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A Research on Catalytic Wet Oxidation of Substituted Phenols: Blank Experiments

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Abstract – The objective of the present paper was to prepare different transition metal impregnated heterogeneous catalysts using coal fly ash as a support and to use these catalysts in the wet oxidation of phenol and substituted phenols (2-chlorophenol, 4- chlorophenol, 2.4-dichlorophenol, 2,4,6-trichlorophenol, 2-nitrophenol and 4- nitrophenol). In all the reactions, hydrogen peroxide is to be used as the oxidizing agent and the reactions are to be carried out in a batch reactor under different sets of process variables. The work consisted of (i) preparation of acid and alkali treated fly ash followed by transition metal [Mn(II), Co(II), Ni(II) and Fe(III)] incorporation by impregnation via reflux method, (ii) characterization of the catalysts with spectroscopic and other techniques, (iii) study of the catalytic activity of the materials for wet oxidation of phenol, 2-chlorophenol, 4-chlorophenol, 2.4-dichlorophenol, 2,4,6-trichlorophenol, 2- nitrophenol and 4-nitrophenol using hydrogen peroxide as the oxidizing agent, (iv) optimization of the reaction conditions, (v) monitoring the products as well as Chemical Oxygen Demand of the reaction mixtures for establishing the mechanism of oxidation and (vi) studying the leaching properties of the catalysts with respect to the incorporated metal cations.

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INTRODUCTION

This chapter describes the catalytic wet oxidation of phenol with the help of catalysts prepared by impregnating transition metal ions [Mn(II), Co(II), Fe(III), Ni(II)] into fly ash. The oxidative reactions are studied varying different reaction parameters, like, (i) pH, (ii) reaction time, (iii) kinetics, (iv) catalyst load, (v) mole ratio of reactant, (vi) reactant concentration and (vii) temperature. Before evaluating the effectiveness of the prepared catalysts in the wet oxidation process, a set of blank reactions were carried out without using any catalyst and using only the parent fly ash as catalysts. The percentage of conversion of the reactant is monitored spectrophotometrically and also by COD measurement. The plausible mechanism of the oxidative degradation of phenol is proposed with the help of GC-MS analysis. After the completion of each reaction, all catalysts are thoroughly washed with distilled water to remove any reactant present on the catalyst surfaces. The catalysts can be further reused up to six cycles with not much loss its catalytic activity. Leachability of all the catalysts is tested so that there will be no secondary contamination of water by the transition metals present in the catalysts.

Phenol and substituted phenols have been identified by the US EPA (Environmental Protection Agency) as major organic pollutants due to their toxic nature towards the ecosystem and humans at very low concentrations. This prompted to set a discharge limit of 10^{-4} g/L for phenol in waste water (Chaliha et al., 2008). Yang et al (2008) have reported that the concentration of phenol in drinking water should be < 0.5 pg/L. According to Indian EPR (1986), the permissible limit of phenol in inland water was set as 10^{-3} g/L and in public sewer and marine coastal areas the limit was 5.0×10^{-3} g/L which was also reported by Gupta et al. (2006). According to Indian standard specifications for drinking water IS: 10500, 1992, the permissible limit for phenol and its related compounds is 1.0×10^{-3} mg/L beyond which it may cause objectionable taste and odour effects.

WET OXIDATION OF PHENOL

Blank experiments : The following blank experiments were carried out on wet oxidation of phenol in water in a batch process by agitating a volume of 50 mL in a 100 ml Erlenmeyer flask in a thermostatic water bath shaker:

(i) Aqueous phenol alone without any catalyst and H_2O_2,

(ii) Aqueous phenol and H_2O_2 (1:1 molar ratio) without any catalyst

(iii) Aqueous phenol with raw fly ash (O) as the catalyst (1.0 g/L)

(iv) Aqueous phenol and H_2O_2 (1:1 molar ratio) with raw fly ash (O) as the catalyst (1.0 g/L)

under the same conditions of temperature (323 K), shaking time interval (300 min) and pH (4.5) of as prepared aqueous phenol solution (5.0×10^{-3} M).

In the set (i), the conversion of phenol was not detectable – indicating that an aqueous phenol solution is quite stable and did not show any signs of degradation.

Similar results were obtained in the set (iii), which indicated that when the aqueous phenol solution was mixed with the raw fly ash under similar conditions and was agitated, no oxidative conversion was again possible. Therefore, the raw fly ash on its own did not have any catalytic properties.

In the set (ii), phenol conversion of ~ 9.2 % was measured; showing that hydrogen peroxide on its own could bring about some amount oxidation of phenol at 323 K after agitating the mixture for 300 min. It is likely that some OH radicals are generated by self-dissociation of hydrogen peroxide under the reaction conditions, bringing about a little oxidation of phenol even without the presence of a catalyst.

In the set (iv), phenol oxidation up to 20.4 % could be detected. Presence of fly ash in the reaction mixture must have some influence on hydrogen; peroxide dissociation.

WET OXIDATION OF SUBSTITUTED PHENOL

1. Wet oxidation of 2-chlorophenol

Blank experiments : Blank experiments, as shown below, were carried out on oxidation of 2-chlorophenol in water before investigating the effectiveness of the transition metal impregnated fly ash (FA) catalysts.

(v) Aqueous 2-chlorophenol alone without any catalyst and H_2O_2,

(vi) Aqueous 2-chlorophenol and H_2O_2 (1:1 molar ratio) without any catalyst

(vii) Aqueous 2-chlorophenol with raw fly ash (O) as the catalyst (1.0 g/L)

(viii) Aqueous 2-chlorophenol and H_2O_2 (1:1 molar ratio) with raw fly ash (O) as the catalyst (1.0 g/L)

under the same conditions of temperature (323 K), time interval (300 min) and pH (i.e., pH of the as prepared aqueous 2-chlorophenol solution of concentration, 5.0×10^{-3} M).

No measurable conversion was recorded in (i) and (iii) while the conversion observed in (ii) and (iv) was ~ 6.8 and 18.0 % respectively. Thus, the following inferences may be made from the blank experiments:

- Aqueous 2-chlorophenol is very stable and shows very little decomposition at 323 K even after 300 min (experiment (i)).

- The fly ash itself has poor catalytic activity (experiment (iii)) with respect to oxidation of aqueous 2-CP.

- The oxidative conversion in (ii) and (iv) was likely to be due to OH radicals produced by partial decomposition of hydrogen peroxide at the temperature of reaction, 323 K and also due to the presence of Fe_2O_3 in the fly ash materials which is likely to act as a Fenton-type catalyst.

Much more oxidation was possible in (iv) since fly ash particles were likely to adsorb OH radicals on their surface for initiation of 2-CP oxidation.

2. Wet oxidation of 4-chlorophenol

Blank experiments: Blank experiments, as shown below, were carried out on wet oxidation of 4-chlorophenol in water before investigating the effectiveness of the transition metal impregnated fly ash (FA) as catalyst:

Aqueous 4-chlorophenol alone without any catalyst and H_2O_2,

(ix) Aqueous 4-chlorophenol and H_2O_2 (1:1 molar ratio) without any catalyst

(x) Aqueous 4-chlorophenol with raw fly ash (O) as the catalyst (1.0 g/L)

(xi) Aqueous 4-chlorophenol and H_2O_2 (1:1 molar ratio) with raw fly ash (O) as the catalyst (1.0 g/L)

under the same conditions of temperature (323 K), time interval (300 min) and the pH of the aqueous 4-chlorophenol solutions (5.0×10^{-3} M) as prepared.

No measurable conversion was recorded in (i) and (iii) while the conversion observed in (ii) and (iv) was ~14.3 and 31.4 % respectively. Thus, the blank experiments show that

- Aqueous 4-chlorophenol is very stable and shows very little decomposition at 323 K (experiment (i)).

- The fly ash itself has poor catalytic activity (experiment (iii)) with respect to oxidation of aqueous 4-CP.

- The oxidative conversion in (ii) and (iv) was likely to be due to OH radicals produced by partial decomposition of hydrogen peroxide at the temperature of reaction, 323 K and also due to the presence of Fe_2O_3 in the fly ash materials which is likely to act as a Fenton's catalyst.

- Much more oxidation was possible in (iv) since fly ash particles were likely to adsorb OH radicals on their surface for initiation of 4-CP oxidation.

3. Wet oxidation of 2,4-dichlorophenol

Blank experiments : A set of blank experiments were carried out (repeated three times) before going for catalytic oxidation to find out if 2,4-dichlorophenol (2,4-DCP) in water undergoes self- oxidation without the need for any oxidant or catalyst and also to find our if the oxidant alone without a catalyst or the catalyst support (fly ash) has any oxidizing capacity for 2,4-DCP. These experiments were

(xiii) Aqueous 2,4-DCP alone without any catalyst and H_2O_2,

(xiv) Aqueous 2,4-DCP and H_2O_2 (1:1 mole ratio) without any catalyst

(xv) Aqueous 2,4-DCP with the raw fly ash (O) as the catalyst (1.0 g/L)

(xvi) Aqueous 2,4-DCP and H_2O_2 (1:1 mole ratio) with raw fly ash (O) as the catalyst (1.0 g/L)

under the same conditions of temperature (323 K), time interval (240 min) and pH (i.e., pH 6.8 of the aqueous 2,4-DCP solution as prepared of concentration, 1.0×10^{-3} M).

Experiments (i) and (iii) did not show any measurable conversion indicating that

- Aqueous 2,4-DCP is very stable and shows very little decomposition at 323 K even after 240 min (experiment (i)).
- The fly ash itself has poor catalytic activity (experiment (iii)) with respect to oxidation of aqueous 2,4-DCP and therefore, has no effect on 2,4-DCP.

The experiments (ii) and (iv) showed 2,4-DCP conversion of ~ 5.9 and 21.4 % respectively. The inferences from these two experiments are:

- Aqueous 2,4-DCP suffers oxidation to a little extent (~ 5.9 %) if it is allowed to stand with the oxidant, H_2O_2 for 240 min at 323 K. This might have occurred due to partial decomposition of H_2O_2 at the higher temperature giving some OH radicals, which attach 2,4-DCP molecules (experiment (ii)).

In experiment (iv), 2,4-DCP suffered oxidation up to 21.4 % which is likely to be due to OH radicals produced by partial decomposition of hydrogen peroxide at the temperature of reaction, 323 K that is aided by the presence of Fe_2O_3 in the fly ash. The fly ash particles are likely to adsorb OH radicals on their surface which interact with 2,4-DCP molecules and partially oxidize them.

4. Wet oxidation of 2,4,6 -trichlorophenol

Blank experiments : Blank experiments were carried out (repeated three times) before going for catalytic oxidation to find out if 2,4,6-trichlorophenol (2,4,6-TCP) in water undergoes self- oxidation without the need for any oxidant or catalyst and also to find out if the oxidant alone without a catalyst or the catalyst support (fly ash) has any oxidizing capacity for 2,4.6-TCP. These experiments were

(xvii) Aqueous 2,4,6-TCP alone without any catalyst and H_2O_2,

(xviii) Aqueous 2,4,6-TCP and H_2O_2 (1:1 mole ratio) without any catalyst

(xix) Aqueous 2,4,6-TCP with the raw fly ash (O) as the catalyst (1.0 g/L)

(xx) Aqueous 2,4,6-TCP and H_2O_2 (1:1 mole ratio) with raw fly ash (O) as the catalyst (1.0 g/L)

under the same conditions of temperature (323 K), time interval (240 min) and pH (i.e., pH 5.5 of the aqueous 2,4,6-TCP solution as prepared of concentration, 1.0×10^{-3} M).

Experiments (i) and (iii) did not show any measurable conversion indicating that

- Aqueous 2,4,6-TCP is very stable and shows very little decomposition at 323 K even after 240 min (experiment (i)).
- The fly ash itself has poor catalytic activity (experiment (iii)) with respect to oxidation of aqueous 2,4,6-TCP and therefore, has no effect on 2,4,6-TCP.

The experiments (ii) and (iv) showed average 2,4,6-TCP conversion of ~ 4.7 and 15.3 % respectively. The inferences from these two experiments are

- Aqueous 2,4,6-TCP suffers oxidation to a little extent (~ 4.7 %) if it is allowed to stand with the oxidant, H_2O_2 for 240 min at 323 K. This might have occurred due to partial decomposition of H_2O_2 at the higher temperature giving some OH radicals, which attack 2,4,6-TCP molecules (experiment (ii)).

In experiment (iv), 2,4,6-TCP suffered oxidation up to 15.7 % which is likely to be due to OH radicals produced by partial decomposition of hydrogen peroxide at the temperature of reaction, 323 K which is likely to be enhanced by the presence of Fe_2O_3 in the fly ash. The fly ash particles are likely to adsorb OH radicals on their surface which interact with 2,4,6-TCP molecules and partially oxidize them.

5. Wet oxidation of 2-nitrophenol

Blank experiments : The following blank experiments were carried out on wet oxidation of 2-nitrophenol (2- NP) in water in a batch process by agitating a volume of 50 mL in a 100 ml Erlenmeyer flask in a thermostatic water bath shaker:

(xxi) Aqueous 2-NP alone without any catalyst and H_2O_2,

(xxii) Aqueous 2-NP and H_2O_2 (1:1 molar ratio) without any catalyst

(xxiii) Aqueous 2-NP with raw fly ash (O) as the catalyst (1.0 g/L)

(xxiv) Aqueous 2-NP and H_2O_2 (1:1 molar ratio) with raw fly ash (O) as the catalyst (1.0 g/L)

under the same conditions of temperature (323 K), shaking time (240 min) and pH (5.2 as prepared) with aqueous 2-NP solution (5.0×10^{-3} M).

In the set (i), the conversion of 2-NP was not detectable – indicating that an aqueous 2-nitrophenol solution is quite stable and did not show any signs of degradation.

Similar results were obtained in the set (iii), which indicated that when the aqueous 2-NP solution was mixed with the raw fly ash under similar conditions and was agitated, no conversion was possible. Therefore, the raw fly ash on its own did not have any catalytic properties.

In the set (ii), 2-NP conversion of ~ 7.9 % was measured; showing that hydrogen peroxide on its own could bring about some amount of oxidation of 2-NP at 323 K after agitating the mixture for 240 min. It is likely that some OH radicals are generated by self-dissociation of hydrogen peroxide under the reaction conditions, bringing about a little oxidation of 2-nitrophenol even without the presence of a catalyst.

In the set (iv), 2-NP oxidation up to 17.6 % could be detected. Presence of fly ash in the reaction mixture must have some influence on hydrogen peroxide dissociation producing more of OH radicals and consequently, conversion of 2-NP was more than what happened in the set (ii).

6. Wet oxidation of 4-nitrophenol

Blank experiments : The following blank experiments were carried out on wet oxidation of 4-nitrophenol (4- NP) in water in a batch process by agitating a volume of 50 mL in a 100 ml Erlenmeyer flask in a thermostatic water bath shaker:

(xxv) Aqueous 4-NP alone without any catalyst and H_2O_2,

(xxvi) Aqueous 4-NP and H_2O_2 (1:1 molar ratio) without any catalyst

(xxvii) Aqueous 4-NP with raw fly ash (O) as the catalyst (1.0 g/L)

(xxviii) Aqueous 4-NP and H_2O_2 (1:1 molar ratio) with raw fly ash (O) as the catalyst (1.0 g/L)

under the same conditions of temperature (323 K), shaking time interval (240 min) and pH (5.5) of as prepared aqueous 4-NP solution (5.0×10^{-3} M).

In the set (i), the conversion of 4-NP was not detectable which indicated that an aqueous phenol solution was quite stable and did not show any sign of degradation.

The set (iii) also showed no detectable conversion. Thus, aqueous 4-NP solution, mixed with the raw fly ash under similar conditions, followed by agitation for 240 min, remained stable and showed no detectable oxidative conversion. Therefore, the raw fly ash on its own does not possess any catalytic properties, despite having a composition with large amount of inorganic oxides.

In the set (ii), 4-NP conversion of ~ 10.8 % was measured; showing that hydrogen peroxide on its own could bring about some amount of oxidation of 4-NP at 323 K after agitating the mixture for 240 min. It is likely that some OH radicals are generated by self-dissociation of hydrogen peroxide under the reaction conditions, bringing about oxidation of 4-nitrophenol to a little extent even without the presence of a catalyst.

In the set (iv), 4-NP oxidation up to 18.9 % could be detected. Since the oxidation normally follows a free radical mechanism based on OH radicals, it is likely that compared to the situation (ii), more OH radicals are present in (iv) with some enhanced contribution through decomposition of H_2O_2 in the presence of fly ash. The presence of Fe_2O_3 in the fly ash might have increased OH radical formation influencing oxidation of 2-NP.

The conclusion that can be drawn from the set of blank experiments clearly shows that hydrogen peroxide alone or in the presence of the raw fly ash, does not bring about considerable oxidation of 4-NP and therefore, some active catalyst is necessary to achieve partial or complete mineralization.

From the blank experiments, it could be concluded that hydrogen peroxide alone or in the presence of the raw fly ash, could not bring about any remarkable oxidation of 2- NP.

CONCLUSION

In the present work, twelve transition metal impregnated fly ash (FA) materials [water washed, acid treated, and alkali treated fly ash impregnated with Mn(II), Co(II), Ni(II), Fe(III)], namely, M1, M2, M3, C1, C2, C3, N1, N2, N3, F1, F2, F3 were used ascatalysts for wet peroxide oxidation of phenol, 2-chlorophenol, 4-chlorophenol, 2,4- dichlorophgenol, 2,4,6-trichlorophenol, 2-nitrophenol, 4-nitrophenol. The reactions were carried out under different conditions to evaluate the effects of (a) reaction time, (b) pH, (c) catalyst load, (d) mole ratio of the reactants, (e) concentration of the reactant, and (f) reaction temperature in the presence of hydrogen peroxide as an oxidant.

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