Chapter 7
WET OXIDATION OF 2,4-DICHLOROPHENOL

Chapter summary
This chapter describes the catalytic wet oxidation of 4-chlorophenol (4-CP) 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) temperature, (iv) mole ratio of reactant, (v) reactant concentration and (vi) catalyst load. 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 mechanisms of the oxidative degradation of 4-chlorophenol 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.

7.1. Wet oxidation of 2,4-dichlorophenol
7.1.1. 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 \( \text{H}_2\text{O}_2 \),
(xiv) Aqueous 2,4-DCP and \( \text{H}_2\text{O}_2 \) (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 \( \text{H}_2\text{O}_2 \) (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, \( 1.0 \times 10^{-3} \text{ M} \)).
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, \( \text{H}_2\text{O}_2 \) for 240 min at 323 K. This might have occurred due to
partial decomposition of \( \text{H}_2\text{O}_2 \) 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 \( \text{Fe}_2\text{O}_3 \) 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.

7.1.2. Effects of reaction time

The oxidation reactions were carried out with Mn(II), Co(II), Ni(II) and Fe(III) incorporated into water washed, acid treated and alkali treated fly ash as catalysts. All the reactions were carried out with aqueous solution of 2,4-dichlorophenol of concentration \( 1.0 \times 10^{-3} \text{ M} \) at a temperature of 323 K and under atmospheric pressure. The reaction time was varied from 5 to 240 min and the oxidative degradation of the reactant was monitored after each time interval. Each experiment was repeated thrice and it was found that the results deviated from each other only by 1 – 3 %. The detailed results are discussed below:

(i) Mn(II)-FA catalysts

The conversion of 2,4-dichlorophenol (2,4-DCP) increased with reaction time (5 – 240 min) till equilibrium conditions were reached (Figure 7.1). The conversion of 2,4-DCP in presence of \( \text{H}_2\text{O}_2 \) in 1:1 mole ratio was 51.1, 53.6 and 43.7 % respectively for Mn(II)-water washed FA (M1), Mn(II)-acid treated FA (M2), Mn(II)-alkali treated FA (M3) after 15 min of reaction. The conversion increased to 61.7, 68.4, and 59.5 % after 240 min. In all three cases, the reactions reached equilibrium after 120 min showing almost constant conversion afterwards.

![Figure 7.1. Effects of reaction time on catalytic wet oxidation of 2,4-dichlorophenol (1.0 x 10^{-3} \text{ M}) with Mn(II)-water washed FA, Mn(II)-acid treated FA and Mn(II)-alkali treated FA catalysts (M1, M2, M3) at 323 K (2,4-DCP: \text{H}_2\text{O}_2 \text{ mole ratio 1:1, catalyst load 1.0 g/L})](image-url)
(ii) Co(II)- FA catalysts

The conversion of 2,4-dichlorophenol increased with reaction time (5 – 240 min) (Figure 7.2). The conversion of 50.0, 54.4 and 48.2 % respectively for Co(II)-water washed FA (C1), Co(II)-acid treated FA (C2), Co(II)-alkali treated FA (C3) after 15 min of reaction increased to 63.5, 69.1, and 58.2 % after 240 min. In all three cases, the reactions reached equilibrium after 120 min (2,4-DCP/H_2O_2 mole ratio 1:1).

![Figure 7.2](image.png)

**Figure 7.2.** Effects of reaction time on wet oxidation of 2,4-dichlorophenol (1.0 x 10^{-3} M) with Co(II)-water washed FA, Co(II)-acid treated FA and Co(II)-alkali treated FA catalysts (C1, C2, C3) at 323 K (2,4-DCP: H_2O_2 mole ratio 1:1, catalyst load 1.0 g/L)

(iii) Ni(II)- FA catalysts

With Ni(II)- FA catalysts, the conversion of 2,4-dichlorophenol increased with reaction time (5 – 240 min) as shown in Figure. 7.3 till equilibrium were reached. The conversion after 15 min was 48.3, 50.8 and 41.1 % respectively for Ni(II)-water washed FA (N1), Ni(II)-acid treated FA (N2), Ni(II)-alkali treated FA (N3) which increased to 67.3, 70.6, and 54.8 % after 240 min (2,4-DCP : H_2O_2 mole ratio 1:1). The equilibrium conditions were reached after 120 min in all the three cases.

(iv) Fe(III)- FA catalysts

For this group of catalysts also, the conversion of 2,4-dichlorophenol increased with reaction time from 47.7 – 65.1 %, 50.9 – 72.4 % and 46.9 – 60.2 % respectively (Figure 7.4) for Fe(III)-water washed FA (F1), Fe(III)-acid treated FA (F2), and Fe(III)-alkali treated FA (F3) catalysts in the reaction time interval of 5 to 240 min (2,4-DCP : H_2O_2 mole ratio 1:1). In all the cases, a steady state in conversion was noticed after 120 min indicating approach to equilibrium conditions.
Figure 7.3. Effects of reaction time on wet oxidation of 2,4-dichlorophenol (1.0 x 10^{-3} M) with Ni(II)-water washed FA, Ni(II)-acid treated FA and Ni(II)-alkali treated FA catalysts (N1, N2, N3) at 323 K (2,4-DCP: H_2O_2 mole ratio 1:1, catalyst load 1.0 g/L)

Figure 7.4. Effect of reaction time on catalytic wet oxidation of 2,4-dichloropnenol (1.0 x 10^{-3} M) with Fe(III)-water washed FA, Fe(III)-acid treated FA and Fe(III)-alkali treated FA catalysts (F1, F2, F3) at 323 K (2,4-DCP: H_2O_2 mole ratio 1:1, catalyst load 1.0 g/L)

Chaliha et al. (2009) have reported an equilibrium time of ~ 180 min for 2,4-dichlorophenol (10^{-3} M) oxidation with transition metal (Co(II)-, Ni(II), Fe(III)-) impregnated MCM41 (2.0 g/L) and oxidation of < 56.0 % in presence of H_2O_2 and < 65.0 % in absence of H_2O_2 at 353 K after 300 min. In the present case, the catalyst, F2,
(Fe(III)-acid treated FA) was found to be the most efficient catalyst with 72.4 % conversion at 240 min with the equilibrium time (60 min), the catalyst load (1.0 g/L) and the reaction temperature (323 K) much lower than those used by Chaliha et al. (2009).

### 7.1.3. Kinetics of wet oxidation of 2,4-dichlorophenol

The reaction rates of the oxidative degradation were tested for conformity with both first and second order kinetics. For first order kinetics, log \( C_t \) (averages of three different sets of measurements under identical conditions) was plotted against time (min) on the basis of the logarithmic form of the first order rate equation:

\[
\log C_t = \log C_0 - \left(\frac{k_1}{2.303}\right) t
\]

The reaction data were also tested for conformity to the second order kinetics by plotting \( 1/C_t \) versus time (min) according to the second order kinetic equation:

\[
\frac{1}{C_t} = k_2 t + \frac{1}{C_0}
\]

where \( C_0 \) and \( C_t \) represent the initial concentration and any concentration at time ‘t’ of the reactant, \( k_1 \) and \( k_2 \) are the first and second order rate coefficients (Atkins et al., 2010). The results are summarized below for the four sets of catalysts used in this work.

### (i) Mn(II)-FA catalysts.

Both first order (Figure 7.5, top) and second order (Figure 7.5, bottom) kinetic plots for Mn(II)-water washed FA (M1), Mn(II)-acid treated FA (M2) and Mn(II)-alkali treated FA (M3) are found to be linear up to 60 min (equilibrium time) (R= 0.99). The values for both first and second order rate coefficient are shown in Table 7.1. Both first and second order rate coefficients follow the order: M2 > M3 > M1 indicating that the acid treated Mn(II)-FA has a higher rate of conversion of 2,4-DCP in aqueous medium.

**Table 7.1.** First order and second order rate coefficients for oxidation of 2,4-dichlorophenol over the catalysts, M1, M2, M3 respectively (reaction temperature 323 K, 2,4-DCP \( 1.0 \times 10^{-3} \) M, catalyst loading 1.0 g/L, pH as prepared (6.8), \( k_1 \) in min\(^{-1} \) and \( k_2 \) in L mol\(^{-1} \) min\(^{-1} \))

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<td></td>
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Figure 7.5. First (top) and Second order (bottom) kinetic plots for wet oxidation of 2,4-dichlorophenol (1.0 x 10^{-3} M) with H_{2}O_{2} at 323 K over Mn(II)-water washed FA (M1), Mn(II)-acid treated FA (M2), Mn(II)-alkali treated FA (M3) respectively (Catalyst 1.0 g/L, 2,4-DCP: H_{2}O_{2} mole ratio 1:1).

(ii) Co(II)-FA catalysts.

The catalysts, Co(II)-water washed FA (C1), Co(II)-acid treated FA (C2) and Co(II)-alkali treated FA (C3), yielded similar linear plots with respect to both first and second order kinetics (Figure 7.6) with R= 0.99 up to the reaction time of 60 min. The rate coefficients (k_{1} and k_{2}, Table 7.2) follow the order: C2 > C1 > C3 for the second order kinetics and C1 > C2 > C3 for the first order kinetics. Taking both the cases together, the alkali treated Co(II)-FA has the slowest rate of conversion of 2,4-dichlorophenol in aqueous medium.

From the values of the regression coefficients, it is difficult to ascertain whether first order or second order mechanism is followed in 2,4-DCP oxidation over Co(II)-FA catalysts.
Figure 7.6. First order (Top) and Second order (Bottom) kinetic plots for wet oxidation of 2,4-dichlorophenol (1.0 x 10\(^{-3}\) M) with H\(_2\)O\(_2\) at 323 K over Co(II)-water washed FA (C1), Co(II)-acid treated FA (C2), Co(II)-alkali treated FA (C3) respectively (Catalyst 1.0 g/L, 2,4-DCP: H\(_2\)O\(_2\) mole ratio 1:1).

Table 7.2. First order and second order rate coefficients for oxidation of phenol over the catalysts, C1, C2, C3 respectively (reaction temperature: 323 K, phenol 5.0 x 10\(^{-3}\) M, catalyst loading 1.0 g/L, pH as prepared (6.8), k\(_1\) in min\(^{-1}\) and k\(_2\) in L mol\(^{-1}\) min\(^{-1}\))

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<td>R(^2) x 10(^2)</td>
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(iii) Ni(II)-FA catalysts.

Both first order and second order plots of Ni(II)-water washed FA (N1), Ni(II)-acid treated FA (N2) and Ni(II)-alkali treated FA (N3) are shown in Figure 7.7. The plots are linear with a regression coefficient of $R^2 = 0.99$ up to the reaction time of 60 min (Table 7.3). In both cases, the rate coefficient has higher values for the acid treated catalyst (N2). The rate coefficients (both first and second order) follow the order: $N2 > N1 > N3$ indicating that the alkali treated Ni(II)-FA has the slowest rate of conversion of 2,4-DCP in aqueous medium.

![Figure 7.7. First order (Top) and Second order (Bottom) kinetic plots for wet oxidation of 2,4-dichlorophenol ($1.0 \times 10^{-3}$ M) with $\text{H}_2\text{O}_2$ at 323 K over Ni(II)-water washed FA (N1), Ni(II)-acid treated FA (N2), Ni(II)-alkali treated FA (N3) respectively (Catalyst 1.0 g/L, 2,4-DCP: $\text{H}_2\text{O}_2$ mole ratio 1:1).]
Table 7.3. First order and second order rate coefficients for oxidation of phenol over the catalysts (N1, N2, N3 respectively; reaction temperature: 323 K, 2,4-DCP: 1.0 x 10^{-3} M, catalyst loading 1.0 g/L, pH as prepared (6.8), k_1 in min^{-1} and k_2 in L mol^{-1} min^{-1})

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<td>k_2</td>
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<td>R^2 x 10^2</td>
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(iv) Fe(III)-FA catalysts. In Figure 7.8, it is observed that both first (Top) and second (Bottom) order kinetics yield very good linear plots and the regression coefficients differ very little from one another. Table 7.4 shows that the rate coefficients (both first and second order) follow the order, F2 > F1 > F3 indicating that the acid treated Fe(III)-FA (F2) has a faster rate of conversion of 2,4-DCP in aqueous medium.

Table 7.4. First order and second order rate coefficients for oxidation of 2,4-dichlorophenol over Fe(III)-water washed, Fe(III)-acid treated and Fe (III)-alkali treated FA catalysts (F1, F2, F3 respectively; reaction temperature: 323 K, 2,4-DCP: 1.0 x 10^{-3} M, catalyst loading 1.0 g/L, pH as prepared (6.8), k_1 in min^{-1} and k_2 in L mol^{-1} min^{-1})

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<th>Fe(III)-FA catalysts</th>
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<td></td>
<td></td>
<td>F1</td>
</tr>
<tr>
<td>1</td>
<td>k_1 x 10^{-3}</td>
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<tr>
<td></td>
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<tr>
<td>2</td>
<td>k_2</td>
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<td>R^2 x 10^2</td>
<td>99.79</td>
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The above results indicate that incorporation of Mn(II), Co(II), Ni(II) and Fe(III) into the fly ash results in obtaining catalysts with different properties for 2,4-dichlorophenol oxidation in aqueous medium. Out of all twelve catalysts under study, Fe(III)-acid treated FA catalyst (F2) has the highest rate coefficient (second order 24.14 L mol^{-1} min^{-1}) and Fe(III)-alkali treated FA catalyst (F3) has the minimum rate coefficient (second order 8.13 L mol^{-1} min^{-1}).

In studying the first order kinetics for aqueous 2,4-dichlorophenol (10^{-3} M) conversion over Co(II)-, Ni(II)-, Fe(III)- impregnated MCM41 at 353 K, Chaliha et al. (2009) showed that the rate coefficients remained in the range of 5.0 to 3.5 (x 10^{-3} L (g catal)^{-1} min^{-1}) with or without H_2O_2 in the reaction mixture. 2,4-dichlorophenol (5.0 x 10^{-4} M) oxidation in a batch reactor by Fenton’s reagent (Fe^{2+}: 2.0 x 10^{-4} M, H_2O_2: 5.0 x 10^{-4} M) followed first order kinetics (Tang et al., 1996) and it was shown that the reaction rate and the rate coefficients were dependant on the reaction parameter like pH, H_2O_2 concentration, Ferrous ion concentration, etc., indicating that the determination of the kinetics of a reaction is a very complex process.
The above examples show that the kinetics of catalytic reactions is very complex, and unlike in the process of adsorption, establishing the kinetics of a catalytic reaction is not an easy task. It is also likely that the metal impregnated FA catalysts have different types of active sites on the surface, with some sites conforming to a first order kinetic mechanism while the others promote second order kinetics.

![Graph showing first and second order kinetic plots](image)

**Figure 7.8.** First order (Top) and Second order (Bottom) kinetic plots for wet oxidation of 2,4-dichlorophenol (1.0 × 10⁻³ M) with H₂O₂ at 323 K over Fe(III)-water washed FA (F1), Fe(III)-acid treated FA (F2), Fe(III)-alkali treated FA (F3) respectively (Catalyst 1.0 g/L, 2,4-DCP: H₂O₂ mole ratio 1:1).
7.1.4. Effects of catalyst load

Five different catalyst loads of 0.4, 1.0, 2.0, 4.0, 8.0 g/L were taken for the wet oxidation of 2,4-dichlorophenol (1.0 x 10^-3 M) in water containing equimolar hydrogen peroxide at a temperature of 323 K and 1.0 atmospheric pressure.

(i) Mn(II)-FA catalysts

When the catalyst loading was increased from 0.4 to 8.0 g/L, the oxidation increased, but the increase was not proportionate to the increase in the catalyst loading. 2,4-dichlorophenol oxidation increased from 58.8 – 64.1 % for Mn(II)-water washed FA (M1), 62.4 – 72.1 % for Mn(II)-acid treated FA (M2) and 57.3 – 61.6 % for Mn(II)-alkali treated FA (M3) only. The results are shown in Figure 7.9. M1 and M3 showed an almost linear increase in conversion in the whole range of catalyst loadings, M2 showed a sharp increase of conversion when the loading increased from 0.4 g/L to 1.0 g/L and after that the conversion increased linearly.

(ii) Co(II)-FA catalysts

Figure 7.10 shows the effects of increasing catalyst load (0.4 to 8.0 g/L) on 2,4-dichlorophenol oxidation. As in the earlier case, no dramatic increase in the conversion was observed. The increase was confined between 60.7 – 65.4 % for Co(II)-water washed FA (C1), 65.7 – 71.3 % for Co(II)-acid treated FA (C2) and 57.4 – 59.4 % for Co(II)-alkali treated FA (C3), which is about 2 – 6 % for the three catalysts.

(iii) Ni(II)-FA catalysts

With Ni(II)-FA catalysts, 2,4-dichlorophenol oxidation increased from 66.7 – 68.6 % for Ni(II)-water washed FA (N1), 68.8 – 72.1 % for Ni(II)-acid treated FA (N2) and 53.2 – 57.7 % for Ni(II)-alkali treated FA (N3) when the catalyst loading was increased from 0.4 to 8.0 g/L, as shown in Figure 7.11. Again, the increase was not proportionate to the increase in catalyst loading. N1 showed an almost linear increase in conversion in the whole range of catalyst loadings, N2 and N3 showed a slight upward trend up to a loading of 2.0 g/L and after this loading the increase was almost linear.
Figure 7.10. Effects of catalyst load on 2,4-dichlorophenol oxidation with Co(II)-water washed FA, Co(II)-acid treated FA and Co(II)-alkali treated FA catalysts (C1, C2, C3) at 323 K (2,4-DCP 1.0 x 10^{-3} M, 2,4-DCP: H_2O_2 mole ratio 1:1, reaction time 240 min)

Figure 7.11. Effects of catalyst load on 2,4-dichlorophenol oxidation with Ni(II)-water washed FA, Ni(II)-acid treated FA and Ni(II)-alkali treated FA catalysts (N1, N2, N3) at 323 K (2,4-DCP 1.0 x 10^{-3} M, 2CP: H_2O_2 mole ratio 1:1, reaction time 240 min, pH as prepared)
(iv) Fe(III)-FA catalysts

In the case of Fe(III)-FA catalysts, increase in the catalyst loading from 0.4 to 8.0 g/L had similar effects on 2,4-dichlorophenol oxidation (Figure 7.12). The oxidation increased from 65.8 – 68.9 % for Fe(III)-water washed FA (F1), 67.1 – 69.7 % for Fe(III)-acid treated FA (F2) and 53.6 – 57.0 % for Fe(III)-alkali treated FA (F3). Again, the increase in conversion remained confined between 2 – 4 % when the catalyst was increased by 20 times.

![Graph showing % Conversion vs Catalyst load (g/L)]

**Figure 7.12.** Effects of catalyst load on 2,4-dichlorophenol oxidation with Fe(III)-water washed FA, Fe(III)-acid treated FA and Fe(III)-alkali treated FA catalysts (F1, F2, F3) at 323 K (2,4-DCP 1.0 x 10^{-3} M, 2,4-DCP: H_{2}O_{2} mole ratio 1:1, reaction time 240 min, pH as prepared)

Chaliha et al. (2009) studied the oxidation of 2,4-dichlorophenol (2,4-DCP 1.0 x 10^{-3} M, H_{2}O_{2} 1.0 x 10^{-3} M, temperature 353 K, reaction time 300 min) using three catalysts, viz. Co(II)-, Ni(II)- and Fe(III)-MCM41 with loadings of 2.0, 4.0, 6.0, 8.0 and 10.0 g L^{-1}. There was enhanced oxidation with increase in catalyst loading (2.0 to 8.0 g/L) reaching saturation level at 10.0 g/L. The conversion of 2,4-dichlorophenol at the highest catalyst load followed the order, Ni(II)- > Co(II)- > Fe(III)-MCM41 and the sequence was explained by higher oxygen chemisorptions on Fe(III)-MCM41 compared to the other two catalysts that subsequently led to lowering of conversion of 2,4-DCP. In the present work, maximum activity was observed with Fe(III)-acid treated FA catalysts indicating that the adsorption of oxygen directly from the atmosphere or from the decomposition of H_{2}O_{2} was not the mechanism of oxidative reaction.

In the present work, even though the catalyst loading was much more (0.4 to 8.0 g L^{-1}), the conversion was not that much and therefore, the possibility of either reduction in the active phase (the transition metal cations) or conversion of the transition metal cations to a lower oxidation state may not be applicable. At the minimum catalyst loading of 0.4 g L^{-1}, more than 50.0 % oxidation of 2,4-dichlorophenol was achieved with all the twelve catalysts. As the oxidative conversion did not improve much with increased catalyst loading, it can be inferred that the catalyst load did not have much influence on the wet oxidation of 2,4-dichlorophenol. A small amount of catalyst load
(0.4 g/L) may be sufficient to bring about a significant amount of conversion under moderate conditions. However, the optimum catalyst loading was taken as 1.0 g/L in this work.

### 7.1.5. Effects of mole ratio

Six different mole ratios of H\textsubscript{2}O\textsubscript{2} with respect to 2,4-dichlorophenol (0, 1.0, 2.0, 5.0, 10.0, 20.0) were taken for the wet oxidation of aqueous 2,4-dichlorophenol (1.0 x 10\textsuperscript{-3} M) for a reaction time 240 min at 323 K and 1.0 atmospheric pressure.

#### (i) Mn(II)-FA catalysts

When the mole ratio of hydrogen peroxide and 2,4-dichlorophenol increased from 1:1 to 20:1 for a reaction time of 240 min, 2,4-dichlorophenol oxidation increased from 61.7 – 95.6 % for Mn(II)-water washed FA (M1), 68.4 – 97.8 % for Mn(II)-acid treated FA (M2) and 59.5 – 94.5 % for Mn(II)-alkali treated FA (M3) as shown in Figure 7.13. When there was no H\textsubscript{2}O\textsubscript{2} used in the reaction mixture, keeping the other parameters constant, the conversion was below 10.0 % in all the three cases.

![Figure 7.13](image_url)

**Figure 7.13.** Effects of mole ratio of H\textsubscript{2}O\textsubscript{2} on catalytic wet oxidation of 2,4-dichlorophenol (1.0 x 10\textsuperscript{-3} M) with Mn(II)-water washed FA, Mn(II)-acid treated FA and Mn(II)-alkali treated FA catalysts (M1, M2, M3) at 323 K (reaction time 240 min, catalyst load 1.0 g/L, atmospheric pressure)

#### (ii) Co(II)-FA catalysts

Figure 7.14 shows the effects of increasing mole ratio of H\textsubscript{2}O\textsubscript{2}: 2,4-DCP (1.0 to 20.0) on oxidation of 2,4-DCP. The conversion increased from 63.5 – 100.0 % for Co(II)-water washed FA (C1), 69.1 – 100.0 % for Co(II)-acid treated FA (C2) and 58.2 – 94.1 % for Co(II)-alkali treated FA (C3). If the reaction was carried out with the same set of conditions as above but without taking H\textsubscript{2}O\textsubscript{2} in the reactant mixture, the conversion of 2,4-dichlorophenol was only 7.3, 9.6 and 4.1 % for C1, C2 and C3 respectively.
Figure 7.14. Effects of mole ratio of H$_2$O$_2$ on catalytic wet oxidation of 2,4-dichlorophenol (1.0 x 10$^{-3}$ M) with Co(II)-water washed FA, Co(II)-acid treated FA and Co(II)-alkali treated FA catalysts (C1, C2, C3) at 323 K (reaction time 240 min, catalyst load 1.0 g/L)

(iii) Ni(II)-FA catalysts

With Ni(II)-FA catalysts, 2,4-dichlorophenol oxidation increased from 67.3 – 97.8 % for Ni(II)-water washed FA (N1), 70.6 – 100.0 % for Ni(II)-acid treated FA (N2) and 54.8 – 93.9 % for Ni(II)-alkali treated FA (N3) when the mole ratio of H$_2$O$_2$ : 2,4-DCP was increased from 1.0 to 20.0 (Figure 7.15). With no H$_2$O$_2$ in the reaction mixture (H$_2$O$_2$ : 2,4-DCP mole ratio = 0:1) keeping other parameters fixed, the conversion of the wet oxidation was only 8.4, 10.2 and 3.7 % for Ni(II)-water washed FA (N1), Ni(II)-acid treated FA (N2), Ni(II)-alkali treated FA (N3) respectively.

Figure 7.15. Effects of increasing H$_2$O$_2$ concentration on oxidation of 2,4-dichlorophenol (1.0 x 10$^{-3}$ M) with Ni(II)-FA, N1, N2, N3 at 323 K (reaction time 240 min, catalyst load 1.0 g/L)
(iv) Fe(III)-FA catalysts

In the case of Fe(III)-FA catalysts, increase in mole ratio of $\text{H}_2\text{O}_2 : 2,4\text{-DCP}$ from 1.0 to 20.0 had similar effects on 2,4-dichlorophenol oxidation (Figure 7.16). The oxidation increased from 67.7 – 97.5 % for Fe(III)-water washed FA (F1), 68.6 – 100.0 % for Fe(III)-acid treated FA (F2) and 55.4 – 95.4 % for Fe(III)-alkali treated FA (F3). If the reaction was carried out with the same set of conditions as above but without taking $\text{H}_2\text{O}_2$ in the reactant mixture, the catalysts, F1, F2 and F3 could convert only 8.1, 12.7, 6.1 % of 2,4-dichlorophenol respectively.

![Figure 7.16. Effects of increasing H2O2 concentration on oxidation of 2,4-dichlorophenol (1.0 x 10^{-3} M) with Fe(III)-FA catalysts (F1, F2, F3) at 323 K (reaction time 240 min, catalyst load 1.0 g/L)](image)

The stoichiometric equation for the complete oxidation of 2,4-dichlorophenol with $\text{H}_2\text{O}_2$ (Equation 3) shows that complete oxidation of 1 mole of 2,4-dichlorophenol requires 12 moles of $\text{H}_2\text{O}_2$:

$$2,4\text{-DCP} : \text{C}_6\text{H}_3\text{Cl}_2 (\text{OH}) + 12 \text{H}_2\text{O}_2 \rightarrow 6 \text{CO}_2 + 13 \text{H}_2\text{O} + 2 \text{HCl}$$

Thus, the results obtained in this work, showing enhancement in oxidation of 2,4-DCP with increasing amount of $\text{H}_2\text{O}_2$ in the feed, are in agreement with the stoichiometric requirement. In all the twelve cases, almost 90 % of 2,4-dichlorophenol conversion was achieved when the $\text{H}_2\text{O}_2$: 2,4-DCP mole ratio was increased 10 times. C1, C2, N2 and F2 showed complete conversion when mole ratio of $\text{H}_2\text{O}_2$: 2,4-DCP mole ratio was increased 20 times.

There are very few reports available in the literature for comparison. Zanjanchi et al (2010) had reported a positive effect up to a certain $\text{H}_2\text{O}_2$ concentration on the photocatalytic degradation of 2,4-dichlorophenol (40.0 mg/L) with sulphonated cobalt phthalocynine- MCM-41 (0.6 g/L) as the catalyst. According to these authors, direct photolysis of the oxidant takes place in the presence of UV-A generating highly reactive hydroxyl radicals that degrade 2,4-dichlorophenol. However, large amount of $\text{H}_2\text{O}_2$ in the reaction mixture did not have much effect on oxidative destruction of the reactant and thus, an optimum concentration of $\text{H}_2\text{O}_2$ was suggested for the degradation of 2,4-dichlorophenol.
In the present work, requirement of higher mole ratio of hydrogen peroxide with respect to the reactant might have been necessary because the oxidant itself is likely to undergo non-selective thermal decomposition at the temperature at which the oxidation reactions were carried out. This is in conformity with the observation that the increase in oxidation of 2,4-DCP was not as much as the increase in mole ratio of the oxidant. However, the success of the present work lies in the fact that > 50.0% conversion could be achieved with a comparatively high concentration of DCP (163 mg/L) with 2,4 DCP : H₂O₂ mole ratio of 1:1. This is true for all the twelve fly ash-based catalysts.

7.1.6. Effects of reaction pH on 2,4-dichlorophenol oxidation

Seven different pHs of the reaction mixture with respect to 2,4-dichlorophenol (3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0) were taken for studying the influence of the pH on the wet oxidation of aqueous 2,4-dichlorophenol (1.0 x 10⁻³ M) at fixed reaction time (240 min), temperature (323 K), catalyst load (1.0 g/L), and atmospheric pressure (1.0 atm).

(i) Mn(II)-FA catalysts

In the pH-range, 3.0 to 7.0 (for a fixed reaction time of 240 min), the oxidation of 2,4-DCP decreased from 69.3 – 59.1 % with Mn(II)-water washed FA (M1) as the catalyst. For Mn(II)-acid treated FA (M2) and Mn(II)-alkali treated FA (M3), the conversion decreased from 70.1 – 51.2 % and 67.7 – 54.8 % as pH changed from 3.0 to 5.0 (Figure 7.17). After pH 5.0, the conversion had an increasing trend and showed 71.8 % conversion for Mn(II)-water washed FA (M1), 74.5 % for Mn(II)-acid treated FA (M2) and 71.4 % for Mn(II)-alkali treated FA (M3) respectively at pH 9.0 of the reaction mixture. At the pH of the as prepared aqueous 2,4-dichlorophenol solution (pH 6.8), the conversion was 61.7 % for M1, 68.4 for M2 and 57.4 % for M3 under similar reaction conditions (reaction time: 240 min, temperature: 323 K, catalyst load: 1.0 g/L, mole ratio 2,4-DCP:H₂O₂: 1:1 and atmospheric pressure: 1.0 atm). Figure 7.17 shows that M1 behaves differently from M2 and M3 with respect to variation of pH.

![Figure 7.17](image-url)
(ii) Co(II)-FA catalysts

Figure 7.18 shows the effects of increasing pH (3.0 to 8.0) on the conversion of 2,4-dichlorophenol. In the pH-range 3.0 to 5.0, the conversion decreased from 59.6 – 58.1 % for Co(II)-water washed FA (C1) and 67.7 – 63.3 % for Co(II)-acid treated FA (C2). For Co(II)-alkali treated FA (C3), the conversion changed from 69.4 – 58.2 % as pH was increased from 3.0 – 6.0. After reaching the minimum value, the conversion again increased for all the three catalysts and gave 100 % conversion at pH 8.0 of the reaction mixture. Under similar reaction conditions, aqueous 2,4-dichlorophenol solution (pH 6.8 as prepared) showed conversion of 63.5 % for C1, 69.1 % for C2 and 58.2 % for C3 respectively.

![Figure 7.18](image)

Figure 7.18. Effects of pH on catalytic wet oxidation of 2,4-dichlorophenol (1.0 x 10^{-3} M) with Co(II)-water washed FA, Co(II)-acid treated FA and Co(II)-alkali treated FA catalysts (C1, C2, C3) at 323 K (reaction time 240 min, catalyst load 1.0 g/L, mole ratio 2,4-DCP:H_{2}O_{2}: 1:1)

(iii) Ni(II)-FA catalysts

With Ni(II)-FA catalysts, 2,4-dichlorophenol oxidation varied from 69.7 – 65.3 % for Ni(II)-water washed FA (N1), 78.1 – 67.0 % for Ni(II)-acid treated FA (N2) as the pH of the reaction mixture varied from 3.0 to 5.0. For Ni(II)-alkali treated FA (N3) the conversion decreased from 66.4 – 53.3 % as the pH increased from 3.0 to 6.0, showing a minimum at pH 6.0 (Figure 7.19). With pH increasing further to alkaline medium, 2,4-DCP conversion increased again to 100.0 % for all the three catalysts. If the oxidation was carried out without adjusting the pH (pH of aqueous 2,4-dichlorophenol was 6.8), conversion of 67.3, 70.6 and 54.8 % was achieved for N1, N2, N3 respectively keeping the other reaction parameters constant.

(iv) Fe(III)-FA catalysts

The effects of pH on 2,4-DCP oxidation with Fe(III)-FA catalysts are shown in Figure 7.20. The conversion changed from 76.9 – 67.6 % for Fe(III)-water washed FA (F1), 71.0 – 68.1 % for Fe(III)-acid treated FA (F2) and 67.1 – 54.5 % for Fe(III)-alkali treated FA (F3) as the pH of the reaction mixture was increased from 3.0 – 6.0. With further increase in pH, the conversion increased very rapidly and showed 100 %
conversion at pH = 8.0. Without adjusting the pH and taking the same reaction conditions, the catalysts viz. F1, F2 and F3 can bring about respectively 67.6, 68.6 and 55.4% conversion of the aqueous 2,4-dichlorophenol solution (pH 6.8).

Figure 7.19. Effects of pH on catalytic wet oxidation of 2,4-dichlorophenol (1.0 x 10^{-3} M) with Ni(II)-water washed FA, Ni(II)-acid treated FA and Ni(II)-alkali treated FA catalysts (N1, N2, N3) at 323 K (reaction time 300 min, catalyst load 1.0 g/L, mole ratio 2,4-DCP:H_{2}O_{2}: 1:1)

Figure 7.20. Effects of pH on catalytic wet oxidation of 2,4-dichlorophenol (1.0 x 10^{-3} M) with Fe(III)-water washed FA, Fe(III)-acid treated FA and Fe(III)-alkali treated FA catalysts (F1, F2, F3) at 323 K (reaction time 300 min, catalyst load 1.0 g/L, mole ratio 2,4-DCP:H_{2}O_{2}: 1:1)
The above results show that all the twelve catalysts (M1, M2, M3, C1, C2, C3, N1, N2, N3, F1, F2, F3) showed similar behavior with respect to pH of the reaction mixture. At the acidic pH, a higher oxidative conversion is possible because 2,4-dichlorophenolate ions, being negatively charged, bind more effectively to the acidic catalyst surface (with a layer of protons in them). However, as the pH of the reaction mixture increases, the concentration of hydroxide ions increases which compete with 2,4-dichlorophenolate ions for the positively charged adsorption sites. This leads to the lowering the overall conversion of 2,4-DCP in the wet oxidation process (as observed at pH 5.0 or 6.0). Under these circumstances, the oxidation mechanism would involve two types of interactions:

(iii) Interaction between the adsorbed 2,4-dichlorophenolate ions (from deprotonation of 2,4-DCP) and the adsorbed OH\(^-\) (from decomposition of \(\text{H}_2\text{O}_2\), present in the reaction mixture) following Langmuir–Hinshelwood mechanism, and

(iv) Interaction between 2,4-dichlorophenolate ions in the aqueous phase and OH\(^-\) ions adsorbed on the catalyst surface following Eley-Rideal mechanism.

At higher pH, the catalyst surface would be occupied by more and more OH\(^-\) ions and the second type of interactions (between the adsorbed OH\(^-\) on the catalyst surface and 2,4-dichlorophenolate ions in the aqueous phase) may dominate and the Eley–Rideal mechanism of catalytic action will follow. This might have given rise to increased conversion at higher pH. The charge on the catalyst surface thus plays an important role on the oxidation reaction as seen from the influence of pH on conversion.

Another explanation for the increase in conversion in the alkaline pH might be the dechlorination of the reactant (2,4-dichlorophenol) molecules. At the alkaline medium, dechlorination of 2,4-DCP might be possible that lead to increased conversion through the formation of HCl. This has an additional support from the decrease in pH of the reaction mixture observed after the reaction.

Tang et al. (1996) had reported that Fenton oxidation of 2,4-DCP (5.0 x 10\(^{-4}\) M) in the presence of \(\text{H}_2\text{O}_2\) (5.0 x 10\(^{-4}\) M) was favoured in the acidic medium with an optimum pH of 3.5. The authors suggested that at appropriate pH, \(\text{H}_2\text{O}_2\) decomposed to OH radicals catalyzed by ferrous ions in Fenton’s reagent (Fe(ClO\(_4\))\(_2\): 2.0 x 10\(^{-4}\) M) in the acidic medium.

7.1.7. Effects of reactant concentration on 2,4-dichlorophenol oxidation

To evaluate the effects of increasing 2,4-dichlorophenol concentration on the wet oxidation process five different concentrations (2.0, 4.0, 6.0, 8.0 and 10.0 (x 10\(^{-4}\) mol/L)) of the reactant (2,4-DCP) were taken with a constant concentration of \(\text{H}_2\text{O}_2\) (1.0 x 10\(^{-3}\)M) under a fixed reaction time 240 min, catalyst load 1.0 g/L, reaction temperature 323 K, pressure 1 atm.

(i) Mn(II)-FA catalysts. With increase in concentration of 2,4-chlorophenol from 2.0 x10\(^{-4}\) – 10.0 x 10\(^{-4}\) mol/L, the conversion showed a downward trend. The conversion came down from 67.4 – 61.7 % for Mn(II)-water washed fly ash (M1), 76.5 – 68.4 % for Mn(II)-acid treated fly ash (M2) and 62.3 – 59.5 % for Mn(II)-alkali treated fly ash (M3). The decrease in conversion is obviously due to the increasing competition faced by 2,4-dichlorophenol molecules (at fixed catalyst load, reaction time and reaction temperature) for the available adsorption sites where the conversion can take place. The
decrease in conversion with increase in 2,4-dichlorophenol concentration is represented graphically in Figure 7.21.

![Graph of conversion vs. 2,4-DCP concentration for different Mn(II)-FA catalysts.](image1)

**Figure 7.21.** Oxidation of 2,4-dichlorophenol (2,4-DCP) at different concentrations with Mn(II)-FA (M1, M2, M3) catalysts (catalyst load: 1.0 g/L, reaction time: 300 min, 2,4-DCP: H$_2$O$_2$ mole ratio 1:1, reaction temperature: 323 K and pressure: 1.0 atm)

(ii) **Co(II)-FA catalysts.** In 2,4-DCP concentration range of $2.0 \times 10^{-4}$ to $10.0 \times 10^{-4}$ M, its conversion decreased from (i) 70.1–63.5 % for Co(II)-water washed fly ash (C1), (ii) 78.3–69.1 % for Co(II)-acid-treated fly ash (C2) and (iii) 61.8–58.4 % for Co(II)-alkali treated fly ash (C3). The influence of 2,4-DCP concentration was the least for C3 and was the maximum for C2. The detailed degradation results and a comparison of the performance of the three catalysts with increasing 2,4-dichlorophenol concentration are shown in Figure 7.22.

![Graph of conversion vs. 2,4-DCP concentration for different Co(II)-FA catalysts.](image2)

**Figure 7.22.** Oxidation of 2,4-dichlorophenol at different concentrations with Co(II)-FA catalysts (catalyst load 1.0 g/L C1, C2 and C3, reaction time 300 min, 2,4-DCP: H$_2$O$_2$ mole ratio 1:1, reaction temperature 323 K and pressure 1.0 atm)
(iii) Ni(II)-FA catalyst. In this case, the conversion decreased with increasing 2,4-DCP concentration from (i) 73.5 – 67.3 % for Ni(II)-water washed fly ash (N1), (ii) 81.7 – 70.6 % for Ni(II)-acid-treated fly ash (N2) and (iii) 60.2 – 54.8 % for Ni(II)-treated fly ash (N3). The decrease was much more for the catalyst N2 compared to N1 and N3. The degradation results and a comparison of the performance of the three Ni(II)-catalysts with increasing 2,4-DCP concentration are shown in Figure 7.23.

![Figure 7.23](image)

**Figure 7.23.** Oxidation of 2,4-dichlorophenol at different concentrations (catalyst load 1.0 g/L for N1, N2 and N3, reaction time 300 min, 2,4-DCP: H2O2 mole ratio 1:1, reaction temperature 323 K and atmospheric pressure)

(iv) Fe(III)-FA catalysts. The decrease in conversion in the wet oxidation of 2,4-DCP with increase in reactant concentration was (i) 72.8 – 67.6 % for Fe(III)-water washed fly ash (F1), (ii) 83.1 – 68.8 % for Fe(III)-acid-treated fly ash (F2) and (iii) 64.7 – 55.4 % for Fe(III)-alkali treated fly ash (F3). The catalyst, Fe(III)-acid-treated fly ash (F2), showed the maximum influence of 2,4-DCP concentration on its conversion. A comparison of the performances of the three Fe(III)-catalysts with increasing 2,4-dichlorophenol concentration is shown in Figure 7.24.

Chaliha et al. (2009) have observed similar results in the catalytic wet oxidation of 2,4-dichlorophenol over Fe(III)-, Co(II)- and Ni(II)-impregnated MCM41 catalysts when the conversion decreased as 2,4-DCP concentration was increased from 2.0 to 10.0 (x 10^{-4} mole/L) at fixed temperature (353 K), catalyst load (2.0 g/L) and time (300 min) giving the most significant effect with Fe(III)-MCM41 (70.0 to 38.6 %). The mechanism for the decreased conversion at higher concentration was explained on the basis of transport mechanism that involve diffusion of both 2,4-DCP from aqueous phase to the surface of the catalysts as well as the diffusion of the products formed by oxidation of 2,4-DCP away from the catalyst surface. Wu et al. (2007) observed a similar decreasing trend with increase in concentration of 2,4-dichlorophenol with polydivinylbenzene-supported Zn phthalocyanine (PDVB-ZnPc) (1.0 g/L) as the catalyst in the photo-degradation of aqueous 2,4-DCP (pH 13) in presence of H2O2 (30.0%, 1.0 ml). It is shown that the rate constant of the photo-degradation of the
reactant after 60 min decreases from $1.89 \times 10^{-2}$ min$^{-1}$ to $0.81 \times 10^{-2}$ min$^{-1}$ as 2,4-DCP concentration increases from 16.3 to 65.2 mg/L.

The catalysts in the present work show that the decrease in conversion with increase in 2,4-DCP concentration is not the same for Mn(II)-, Co(II)-, Ni(II)- and Fe(III)-FA catalysts and therefore, the metal ions have an important role in determining the conversion of 2,4-DCP concentration. In the present work, the effects of concentration are most significant with Fe(III)-acid treated fly ash (F2) catalyst with 14.3 % rise in oxidation of 2,4-DCP for an increase in concentration from $2.0 \times 10^{-4}$ to $10.0 \times 10^{-4}$ M keeping other parameters constant.

7.1.8 Effects of the reaction temperature on 2,4-dichlorophenol oxidation

To observe the influence of reaction temperature on the catalytic wet oxidation reactions of 2,4-dichlorophenol, five different temperatures, from 303 to 343 K in steps of 10 K were taken. All the reactions were carried out at atmospheric pressure with fixed 2,4-DCP concentration of $1.0 \times 10^{-3}$ M, catalyst load of 1.0 g/L, 2,4-DCP: H$_2$O$_2$ mole ratio 1:1 and a reaction time of 300 min. It was found that the reaction temperature had a positive influence on 2,4-dichlorophenol oxidation. The results are described below.

(i) Mn(II)-FA catalysts

When the reaction temperature was increased from 303 to 343 K for a reaction time of 240 min, 2,4-dichlorophenol oxidation varied from 55.9 – 67.2 % for Mn(II)-water washed FA (M1), 61.2 – 73.3 % for Mn(II)-acid treated FA (M2) and 53.8 – 62.5 % for Mn(II)-alkali treated FA (M3) as shown in Figure 7.25. It is observed from the trends that the increase in conversion with increase in temperature was smaller than expected,
but the increasing trend showed that still higher conversion is possible at temperatures > 343 K.

**Figure 7.25.** Effects of reaction temperature on catalytic wet oxidation of 2,4-dichlorophenol (1.0 x 10^{-3} M) with Mn(II)-water washed FA, Mn(II)-acid treated FA and Mn(II)-alkali treated FA catalysts (M1, M2, M3) (reaction time 240 min, 2,4-DCP: H_2O_2 mole ratio 1:1, catalyst load 1.0 g/L)

**(ii) Co(II)-FA catalysts**

Figure 7.26 shows the effects of increasing reaction temperature on the conversion of 2,4-dichlorophenol. As the reaction temperature was increased from 303 to 343 K, 2,4-dichlorophenol oxidation increased from 58.1 – 67.2 % for Co(II)-water washed FA (C1), 63.4 – 75.8 % for Co(II)-acid treated FA (C2), 52.1 – 62.6 % for Co(II)-alkali treated FA (C3).

**Figure 7.26.** Effects of reaction temperature on catalytic wet oxidation of 2,4-dichlorophenol (1.0 x 10^{-3} M) with Co(II)-water washed FA, Co(II)-acid treated FA and Co(II)-alkali treated FA catalysts (C1, C2, C3) (reaction time 240 min, 2,4-DCP: H_2O_2 mole ratio 1:1, catalyst load 1.0 g/L)
(iii) Ni(II)-FA catalysts
With Ni(II)-FA catalysts, 2,4-dichlorophenol oxidation varied from 62.3 – 69.6 % for Ni(II)-water washed FA (N1), 64.9 – 74.1 % for Ni(II)-acid treated FA (N2) and 48.4 – 57.6 % for Ni(II)-alkali treated FA (N3) in the temperature range of 303 to 343 K (Figure 7.27). All the three Ni(II)-FA catalysts exhibited an increasing trend in conversion.

Figure 7.27. Effects of reaction temperature on catalytic wet oxidation of 2,4-dichlorophenol (1.0 x 10^{-3} M) with Ni(II)-water washed FA, Ni(II)-acid treated FA and Ni(II)-alkali treated FA catalysts (N1, N2, N3) (reaction time 240 min, 2,4-DCP: H_{2}O_{2} mole ratio 1:1, catalyst load 1.0 g/L).

(iv) Fe(III)-FA catalysts
In the case of Fe(III)-FA catalysts, increase in reaction temperature from 303 to 343 K had similar effects on 2,4-dichlorophenol oxidation (Figure 7.28). The oxidation increased from 61.7 – 70.4 % for Fe(III)-water washed FA (F1), 62.9 – 72.4 % for Fe(III)-acid treated FA (F2) and 50.3 – 58.2 % for Fe(III)-alkali treated FA (F3). It is observed that Fe(III)-alkali treated FA (F3) is much less effective in 2,4-DCP conversion compared to Fe(III)-water washed FA (F1) and Fe(III)-acid treated FA, which could achieve almost similar conversions.

The results of the influence of temperature on 2,4-DCP oxidation show that the oxidation of 2,4-dichlorophenol increased with temperature for all the metal incorporated catalysts, although the magnitude of increase was different for the catalysts. The positive trend is due to the increased mobility of the reactant molecules at higher temperatures and consequently, they reach the catalyst surface quickly without having to go through the slow diffusion process. This leads to an increased conversion in the wet oxidation process. The influence of temperature in case of all the catalysts is almost a linear increase in the conversion in the given temperature ranges, but the
influence was different for the different catalysts. Out of all the twelve catalysts, Fe(III)-acid treated FA (F2) gives the maximum conversion (72.4 %) at 343 K.

![Figure 7.28](image.png)

**Figure 7.28.** Effects of reaction temperature on catalytic wet oxidation of 2,4-dichlorophenol (1.0 × 10^{-3} M) with Fe(III)-water washed FA, Fe(III)-acid treated FA and Fe(III)-alkali treated FA catalysts (F1, F2, F3) (reaction time 240 min, 2,4-DCP: H_{2}O_{2} mole ratio 1:1, catalyst load 1.0 g/L).

Chaliha et al. (2008) have studied the oxidation of 2,4-dichlorophenol (2,4-DCP) in the temperature range of 333 – 413 K using Mn(II)-MCM41 catalysts (2.0 g/L) under the conditions of 0.2 MPa pressure, 300 min reaction time, 180 rpm stirring rate. Reaction temperature increase was found to influence 2,4-DCP (1.0 × 10^{-3} M) conversion positively as the conversion increased from 54.9 to 65.2 % in presence of H_{2}O_{2} and 60 to 63 % in absence of H_{2}O_{2}. However the extent of increase was not proportionate to the increase in temperature and thus an optimum temperature of 353 K was suggested for the reaction.

In the present case, more than 50.0 % conversion was achieved at a moderate temperature of 323 K with all the twelve catalysts under study. Therefore, the optimum temperature for the wet oxidation of 2,4-DCP in the present case could be considered as 323 K which is much lower than that used by Chaliha et al. (2008).

7.1.9. Monitoring of 2,4-dichlorophenol oxidation with COD measurement

Reduction in COD load of the reaction mixture was another clear indication of 2,4-dichlorophenol mineralization. For Mn(II)-FA catalysts, it was observed that the initial COD load of the reaction mixture (2,4-DCP: 1.0 × 10^{-3} M, H_{2}O_{2}: 1.0 × 10^{-3} M, catalyst load: 1.0 g L^{-1}, temperature 323 K, reaction time 0 – 240 min) decreased from 1560 to 580, 440, 620 mg/L respectively for Mn(II)-water washed FA, Mn(II)-acid treated FA and Mn(II)-alkali treated FA (Figure 7.33) (overall COD reduction was 62.8, 71.8 and 60.3 %). This is in contrast to the increase in conversion of 2,4-DCP oxidation (Figure. 7.29) where a significant amount of oxidation was obtained within the first 15 min of reaction time (51.1, 53.6, 43.7 for M1, M2 and M3 respectively). Thus, COD reduction and 2,4-DCP degradation did not occur at the same rate and the rate of COD reduction
was slower in comparison to the increase in conversion. However, with increase in reaction time, COD reduction became larger than 2,4-DCP conversion (for example, after 240 min, COD reduction was 62.8, 71.8 and 60.3 % for the catalysts Mn(II)-water washed FA, Mn(II)-acid treated FA and Mn(II)-alkali treated FA respectively compared to 2,4-DCP oxidation of 61.7, 68.4, and 59.5 % in the same time interval). It was observed that M3 showed the minimum difference between the COD reduction and 2,4-DCP conversion. Large decrease in COD loading pointed to an approach towards complete mineralization.

![Figure 7.29](image)

**Figure. 7.29.** COD reduction in 2,4-DCP oxidation over Mn(II)-water washed, Mn(II)-acid treated and Mn(II)-alkali treated FA catalysts (M1, M2, M3 respectively; reaction temperature 323 K, 2,4-DCP 1.0 x 10^{-3} M, catalyst loading 1.0 g/L).

Similar results were observed for the other metal incorporated FA based catalysts. For Co(II)-FA catalysts, the COD load of the reaction mixture (Figure 7.30) decreased from 1560 to 540, 380, 640 mg/L for reaction time of 0 to 240 min (overall COD reduction was 65.4, 75.6 and 58.9 % respectively) for Co(II)-water washed FA, Co(II)-acid treated FA and Co(II)-alkali treated FA. At 240 min, the conversion of 2,4-DCP is 63.5, 69.1, 58.2 for C1, C2 and C3 respectively showing a significant difference between the COD reduction and conversion of 2,4-DCP.

In case of Ni(II)-catalysts, the COD load of the reaction mixture (Figure. 7.34) decreased from 1560 to 480, 320, 700 mg L^{-1} for reaction time of 0 to 240 min (overall COD reduction achieved was 69.2, 79.5 and 55.1 % respectively) for Ni(II)-water washed FA, Ni(II)-acid treated FA and Ni(II)-alkali treated FA respectively.

For Fe(III)-catalysts, the COD load of the reaction mixture (Figure. 7.32) decreased from 1560 to 500, 240, 360 mg L^{-1} for reaction time of 0 to 240 min (overall COD reduction was 67.9, 84.6 and 61.5 % respectively) for Fe(III)-water washed FA, Fe(III)-acid treated FA and Fe(III)-alkali treated FA respectively.
Figure. 7.30. COD reduction in 2,4-DCP oxidation over Co(II)-water washed, Co(II)-acid treated and Co(II)-alkali treated fly ash catalysts (C1, C2, C3 respectively; reaction temperature 323 K, 2,4-DCP 1.0 \times 10^{-3} \text{ M}, catalyst loading 1.0 \text{ g/L}).

Figure. 7.31. COD reduction in 2,4-DCP oxidation over Ni(II)-water washed, Ni(II)-acid treated and Ni(II)-alkali treated fly ash catalysts (N1, N2, N3 respectively; reaction temperature 323 K, 2,4-DCP 1.0 \times 10^{-3} \text{ M}, catalyst loading 1.0 \text{ g/L}).
Figure. 7.32. COD reduction in 2,4-dichlorophenol oxidation over Fe(III)-water washed, Fe(III)-acid treated and Fe(III)-alkali treated fly ash catalysts (F1, F2, F3 respectively; reaction temperature 323 K, 2,4-DCP 1.0 x 10^{-3} M, catalyst loading 1.0 g/L).

Table 7.5 COD removal and % conversion on catalytic wet oxidation of 2,4-dichlorophenol (1.0 x 10^{-3} M) with metal impregnated fly ash catalysts (M1, M2, M3, C1, C2, C3, N1, N2, N3, F1, F2, F3) at 323 K (reaction time 240 min, catalyst load 1.0 g/L, pH 6.8) with 2,4-DCP: H_{2}O_{2} mole ratio 1:1).

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>COD reduction (%)</th>
<th>2-CP conversion (%)</th>
<th>Difference (X_{COD} - X)</th>
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</thead>
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<tr>
<td>M1</td>
<td>62.8</td>
<td>61.7</td>
<td>1.1</td>
</tr>
<tr>
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<tr>
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Ojeda et al. (2005) have reported that in CWAO of industrial waste water containing 2-CP with activated carbon (AC) as catalyst, the COD reduction came down with increase in time and at the saturation time (16 h), 48% of COD reduction was observed.
at 413 K and 13.1 bar pressure. These authors have also observed a lower COD reduction compared to 2-CP oxidation percentage, which the authors explained as due to the presence of partially oxidized products formed in the reaction mixture. It should be pointed out that the higher the difference between 2-CP conversion and COD reduction, higher would be the amount of partially oxidized products in the liquid effluent. Rao et al. (2003) have found ~ 93% COD reduction for photocatalytic degradation of 2-chlorophenol (100 mg/L) using TiO$_2$ (0.02 g) as a catalyst for 120 min with a 400 W Hg lamp as the photon source and at pH 5.5 during the initial 60 min at an initial rate of 2.46 mg L$^{-1}$ min$^{-1}$.

The present work demonstrated 84.6 % COD removal in CWAO process at 323 K with Fe (III)-acid-treated FA catalyst (F2) (Table. 7.1). The difference between the 2,4-DCP conversion and COD removal was the largest for the catalyst F2 (28.2) and it could be inferred that F2 gave rise to more partially oxidized products in comparison to the other catalysts, thus leading to higher reduction in COD and thus, showed a higher selectivity towards complete mineralization.

**7.1.10 Mechanism of oxidative destruction**

On the basis of the GC−MS identification of some of the intermediate products of 2,4-DCP oxidation and the likely products of oxidation as reported in the literature, a probable mechanism is suggested for the catalytic oxidation of 2,4-dichlorophenol.

GC−MS analysis of the product mixtures (Fig.7.35) showed characteristic peaks at m/z of (i) 86.4, 87.7 (ii) 82.8, (iii) 81.7, (iv) 80.2, (v) 79.1, (vi) 96.8 (vii) 134.8 (viii) 157.2. Some of these peaks could be assigned to 1- butanoic acid (m/z: 88.0), phenol (m/z: 94.0), hydroquinone (m/z: 112), 4-chloro-cyclohexanone ((m/z: 132), chlorocatechol (m/z: 144), and chlorobenzoquinone (m/z: 142).

Based on the literature and also considering the likely products of oxidation by a free radical mechanism suggested by other workers (Lin et al., 1998; Lu et al., 2006; Temel et al., 2011; Catrinescu et al., 2011; Xing et al., 2013), a mechanism for the oxidation of 2,4-dichlorophenol is proposed in Fig. 7.36. According to Lin et al. (1998), both oxygen and hydrogen peroxide initiate the chain reaction via two mechanisms, namely,

(a) Oxygen directly reacts with the organic reactant to form organic radicals and hydroperoxyl radicals (HO$_2$ radicals), and
(b) H$_2$O$_2$ thermally decomposes to .OH radicals.

Both HO$_2$ and OH radicals may actively take part in the oxidation of an organic pollutant that follows hydrogen abstraction mechanism. Lin et al. (1998) oxidized DCP with super critical water (SCWO) at 673 K and it was shown that DCP underwent condensation reaction to form heavier products. In the present study, condensation to higher products may be possible as some GC-MS peaks at higher molar mass were also observed (Figure 7.34). According to Li et al. (2006), hydroxylation of 2,4-DCP takes place that lead to ring opening of the organic compound and ultimately to low molecular weight carboxylic acids (oxalic acid, maleic acid etc) and eventually to complete degradation into CO$_2$ and H$_2$O. Considering all the alternatives, a possible mechanism for the oxidation of 2,4-dichlorophenol is presented below:
Figure 7.33. GC-MS of the product mixture of 2,4-dichlorophenol oxidation over Mn(II)-water washed fly ash (M1, load 1.0 g/L, reaction time 240 min, temperature 323 K, 2,4-DCP/H₂O₂ mole ratio 1:5).
Fig. 7.34. Reaction scheme showing the pathways for product formation in catalytic wet oxidation of 2,4-DCP with H$_2$O$_2$ over Mn(II)-, Co(II)-, Ni(II)- and Fe(III)-FA as the catalyst.

In the scheme of mechanism, an electrophilic OH radical attacks 2,4-DCP (I) at the positions of the two Cl-atoms and replace the electron-withdrawing Cl-atoms, converting 2,4-DCP (I) first to chlorocatechol (II, III), then to chlorobenzoquinone (IV) and finally to unsaturated dicarboxylic acids (V). OH groups also interact with the unsaturated dicarboxylic acids transforming them into simple acids like acetic acid, oxalic acid, etc., as the final products.

7.2.11. Conclusion

The transition metal cations, Fe(III), Co(II), Ni(II) and Mn(II), impregnated into fly ash produce active oxidation catalysts for the treatment of water contaminated with 2,4-dichlorophenol. The fly ash, as such, has very little activity towards the oxidation process. There was also little conversion without using H$_2$O$_2$. In presence of sufficient quantity of H$_2$O$_2$ (10:1 mole ratio with 2,4-DCP) in the reaction mixture, more than 90% conversion could be achieved. The results showed that the total conversion of 2-chlorophenol increases with an increase in the reaction time from 5 to 300 min. A significant amount of conversion is observed at a very short time (15 min) for all the metal impregnated catalysts. The reactions were found to follow second order kinetics and with respect to the rate of conversion, the catalysts are in the order N2 > F2 > N1 > M2 > C2 > C1 > M3 > F1 > C3 = M1 > N3 > F3.

The leaching of the metal ions from the fly ash based catalysts was not very high and found to be within the limit prescribed by the regulatory authorities if the oxidation is carried out at the pH (6.8) of the as prepared 2,4-dichlorophenol aqueous solution.