

Treatment of water containing Phenol with catalytic wet oxidation

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Abstract

The effluents from chemical, petrochemical, pharmaceutical and coal processing industries discharge toxic phenolic contaminants, viz. phenol, substituted phenols etc., into water bodies and these may cause considerable damage to the ecosystem apart from having direct and indirect impact on human health. Catalytic processes provide a pathway for destroying persistent and toxic organic compounds in water. Oxidative destruction of phenol in water is carried out in batch reactor stirring at 172 rpm at 353 K under atmospheric pressure by using commercial Fe_2O_3 and MnO_2 as catalysts in the presence of H_2O_2 . The results have been characterized in terms of percentage destruction of the phenol. MnO_2 (1 g/L) could convert 57.8 % of phenol in presence of H_2O_2 compared to only 10.2 % for Fe_2O_3 . When catalyst load was increased to 20 g/L, the conversion with both the catalysts improved (MnO_2 : 57.8 to 100 %, Fe_2O_3 : 10.2 to 19.3 %). The catalyst MnO_2 was found to be a more efficient eliminator of phenol and it could oxidize the phenol even in the absence of H_2O_2 . MnO_2 could give 100 % conversion with loadings of 6 g/L or more. The influence of catalyst load was most prominent in case of MnO_2 . When the load was increased from 1 to 6 g/L, the destruction of phenol in the presence of H_2O_2 , increased from 62.3 % to 100% with MnO_2 , but the increase was from 22.2 to 28.3 % with Fe_2O_3 at a constant reaction time of 5 h with phenol : H_2O_2 ratio was 1:10. The results are likely to have important practical application.

Keywords: phenol, catalytic wet oxidation, hydrogen peroxide, iron oxide, manganese oxide

Introduction

Phenols are widely used in domestic products such as disinfectants. Industries also used for cleaning and manufacturing certain pesticides and pharmaceuticals. So phenolic compounds are often found in industrial effluent. Discharge of these compounds without treatment may lead to serious health risks to human, animals and aquatic systems [1]. Phenol has been designated as a priority pollutant by the US Environmental Protection Agency (EPA) and the National Pollutant Release Inventory (NPRI) of Canada [2].

Phenols can cause damage to the cells of the living organisms. It has been shown that a long-time intake of phenols by experimental animals leads to changes in the skin, lungs, liver, mucous membranes, oesophagus and in the kidneys [3]. As a result of phenol penetration through the man's skin, its darkening and weakening of the muscles are observed. Lethal doses cause structural and functional changes in the brain, necrosis of the liver, and emphysema [4]. Poisoning caused by phenol compounds provoke such symptoms as headaches, dryness of the throat, dyspnoea, nausea, vomiting, diarrhoea, [5]. According to other reports phenols have cytotoxic effect on skeletal muscle and neurotoxic effect on pyramidal neurones [6].

These reasons call for the development of more feasible, effective and efficient effluent treatment technologies, which accomplish the destruction of these wastes into non-toxic or biodegradable end products.

Processes like chemical oxidation, electrochemical treatment, photo-catalytic oxidation, photo-electrochemical oxidation, and wet oxidation processes under sub- and supercritical conditions and incineration have been tested for the effective removal of the phenolic pollutants [7].

Wet Air Oxidation (WAO) has been known to be a process with well known capacity for breaking down biologically refractory compounds to simple, easily treatable materials before they are released into the environment. WAO is considered as one of the most promising and simplest techniques for partial oxidation of parent pollutants into more biologically amenable intermediates. The efficiency of aqueous phase oxidation can be largely improved by the use of catalysts, either in the form of solids or as homogeneous catalysts. Compared to conventional WAO, catalytic wet-air oxidation (CWAO) offers lower energy requirements. Current literature shows that among the wastewater treatment techniques, catalytic wet oxidation (CWO) of organic wastes in water seems to be effective and promising [8]. In the CWAO process, organics are oxidized to innocuous inorganic compounds such as CO_2 , H_2O at much lower temperature and pressures than in uncatalysed thermal process. Transition-metal oxides have proved to be active in the catalytic oxidation of phenol and its derivatives to CO_2 and H_2O [9– 11]. Phenol supercritical water oxidation (SCWO) have been reviewed in which the formation of dimers and other intermediates like single-ring compounds (e.g. hydroquinone), ring-opening products (e.g. maleic acid, glyoxylic acid, acetic acid and other organic acids) and gases (e.g. CO , CO_2) are reported[12].

The present work investigates the catalytic destruction of phenol in batch reactor at 353 K under atmospheric pressure by using Fe_2O_3 and MnO_2 , near neutral conditions ($\text{pH}\sim 7$) in the presence and absence of H_2O_2 as an oxidizing agent at different reaction times. The other variables were the ratios of phenol and H_2O_2 in the reaction mixture, influence of different catalyst load etc.

Material and methods

The chemicals used in this work were iron oxide, Fe_2O_3 (Howards of Ilford Limited, England), hydrogen peroxide H_2O_2 (E. Merck, Mumbai), phenol (E. Merck, Mumbai) and MnO_2 (BDH, England). All other chemicals used were of analytical grade and the solutions were made in double distilled, deionized water.

The reactions of phenol (1×10^{-3} M) were carried out in batch reactor stirring at 172 rpm at 353 K under atmospheric pressure. Using a UV-Visible spectrophotometer (Hitachi 3210), phenol remaining unconverted after the reaction was monitored and the percentage conversion was calculated.

Results and discussion

The experiments were carried out with catalyst amounts of 1, 2, 3, 4, 6, 8, 10 and 20 g/L at 353 K with two mole ratios of phenol : H_2O_2 of 1:1 and 1:10 when the external oxidant was used. As

the amount of catalyst increased, conversion of phenol increased in all the cases. For phenol : H₂O₂ mole ratio of 1:1 (Table 1), MnO₂ (1 g/L) could convert 57.8 % of phenol in presence of H₂O₂ compared to only 10.2 % for Fe₂O₃ . When catalyst load was increased to 20 g/L, the conversion with both the catalysts improved (MnO₂ : 57.8 to 100 %, Fe₂O₃ : 10.2 to 19.3 %). MnO₂ could give 100 % conversion with loadings of 6 g/L or more. Such high conversion was however not observed with the catalyst Fe₂O₃ even with a high load of 20 g/L. It is seen that the increase in the catalyst amount causes an increase in the oxidation efficiency. This shows that the reaction proceeds on the catalyst surface through a heterogeneous mechanism, and does not take place homogeneously.

The same reaction was done also in absence of H₂O₂ (Table 2). In absence of the external oxidant, the lowest catalyst load of 1 g/L gave very poor conversion 8.9 % with Fe₂O₃ but the same loading of MnO₂ gave 84.5 % conversion. In this case, also, MnO₂ load of 6 g/L or more brought out 100 % conversion of phenol. The improvement with increase in catalyst loading was not very significant for Fe₂O₃ catalyst, which had almost similar conversion of phenol both in presence and in absence of the oxidizing agent. The UV profiles of phenol before and after wet air oxidation (without using H₂O₂ as an external oxidant) when MnO₂ was used as the catalyst are shown in Fig. 1. It was clearly observed that with MnO₂ load of ≥ 6 g/L, 100 % conversion of phenol (10⁻³ M) could be achieved.

When phenol : H₂O₂ mole ratio was increased to 1:10, MnO₂ could convert 62.3 % of phenol in presence of H₂O₂ compared to only 22.2 % for Fe₂O₃ with a loading of 1 g/L. When the same reaction was done in absence of H₂O₂, the catalyst Fe₂O₃ (1 g/L) gave only 7.3 % conversion, less than what it achieved in presence of H₂O₂. The performance of MnO₂ (1 g/L) was better in absence of the external oxidant with a conversion of 71.8 % compared to 62.3 % conversion when the oxidant was present (reactants mole ratio 1:10).

Table 1: Effects of catalyst load on wet oxidation of phenol at 353 K (Reaction time 5 h, phenol 10⁻³ M, phenol : H₂O₂ mole ratio 1:1 when the oxidant was used)

| Catalyst load (g/L) | Percentage conversion of phenol | | | |
|------------------------|--|------------------|---|------------------|
| | In presence of H ₂ O ₂ | | In absence of H ₂ O ₂ | |
| | Fe ₂ O ₃ | MnO ₂ | Fe ₂ O ₃ | MnO ₂ |
| 1 | 10.2 | 57.8 | 8.9 | 84.5 |
| 2 | 10.9 | 69.7 | 9.7 | 84.8 |
| 3 | 11.7 | 88.4 | 10.7 | 94.2 |
| 4 | 12.8 | 96.8 | 11.2 | 98.5 |
| 6 | 13.3 | 100 | 12.3 | 100 |

| | | | | |
|----|------|-----|------|-----|
| 8 | 15.4 | 100 | 12.9 | 100 |
| 10 | 17.2 | 100 | 14.6 | 100 |
| 20 | 19.3 | 100 | 18.8 | 100 |

Table 2: Effects of catalyst load on wet oxidation of phenol at 353 K (Reaction time 5 h, phenol 10^{-3} M, phenol : H_2O_2 mole ratio 1:10 when the oxidant was used)

| Catalyst load (g/L) | Percentage conversion of phenol | | | |
|------------------------|---------------------------------|---------|------------------------|---------|
| | In presence of H_2O_2 | | In absence of H_2O_2 | |
| | Fe_2O_3 | MnO_2 | Fe_2O_3 | MnO_2 |
| 1 | 22.2 | 62.3 | 7.3 | 71.8 |
| 2 | 25.4 | 71.2 | 8.8 | 87.3 |
| 3 | 26.8 | 93.9 | 9.3 | 90.1 |
| 4 | 27.3 | 95.5 | 10.8 | 98.6 |
| 6 | 28.3 | 100 | 12.5 | 100 |
| 8 | 28.9 | 100 | 14.9 | 100 |
| 10 | 29.7 | 100 | 18.3 | 100 |
| 20 | 31.3 | 100 | 21.5 | 100 |

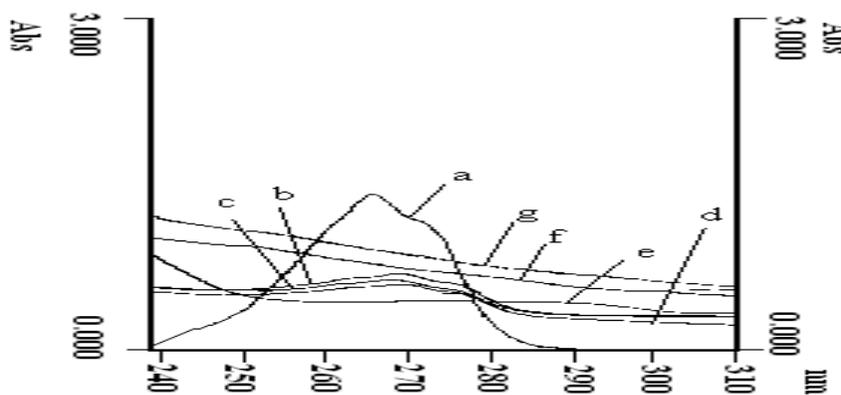


Fig. 1: UV spectrum profiles of phenol before and after wet air oxidation (in absence of H_2O_2) at 353 K in a stirred reactor (reaction time 300 min, phenol 10^{-3} M, a phenol before reaction, MnO_2 load b 1 g/L, c 2 g/L, d 3 g/L, e 4 g/L, f 10 g/L, g 20g/L).

Conclusion

The results of the present study reveal that it is possible to develop a catalytic method for the detoxification of phenol-containing waste waters. Relatively inexpensive materials like Fe_2O_3 , and MnO_2 , can have very important potential application in destroying persistent organic pollutants such as phenol in water.

Catalyst load has appreciable influence on conversion of phenol. It is found that a catalyst loading of 6 g/L with respect to MnO_2 could oxidize 100 % of phenol when phenol: H_2O_2 mole ratio is 1:1 and 1:10. Interestingly, the catalyst MnO_2 shows brings about 100 % oxidative conversion of phenol with the same loading in absence of H_2O_2 , i.e. in wet air oxidation. The main advantage of the present work is that phenol could be completely oxidized to harmless end products at room temperature. For this purpose, MnO_2 has been found to be the more active catalyst whether H_2O_2 is present or not in the reaction mixture..

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