oxidation of 2,4,6-TCP

Catalytic oxidation was carried out in a high-pressure stirred reactor (Toshniwal Instruments, India) with equal volumes (25 mL each) of the reactant (2,4,6-TCP: 2×10^{-3} M) and H₂O₂ (2×10^{-3} M), catalyst load of 2 g/L at 353 K under an autogenous pressure of 0.2 MPa and stirrer speed of 180 rpm for 6 h. The reactants were mixed together at room temperature, introduced into the reactor and then the heating was started to obtain the desired temperature. When evaluating the effects of a particular variable, appropriate changes were made in the values of the variable. When no H₂O₂ was used, the total volume was kept at 50 mL. After the reaction was over, the mixture was centrifuged (Remi Research Centrifuge, R24) and the unconverted reactant was estimated in the supernatant layer spectrophotometrically (Hitachi UV-visible U3210).

3. Results and discussion

3.1. Characterization of the catalysts

3.1.1. XRD study

Peaks at $2\theta = 7.4^\circ$ ($d = 10.8 \text{ \AA}$) and 23.2° ($d = 4.18 \text{ \AA}$) in the XRD pattern are characteristics of ZSM5.

XRD pattern of the modified HZSM-5 completely matched with that of the parent HZSM-5, which indicates that the modification has no obvious effect on the parent zeolite structure. There was also no new phase formation during heat treatment and zeolite modification. The XRD pattern of the modified zeolites indicates that the zeolite structure remains intact after loading metals on to HZSM-5. No peaks related to the metals were found from the diffractograms. The XRD patterns are shown in the fig.1.

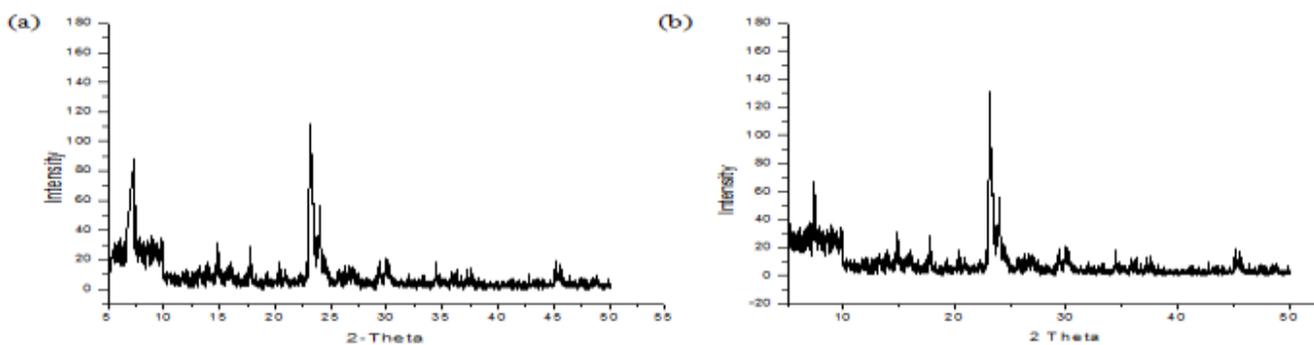


Fig1: XRD pattern for (a) HZSM5 and (b) Fe(III)-ZSM5

3.1.2. FT-IR study

The FTIR analysis (fig.2) shows bands at 1110.3 cm^{-1} for ZSM5 and 1089.28 cm^{-1} for Fe(III)ZSM5 (asymmetrical stretching), 615 cm^{-1} for ZSM5 and 766 cm^{-1} for Fe(III)ZSM5 (symmetric stretching), 482 cm^{-1} for ZSM5 and 464 cm^{-1} for Fe(III)ZSM5 (bending vibration) of (Si, Al)O₄. The broad band at 3446.2 cm^{-1} for ZSM5 and 3465 cm^{-1} for Fe(III)ZSM5 correspond to the stretching vibration of -OH. The band around $\sim 1640 \text{ cm}^{-1}$ (H₂O bending) indicates presence of adsorbed water.

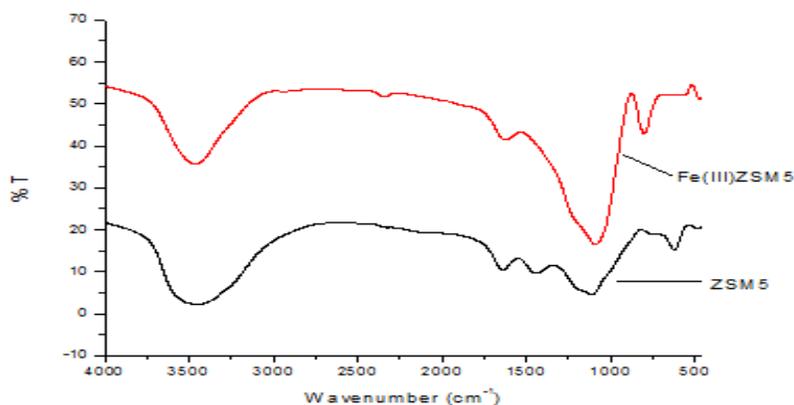


Fig1: XRD pattern for ZSM5 and Fe(III)-ZSM5

3.1.3. AAS measurement

AAS measurement shows that Fe in Fe(III)ZSM5 is 2.68 mg g^{-1} .

3.2. Wet oxidation of 2,4,6-TCP

3.2.1. Blank Experiment

Before investigating the effectiveness of the catalyst for wet oxidation of 2,4,6-TCP in water ($2 \times 10^{-3} \text{ M}$ 2,4,6-TCP), a set of blank experiment were carried out for the following system.

- (i) Reaction without catalyst and H_2O_2
- (ii) Reaction with H_2O_2 (mole ratio 1:1) and without catalyst
- (iii) Reaction without H_2O_2 and with catalyst (2 gL^{-1})
- (iv) Reaction with H_2O_2 (mole ratio 1:1) and HZSM5 as catalyst (2 gL^{-1})

Under the same condition of temperature and pressure and time interval (5h), no measurable conversion were observed for (i) and (iii), however, a small amount of decomposition observed in (ii) (7.6%) and (iv) (19.4%) due to presence of H_2O_2 .

3.2.2. Effect of Reaction time

In the time interval of 30-300 min 36.1 to 69.9% conversion could be observed. The equilibrium time was found to be 210 min.

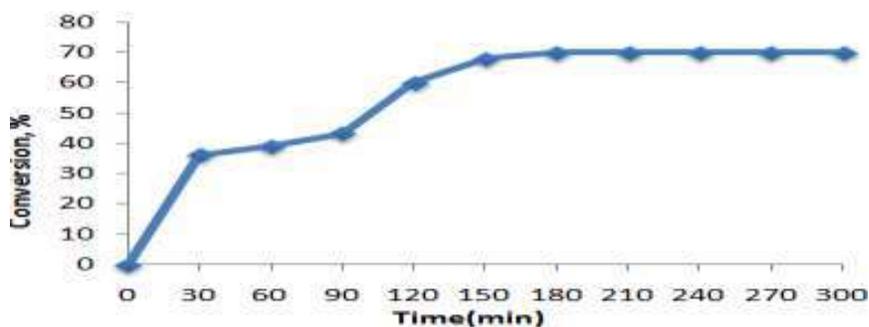


Fig3: Effect of reaction time on oxidation of 2,4,6-TCP

3.2.3. Effects of concentration

When the concentration of reactants were increased from 2×10^{-4} M to 12×10^{-4} M keeping the concentration of H_2O_2 constant in the reaction mixture, the conversion comes down. When there is a large no of 2,4,6-TCP molecules in the liquid phase, their transport to and adsorption on the catalyst surface will be competing one another.

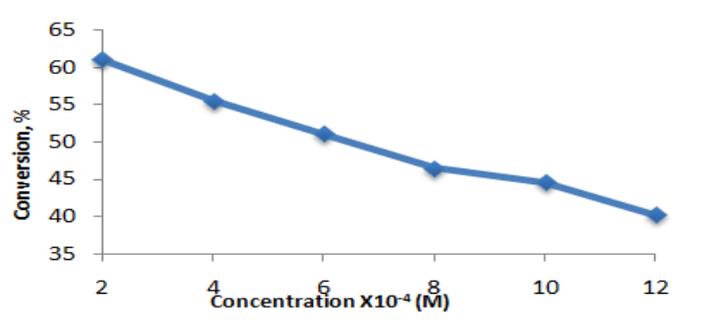


Fig3: Effect of reactant concentration on oxidation of 2,4,6-TCP

3.2.4. Effect of Catalyst load

Five different catalyst loadings of 2, 4, 6, 8 and 10 g/L were used to carry out the oxidation reactions at constant reaction time of 300 min and reactant: H_2O_2 mole ratio of 1:1. The results (Fig. 4) show that the catalyst load did not have much influence on the conversion.

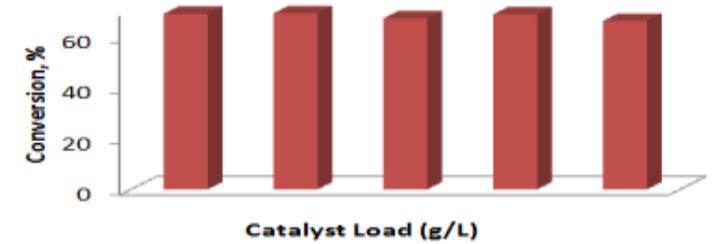


Fig.4: Effect of catalyst load on oxidation of 2,4,6-TCP

3.2.5. Effect of mole ratio of the reactants

To investigate the effects of increasing amount of H_2O_2 , the mole ratio of hydrogen peroxide and the reactant was increased from 1:1 to 20:1 with respect to H_2O_2 for a constant reaction time of 300 min at catalyst load 2 g/L (Fig.5). It was obvious that a large excess of H_2O_2 did not particularly help the conversion. At the comparatively high temperature H_2O_2 itself may undergo some amount of decomposition aided by the presence of the catalyst. Such decomposition has been recognized as a factor determining the overall rate of reaction as well as the product yield.

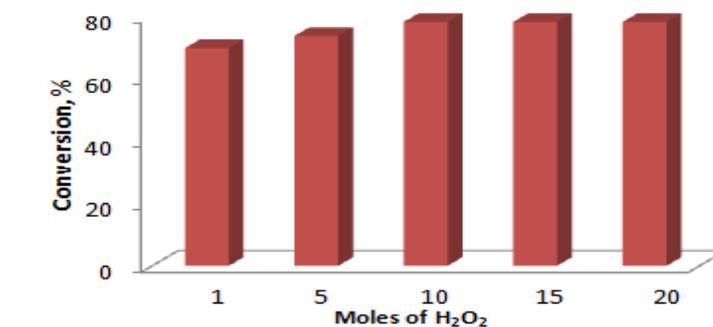


Fig.5: Effect of catalyst load on oxidation of 2,4,6-TCP

4. Conclusion

Incorporation of transition metal Fe (III) into ZSM5 could convert it into a very active catalyst for treating water contaminated with 2,4,6-trichlorophenol. The results of the present study shows that the conversion of 2,4,6-TCP increases smoothly with increase in the reaction time from 30 to 300 min. A small amount of catalyst (2g/L) was sufficient for maximum oxidative destruction of 2, 4, 6-TCP in water. The main advantage of the present work is that 2,4,6-TCP could be oxidized to harmless end products which do not have persistent nature and are likely to undergo complete mineralization.

References

- [1]. M. Pera-Titus, V. Garcya-Molina, M.A. Banos, J. Gimenez, S. Esplugas, Degradation of chlorophenols by means of advanced oxidation processes: a general review, *Appl. Catal. B: Environ.* 47 (2004) 219–256.
- [2]. S. Sabhi, J. Kiwi, Degradation of 2,4-dichlorophenol by immobilized iron catalysts, *Water Res.* 35 (2001) 1994–2002.
- [3]. R. Bauer, G. Waldner, S. Hager, S. Malato, P. Maletzky, The photo-Fenton reaction and the TiO₂/UV process for wastewater treatment—novel developments, *Catal. Today* 53 (1999) 131–144.
- [4] J. Arana, E. Tello-Rendon, J.M. Dona-Rodriguez, C. Valdes do Campo, J.A. Herrera-Melidan, O. Gonzalez-Diaz, J. Perez-Pena, Highly concentrated phenolic wastewater treatment by heterogeneous and homogeneous photocatalysis: mechanism study by FTIR-ATR, *Water Sci. Technol.* 44(2001) 229–236.
- [5] R.-A. Doong, R.A. Maithreepala, S.-M. Chang, Heterogeneous and homogeneous photocatalytic degradation of chlorophenols in aqueous titanium dioxide and ferrous ion, *Water Sci. Technol.* 42 (2000) 253–260.
- [6] S. Verenich, A. Laari, M. Nissen, J. Kallas, Combination of coagulation and catalytic wet oxidation for the treatment of pulp and paper mill effluents, *Water Sci. Technol.* 44 (2001) 145–152.
- [7] F.W. Wiese, H.C. Chang, R.V. Lloyd, J.P. Freeman, V.M. Samokyszyn, Peroxidase-catalyzed oxidation of 2,4,6-trichlorophenol, *Arch. Environ. Contam. Toxicol.* 34 (1998) 217–222.
- [8] Elisa Leyva, Ismael Crispin, Edgar Moctezuma, and Socorro Leyva, Selective chemical oxidation or reduction of chlorophenols with potassium nitrosodisulfonate, *ARKIVOC* 2003 (xi) 203-212.