

Fe (III)-ZSM5 AS AN ENVIRONMENT-FRIENDLY CATALYST TO OXIDIZE 2, 4, 6-TRICHLOROPHENOL IN AQUEOUS SOLUTION

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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 1 M Fe (NO₃)₃·6H₂O for 6 hr. 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.

Key words: 2,4,6-TCP, Catalytic wet oxidation, Fe(III)-ZSM5.

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 periods¹. 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 is the common effluent treatment in practice for 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 H₂O₂, which does not form any harmful byproduct. H₂O₂ is an eco-friendly oxidizing reagent. CWPO 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 cost⁸.

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.

EXPERIMENTAL

Materials and method

Chemicals used

The following commercially available chemicals were used without further purification.

- (i) Sodium Silicate (Sigma)
- (ii) Al₂(SO₄)₃.16H₂O (E. Merck)
- (iii) Sulphuric acid (98%, BDH Analytical Grade)
- (iv) Tetrapropylammoniumbromide (TPABr) (HIMEDIA reagent)
- (v) Fe(NO₃)₃.6H₂O (E. Merck, Mumbai, India)
- (vi) 2,4,6-Trichlorophenol (TCP) (Merck)
- (vii) Hydrogen Peroxide (H₂O₂) (E Merck)

Synthesis of Fe (III)-ZSM5

Aluminium sulphate (1.563 g) and sulphuric acid (4.16 g) 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. 29 Na₂O. Al₂O₃ 88.80 SiO₂.3526 H₂O. 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 36 hr. 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 (NH₄)₂NO₃ to produce NH₄ZSM5, which was calcined at 873 K in a muffle furnace to obtain HZSM5. Fe is incorporated by refluxing HZSM5 With 1 M Fe(NO₃)₃.9H₂O for 6 hr filtered, washed and dried in an oven. The material was calcined at 873 K before using as a catalyst.

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 SpectrAA 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.

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 H_2O_2 (2×10^{-3} M), catalyst load of 2 g/L at 353 K under autogenous pressure of 0.2 MPa and stirrer speed of 180 rpm for 6 hr. 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 H_2O_2 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).

RESULTS AND DISCUSSION

Characterization of the catalysts

XRD study

Peaks at $2\theta = 7.4^\circ$ (d 10.8 Å) and 23.2° (d 4.18 Å) 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 indicate 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 Fig. 1.

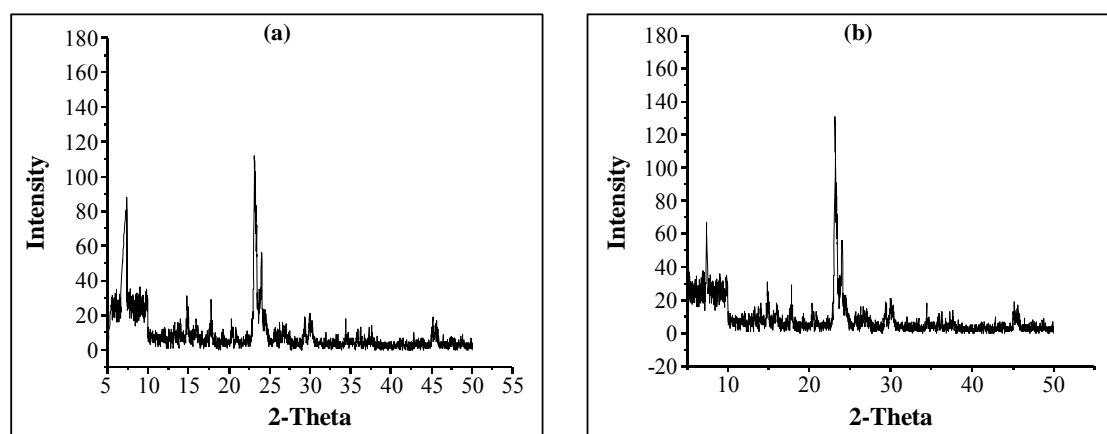


Fig. 1: XRD pattern for (a) HZSM5 and (b) Fe(III)-ZSM5

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 $(\text{Si}, \text{Al})\text{O}_4$. The broad bend at 3446.2 cm^{-1} for ZSM5 and 3465 cm^{-1} for Fe(III) ZSM5 correspond to the stretching vibration of $-\text{OH}$. The band around $\sim 1640 \text{ cm}^{-1}$ (H_2O bending) indicates presence of adsorbed water.

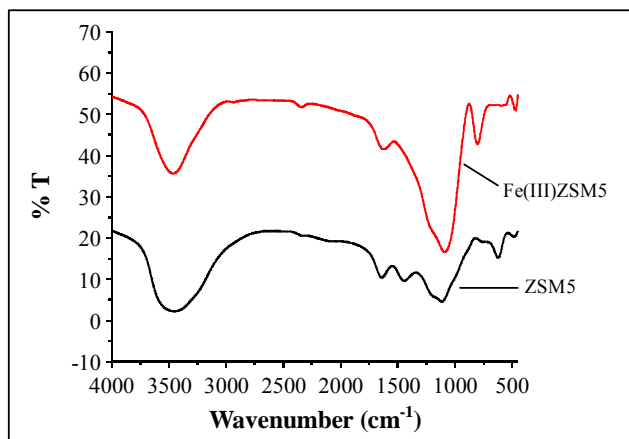


Fig. 2: XRD pattern for ZSM5 and Fe(III)-ZSM5

AAS measurement

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

Wet oxidation of 2, 4, 6-TCP

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 (5 hr), 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 .

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.

Effects of concentration

When the concentration of reactants were increased from $2 \times 10^{-4} \text{ M}$ to $12 \times 10^{-4} \text{ M}$ keeping the concentration of H_2O_2 constant in the reaction mixture, the conversion comes down. When there is a large number of 2,4,6-TCP molecules in the liquid phase, their transport to and adsorption on the catalyst surface will be competing one another.

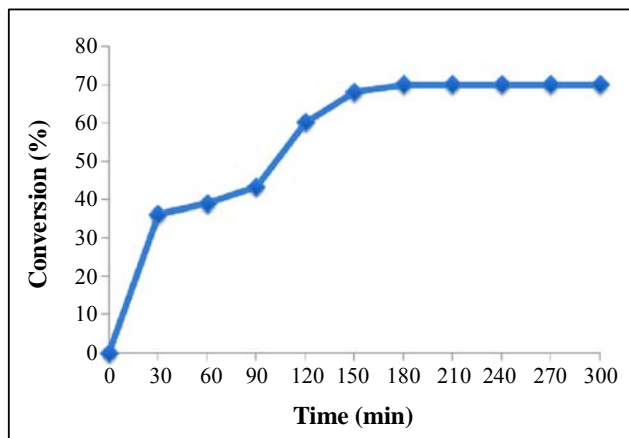


Fig. 3: Effect of reaction time on oxidation of 2, 4, 6-TCP

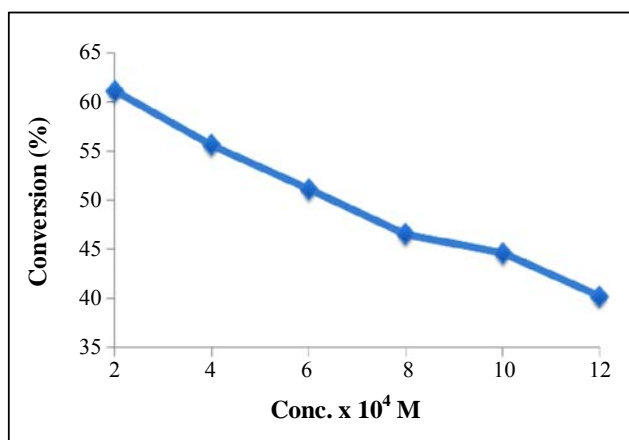


Fig. 4: Effect of reactant concentration on oxidation of 2, 4, 6-TCP

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: H₂O₂ mole ratio of 1:1. The results (Fig. 5) show that the catalyst load did not have much influence on the conversion.

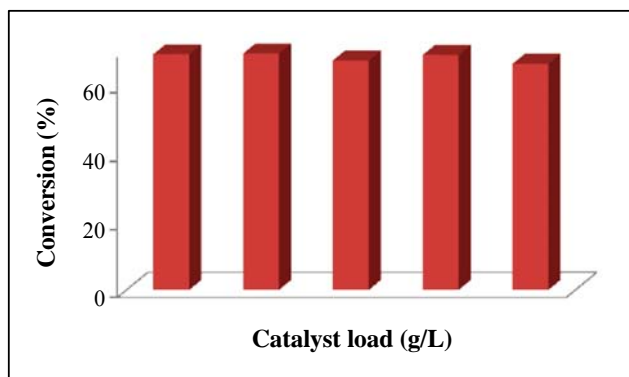


Fig. 5: Effect of catalyst load on oxidation of 2, 4, 6-TCP

Effect of mole ratio of the reactants

To investigate the effects of increasing amount of H₂O₂, the mole ratio of hydrogen peroxide and the reactant was increased from 1:1 to 20:1 with respect to H₂O₂ for a constant reaction time of 300 min at catalyst load 2 g/L (Fig. 6). It was obvious that a large excess of H₂O₂ did not particularly help the conversion. At the comparatively high temperature H₂O₂ 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.

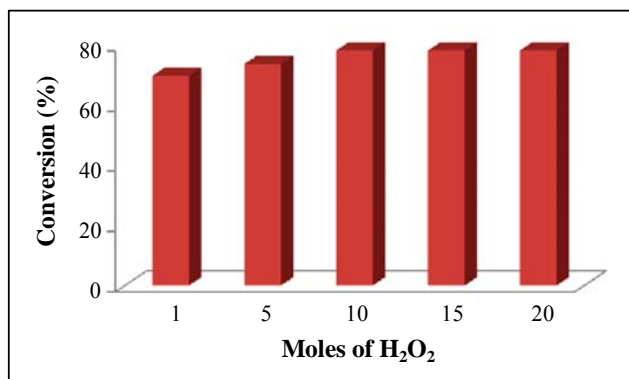


Fig. 6: Effect of catalyst load on oxidation of 2, 4, 6-TCP

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 show 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 (2 g/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.

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