Catalytic wet oxidation of phenol and its derivatives with Fe$_2$O$_3$ and MnO$_2$

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Wet oxidation of phenol, 2-chlorophenol, 4-chlorophenol and 2-nitrophenol over iron oxide and manganese dioxide catalysts was tested in this work with or without hydrogen peroxide in the reaction mixture. Influence of factors such as catalyst load, reactant-hydrogen peroxide mole ratio, and reaction time was monitored for all the phenols. Increase in the amount of hydrogen peroxide in the feed composition resulted in a better conversion in all the cases and by using 5 – 10 moles of hydrogen peroxide for each mole of the reactant, conversion was better than 80%. The oxidation reaction was sufficiently fast except in the case of 2-nitrophenol. The wet oxidation could be carried out in air by using either iron oxide or manganese dioxide catalyst without adding hydrogen peroxide to the reaction mixture. The direct oxidation is more effective for 2-chlorophenol and 4-chlorophenol with iron oxide while manganese dioxide was more effective for phenol, 2-chlorophenol and 4-chlorophenol. In both cases, 2-nitrophenol was found to be more resistant to oxidation.

Keywords: Wet oxidation, Phenol, Chlorophenol, Nitrophenol, Iron oxide, Manganese dioxide, Hydrogen peroxide

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Phenol and its derivatives are considered as Persistent Organic Pollutants (POPs), and are listed by the USEPA as priority pollutants$^{1,3}$, which are toxic and capable of causing considerable damage to human health and the ecosystem. Catalytic processes are used for destroying such persistent and toxic organic compounds in wastewater. Phenolic pollutants enter water streams from coal gasification, coke oven batteries, oil refineries and petrochemical plants$^4$. Chlorinated compounds present in aqueous system cause severe environmental problems. Most chlorophenols are released into the environment from the plastic and pesticide industries$^1$. Nitrophenols, known to be toxic, inhibitory and biorefractory in nature are extensively used in chemical industries for the manufacture of pesticides, dyes and pharmaceuticals$^{5-7}$.

Environmental concerns have led to extensive research on the removal of harmful organic compounds from industrial waste streams$^8$. Wet oxidation is a well-established process for destroying the harmful organic pollutants$^9$ and numerous catalysts such as Fe, Mn, Zn, Cu have been tested for increasing the rate of the process. The process has either been modified or a suitable combination of processes has been used to increase the efficiency of wet oxidation. Various catalysts have been tested for decreasing the pressure and the temperature of the process$^{10-13}$. The organic load in the case of pulp mill effluent could be reduced by using heterogeneous catalysts, such as Pd/Al$_2$O$_3$, Pt-Pd(I)Ce(IV)/Al$_2$O$_3$, Fe/Mn-C, Cu/Co/Bi-C, by up to 60-80% under relatively mild conditions (423-463 K and pressure of 1-1.5 MPa). Despite these developments, wet oxidation with hydrogen peroxide has remained the most attractive process$^{14}$. The use of various catalysts is accompanied by the problem of leaching of active metals into water, which makes post-treatment necessary for metal removal. Use of hydrogen peroxide in wet catalytic oxidation processes has also been shown to bring about significant improvement in the oxidation of water pollutants.

Ferrous salts are equally efficient as catalysts in wet oxidation$^{15}$. The oxidation of organic compounds by Fenton’s reagent is gaining an increasingly important role in the development of alternative technologies for water and wastewater remediation. Advantages of Fenton’s reagent$^{16}$ over other oxidizing treatments are numerous, which include simplicity, suitability to treat a wide range of substances, no need for special equipment, etc.

The basic reaction mechanism of the Fenton oxidation system has been discussed by Haber and Weiss$^{17}$, Barb$^{et al.}$, and Yoon$ et al.$ Walling$^{19}$.
investigated the reactivity of OH to various organic substrates in the Fenton system and the fate of the resultant radical intermediates. De Laat and Gallard demonstrated the mechanistic elimination of organic pollutants at various reagent conditions, using kinetic stimulation based on the established Fenton reaction mechanism.

Transition metal oxides have been proved to be effective in the catalytic degradation of phenols, various chlorophenols and nitrophenols in wastewater. The activity and selectivity of the oxide catalysts depend upon the oxidation state of the metal ions and their co-ordination in the lattice, the surface cation - oxygen bond strength, the extent of active oxygen (both total and surface), and the morphology of the material.

The present work investigates catalytic wet oxidation of phenol, 2-chlorophenol, 4-chlorophenol, and 2-nitrophenol using two oxide catalysts, Fe$_2$O$_3$ and MnO$_2$ with or without an oxidant (H$_2$O$_2$) by varying reaction time, catalyst load and mole ratio of the reactant and the oxidant.

**Experimental Procedure**

Commercially available chemicals, phenol (E Merck, Mumbai), 2-nitrophenol (LobaChemie, Mumbai), 2-Chlorophenol (B.D.H., England), 4-Chlorophenol (B.D.H, England), H$_2$O$_2$ (E. Merck, Mumbai), Fe$_2$O$_3$ (Howard of Ilford Limited, London), and MnO$_2$ (B.D.H., England) were used without further purification. Stock solutions of the phenols and H$_2$O$_2$ of concentration $10^{-3}$ M were prepared in double distilled water and all solutions for subsequent reaction study were prepared by appropriate dilution.

The reactions were carried out in 100 mL capped Erlenmeyer flasks kept agitated in a water bath shaker (NSW, India) at room temperature (305 K) and atmospheric pressure. The total volume of the reaction mixture was kept at 50 mL. After the reaction was carried out for a particular time interval, the reaction mixture was centrifuged (Remi Research Centrifuge, R24) and the unconverted reactant was estimated in the centrifugate spectrophotometrically (Hitachi U3210) after thorough calibration.

**Results and Discussion**

**Effect of catalyst load**

A set of reactions was carried out by increasing the catalyst load (Fe$_2$O$_3$) from 10 to 70 g/L while keeping the phenol : H$_2$O$_2$ mole ratio at 1:1 and reaction time 1 h. For the range of catalyst loads, the conversion increased from 54.5 to 75.0%, which is quite remarkable (Fig. 1). The oxidative degradation of 2-CP, 4-CP and 2-NP was carried out subsequently at a constant catalyst load of 70 g/L. With MnO$_2$ as the catalyst, all reactions were carried out with a constant catalyst load of 10 g/L as it was found that this was sufficient to bring about very large conversion of phenol and its derivatives.

**Effect of mole ratio**

The oxidative degradation of phenol and its derivatives was influenced by the mole ratio of the reaction mixture. With the phenol : H$_2$O$_2$ mole ratio increasing from 1:1 to 1:5, the degradation was enhanced from 52.4 to 84.1% at constant reaction time of 1 h and Fe$_2$O$_3$ load of 70 g/L (Fig. 2). The conversion of 2-chlorophenol was only 31.3% when the mole ratio was 1:1, but the conversion increased to 82.0% when the mole ratio was 1:5 and to 88.0% when the mole ratio was 1 : 10. The conversion of 4-chlorophenol was 85.3% with a mole ratio of 1:1 and was 97.4% with a mole ratio of 1:10. For 2-nitrophenol, highest conversion of 95.1% was obtained for the mole ratio 1:10 although the conversion was very high (78.0%) even with the mole ratio 1:1. Thus, the amount of H$_2$O$_2$ in the reactant feed has profound influence, particularly, on conversion of phenol and 2-chlorophenol. The influence was relatively small in case of
4-chlorophenol and 2-nitrophenol which give ~80% conversion even with a 1:1 reactant mixture. It is significant that as much as 85% conversion could be obtained with an equimolar mixture of 4-chlorophenol and hydrogen peroxide.

With MnO₂ as the catalyst (load 10 g/L), phenol: H₂O₂ mole ratio was varied from 1:1 to 1:10 at constant reaction time of 2 h. When the mole ratio was increased, conversion of phenol to its oxidative degradation products also significantly increased and the total conversion improved from 60.5 to 94.4% (Fig. 3). In the same mole ratios, 2-chlorophenol conversion was only 92.1 to 95.2% with a reaction time of 2.5 h. The reactant mole ratio thus has very little effect when MnO₂ was the catalyst and there is no need for using a large excess of H₂O₂ to bring out the desired degradation. In case of 4-chlorophenol oxidation, MnO₂ behaved in a way very similar to that of Fe₂O₃ catalyst. Conversion to the extent of 85.1 to 97.2% was possible with MnO₂ load of 10 g/L (reaction time 2 h). The mole ratio has very clear trend of influence on oxidative conversion of 2-nitrophenol. A large excess of hydrogen peroxide in the reaction mixture favours degradation of 2-nitrophenol in such a way that the conversion increased from 48.0 to 89.3% as the ratio of 2-nitrophenol and hydrogen peroxide increased from 1:1 to 1:10.

**Effect of reaction time**

Reaction time had considerable influence in all the cases. The conversion of phenol was quite reasonable at 37.8% even when the reaction time was only 15 min for a reactant feed of phenol : H₂O₂ in the mole ratio of 1:1 and Fe₂O₃ load of 70 g/L (Fig. 4). The conversion increased to 57.8% after 60 min and then it remained constant with further increase in reaction time. For 2-chlorophenol, conversion enhanced from 62.5 to 75.8% in the time interval of 15 to 120 min (reactant molar ratio of 1:1, catalyst load of 70 g/L). It is remarkable that as much as 62.5% conversion could be achieved just after 15 min. The reaction thus is very fast initially, but slows down later. For an equimolar mixture of 4-chlorophenol and H₂O₂, the conversion of the hydrocarbon increased....

Fig. 2—Effect of mole ratio of feed (H₂O₂ : reactant) on conversion at 305 K with Fe₂O₃ (70 g/L, 1 h) as the catalyst.

Fig. 3—Effect of mole ratio of feed (H₂O₂ : reactant) on conversion at 305 K with MnO₂ (10 g/L, 2 h) as the catalyst.

Fig. 4—Influence of reaction time on conversion at 305 K with Fe₂O₃ (70 g/L) as the catalyst (Reactant : H₂O₂ 1:1 excepting 2-NP when the ratio was 2:1).
from 78.6 to 95.7% as the reaction time was changed from 15 to 60 min. Although the degradation did not increase any further if the reaction was carried out for a longer time, it is clear that almost complete elimination of 4-chlorophenol in aqueous phase is possible. The reaction time, on the other hand, did not have much influence on the oxidative conversion of 2-nitrophenol. The conversion remained between 39.7 to 42.3% when the reaction time was varied from 15 to 120 min (2-nitrophenol-hydrogen peroxide mole ratio 2:1, catalyst load 70 g/L). The considerably low conversion can be attributed to the use of less hydrogen peroxide in the reaction mixture.

With MnO₂ as the catalyst (Fig. 5), oxidation with equimolar quantities of H₂O₂ was very high for 4-chlorophenol, starting with 96.6% at 15 min and increasing to 98.3% at 120 min reaction time. The conversion was in the order of 4-CP > 2-CP > phenol > 2-NP.

**Direct oxidation**

Direct oxidation carried out by agitating the reaction mixture in air with the catalyst alone was tried in a different set of experiments. H₂O₂ and other external oxidants were not used. The results are very significant.

With Fe₂O₃, a fixed load of 70 g/L was used with constant reaction time of 1 h at temperature (305 K). The conversion decreased from 42.0 to 37.3% as the phenol concentration was varied from 2.5 × 10⁻⁵ to 5.0 × 10⁻⁵ mol L⁻¹ (Fig. 6). Under similar conditions and in the same concentration range, the conversion of 2-chlorophenol decreased from 80.0 to 70.0%, that of 4-chlorophenol from 99.1 to 88.5% and that of 2-nitrophenol from 68.3 to 33.3%.

When MnO₂ was used as the catalyst (load 10 g/L) in direct oxidation at room temperature (305 K), the conversions followed a similar pattern. For phenol (concentration range 2.5 × 10⁻⁵ to 5.0 × 10⁻⁵ mol L⁻¹), the conversion changed from 91.3 to 61.2% as the concentration increased (Fig. 7). The decrease was from 80.8 to 70.0% for 2-chlorophenol, 99.1 to 81.2% for 4-chlorophenol and 43.0 to 9.7% for 2-nitrophenol in the same concentration range of 2.5 × 10⁻⁵ to 5.0 × 10⁻⁵ mol L⁻¹ at 305 K.

The above results show that wet oxidation with air is possible for phenol and its derivatives and use of a strong oxidant is not necessary. With Fe₂O₃, direct oxidation is more effective for 2-chlorophenol and 4-chlorophenol, but the extent of oxidations is much less for phenol and 2-nitrophenol. MnO₂ is a better catalyst for direct oxidation as it brings out almost complete oxidative destruction of phenol, 2-chlorophenol and 4-chlorophenol, but is less effective for 2-nitrophenol. In general, the nitro-substituted phenol was found to be more resistant to oxidation.
Huang et al. carried out oxidation of 2-CP at 303 K in the presence of a few oxides and observed only a little reduction of 2-CP (less than 4%) over granular ferrihydrite, while a percentage reduction of 9 was observed with goethite. Hematite showed the greatest catalytic effect on 2-CP degradation, causing a percentage reduction of approximately 15. These authors have found that it was mostly hydrogen peroxide which decomposed in presence of iron oxide rather than 2-CP. A much higher decomposition of phenol and its derivatives in the present work, when no hydrogen peroxide was used, is in conformity with the above work. Santos et al. have proposed a Fenton-type route for phenol oxidation over a copper catalyst in the temperature range 413-433 K through formation of catechol and hydroquinone as intermediates. They detected some oligomerization and polymerization products at low catalyst loading (4 g/L), which were finally oxidized to acid intermediates. The catalytic decomposition of phenol decreased with rising catalyst loadings (4 to 1550 g/L). Such high catalyst loadings were not used in the present work, but it was observed that the phenol decomposition in presence of hydrogen peroxide increased when iron oxide loading was increased from 10 to 50 g/L after which the decomposition remained almost constant. Phenol oxidation may take place on the surface of the catalyst (heterogeneous mechanism) or after initiation of the reaction on the catalyst surface, the reaction may proceed in the bulk of the liquid phase (heterogeneous-homogeneous mechanism), and therefore, both contributions must be taken into account in the overall conversion. In order to establish the mechanism, the dependence of the catalytic activity on the catalyst amount is usually investigated. With Ni-oxide as the catalyst, the increase in the catalyst amount was found to cause an increase in the oxidation efficiency. This indicates the reaction to proceed only on the catalyst surface, and not homogeneously. The effect of the catalyst concentration on the efficiency of the process is manifest through the active oxygen of the catalyst that takes part in the oxidation while the dissolved oxygen reoxidizes the reduced catalyst surface (reduction/oxidation mechanism). The larger is the amount of the active oxygen (the mass of the oxide catalyst), the larger is the amount of the OH radicals formed, which causes an increase in the rate of the oxidation process. The present results agree with this mechanism.

Christoskova and Stoyanova carried out a low-temperature liquid-phase oxidation of phenol over Ni-oxide and obtained a complete conversion of phenol under ordinary conditions (pH, T, catalyst amount). The identified reaction products were CO₂ (mainly) and carboxylic acids. These authors showed that the oxidation of phenol proceeded even at 288 K. A complete degradation was achieved after 90 min at 288 K and after 30 min at 338 K. In the present work, degradation of phenol and 2-nitrophenol was relatively less, but the catalysts, iron oxide and manganese oxide, could bring about almost complete conversion of 2-chlorophenol and 4-chlorophenol.

In the familiar Fenton mechanism, hydrogen peroxide (H₂O₂) reacts with Fe(II) to yield hydroxyl radicals (OH⁻) and Fe(III). Fe(III) is reduced back to Fe(II) via reaction with H₂O₂ or superoxide radical (O₂⁻). Both H₂O₂ and OH⁻ can participate in a variety of reactions, making it difficult to anticipate OH⁻ activity and rates of OH⁻ dependent reactions. They can also destroy non-target chemical species such as HCO₃⁻, other inorganic constituents, along with the target contaminants.

Conclusion

The results have indicated that oxidative degradation of phenol depended on phenol : H₂O₂ mole ratio and also on the catalyst load. 75% conversion could be achieved with a catalyst load of 70 g/L. It was found that the oxidation could be carried out without the presence of H₂O₂ with atmospheric oxygen by shaking phenol solution with the catalyst in which case MnO₂ gave better results. The results were similar for 2- and 4-chlorophenols. Oxidation of 2-nitrophenol showed very similar trends with mole ratio of the reactants, catalyst load and reaction time, but Fe₂O₃ was better than MnO₂ in bringing about catalytic destruction of 2-nitrophenol. Optimization of the reaction conditions and other relevant considerations will require systematic experiments under various environmental conditions, which are being pursued.

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