Chapter 9

WET OXIDATION OF 2-NITROPHENOL

Chapter summary
This chapter describes the catalytic wet oxidation of 2-nitrophenol (2-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) 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 mechanisms of the oxidative degradation of 2-nitrophenol 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.

9.1. 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:

(xxı) Aqueous 2-NP alone without any catalyst and H$_2$O$_2$,  
(xxıı) Aqueous 2-NP and H$_2$O$_2$ (1:1 molar ratio) without any catalyst  
(xxııı) Aqueous 2-NP with raw fly ash (O) as the catalyst (1.0 g/L)  
(xxıv) Aqueous 2-NP and H$_2$O$_2$ (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 ($5.0 \times 10^{-3}$ 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).
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.

9.2. Effects of reaction pH on 2-nitrophenol oxidation

To find out the influence of pH of the reaction mixture on the wet oxidation of aqueous 2-NP (5.0 x 10^{-3} M), the reaction was carried out at seven different pHs (3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0) under fixed reaction time of 240 min, temperature 323 K, catalyst load 1.0 g/L under atmospheric pressure. The influence of pH of the reaction mixture on 2-NP oxidation was not very large as a whole and the different catalysts acted differently to changes in pH for the oxidative conversion of 2-NP. The detailed observations for the different fly ash-based catalysts are given below:

(i) Mn(II)-FA catalysts

With increase in pH of the reaction mixture from 3.0 to 9.0, 2-NP oxidation decreased slowly from 60.7 – 58.9 % only for Mn(II)-water washed FA (M1) and 65.1 – 62.6 % for Mn(II)-acid treated FA (M2). However, in case of Mn(II)-alkali treated FA (M3), a sudden decrease in the conversion was observed between pH 4.0 and 6.0 (59.4 – 56.3 %) which stabilized if the pH was increased more (Figure 9.1).

![Figure 9.1. Effects of pH on oxidation of 2-nitrophenol (5.0 x 10^{-3} M) with Mn(II)-FA catalysts, M1, M2, M3 at 323 K (time 240 min, catalyst load 1.0 g/L, 2-NP: H_2O_2 mole ratio 1:1)](image)

At the natural pH of aqueous 2-NP (5.2), the catalysts, M1, M2, M3 showed 50.9, 57.5 and 48.8 % conversion under similar reaction conditions.

(ii) Co(II)-FA catalysts

Figure 9.2 shows the effects of increasing pH on the conversion of aqueous 2-NP in presence of equimolar H_2O_2. Oxidation of 2-NP with Co(II)-water washed FA (C1) as the catalyst was 58.4 to 52.1 % as the pH was increased from 3.0 to 9.0.
Figure 9.2. Effects of pH on oxidation of 2-nitrophenol (5.0 x 10^(-3) M) with Co(II)-FA catalysts (C1, C2, C3) at 323 K (time 240 min, catalyst load 1.0 g/L, 2-NP: H_2O_2 mole ratio 1:1)

In case of Co(II)-acid treated FA (C2) and Co(II)-alkali treated FA (C3), the effects of pH of the reaction mixture were similar. In all the cases, minimum oxidation was obtained at the pH 6.0. As a whole, the conversion did not change much in the alkaline region. In general, 2-NP conversion varied from 65.9 – 59.2 % for Co(II)-acid treated FA (C2) and 52.4 – 50.2 % Co(II)-alkali treated FA (C3), showing that the influence of pH was maximum for the catalyst Co(II)-acid treated FA (C2) while the other two catalysts showed much less influence of pH. At the natural pH of the aqueous 2-NP solution (5.2), the catalysts, C1, C2 and C3, gave 2-NP conversion of 51.2, 58.4 and 45.3 %.

(iii) Ni(II)-FA catalysts

With Ni(II)-water washed FA (N1), 2-NP oxidation showed a negative trend of conversion (67.7 – 59.7 %) with the increase in the reaction mixture pH from 3.0 to 9.0. For the treated catalysts, the conversion decreased up to pH 6 and then the conversion showed a slight increasing trend in the alkaline region. For Ni(II)-acid treated FA (N2), the conversion changed from 64.1 – 62.8 % showing a minimum at pH 6 (60.8 %). Ni(II)-alkali treated FA (N3) showed a decrease in 2-NP oxidation from 57.8 – 51.7 % in the pH range of 3.0 to 9.0 showing a minimum at pH 6 (50.8 %) (Figure 9.3). Although the pH did not have a very large influence on 2-NP oxidation, the decrease was much more for the catalyst, Ni(II)-alkali treated FA (N3) followed by Ni(II)-water washed FA (N1) and then, Ni(II)-acid treated FA (N2). At the natural pH of 2-NP (5.2), the oxidation achieved with N1, N2 and N3 was respectively 54.9, 61.3 and 41.7 %.
(iv) Fe(III)-FA catalysts

In the case of Fe(III)-FA catalysts, increase in reaction mixture pH from 3.0 to 9.0 had similar effects on 2-NP oxidation for both F1 and F2 (Figure 9.4). For Fe(III)-water washed FA (F1), the oxidative conversion of aqueous 2-nitrophenol decreased very slowly reaching a minimum at the pH 6.0 and then there was an increasing trend. The overall decrease was from 63.2 – 57.7 %. For Fe(III)-acid treated FA (F2), a continuous decrease in conversion (67.1 – 64.1 %) was observed from pH 3.0 to 9.0. For Fe(III)-alkali treated FA (F3), the oxidation of 2-NP decreased from 51.1 – 50.3 % in the pH range, 3.0 to 6.0, and then increased to 51.6 % at pH 9.0. At the natural pH (5.2) of aqueous 2-NP solution, the catalysts viz. F1, F2, F3 showed 53.8, 63.7, 50.4 % conversion under identical reaction conditions, indicating that the catalyst, F2 had the best oxidation potential.

Figure 9.3. Effects of pH on oxidation of 2-nitrophenol (5.0 x 10^{-3} M) with N1, N2, N3 at 323 K (time 240 min, catalyst load 1.0 g/L, 2-NP: H_2O_2 mole ratio 1:1)

Figure 9.4. Effects of pH on oxidation of 2-nitrophenol (5.0 x 10^{-3} M) with the catalysts (F1, F2, F3) at 323 K (time 240 min, catalyst load 1.0 g/L, 2-NP: H_2O_2 mole ratio 1:1)
The general observation from all the above sets is that increasing the pH had a
negative effect till almost neutral conditions (pH 6.0 to 7.0) and then a slightly positive
or no influence on 2-nitrophenol oxidation in the alkaline medium. However, it is to be
noted that the effects of pH are dependent on various factors like (i) the nature of the
metal introduced into the fly ash, (ii) how the catalyst was treated compared to the raw
fly ash, etc. Doong et al. (2000) have observed that the photo-degradation of 2-
chlorophenol was favored at higher pH and the behaviour was dependent on factors like
the reactant, catalyst, general environment of oxidation, mechanism of reaction etc.

Egerton et al. (2005) have reported a 70 % increase in 2-NP conversion when the pH
was varied from 5.8 to 7.7 in the photo-catalytic oxidation with TiO₂. However, the
oxidation was enhanced by only 10% if the pH was further increased from 5.8 to 7.7.
Wang et al. (1999) reported that the photo catalytic oxidation of 2-NP by TiO₂ (2-NP
0.1 mM, TiO₂ 2.0 g/L, 2.25 mW/cm², reaction time 140 min) followed the order, pH 9 >
pH 7 > pH 3. They suggested a complex role of pH by proposing a free radical
mechanism as well as surface adsorption mechanism on TiO₂. At higher pH (> 6.3 to
6.6), TiO⁺ species dominate the catalyst surface and 2-NP exist in the molecular form
bound to the catalyst surface through H-bonding. The authors suggested that adsorp-
tion and decomposition of 2-NP took place favourably at the alkaline range of pH.

Similar results were shown by Asha et al. (2013) on photo-catalytic degradation of
2-NP over Ag- impregnated TiO₂ (2-NP 50 mg/L, time 2 h, catalyst dose 1.5 g/L,
temperature 30 ± 2 °C). According to these authors, at pH < pH_{ZPC}, the catalyst surface
is positively charged forming TiOH₂⁺ species and when the pH > pH_{ZPC}, the catalyst
surface is negatively charged forming TiO⁻ and TiOH species over the catalyst surface.
At lower pH_{ZPC} (7.4), the formation of OH radicals takes place that enhances the
decomposition of 2-NP. Although these works deal with the photo-oxidation of 2-NP
and the results are opposite to those observed the present work (conversion decreasing
with the rise in pH), the influence of pH on 2-NP conversion in wet catalytic oxidation
was just as drastic as in the photochemical oxidation. It is likely that as the pH of the
reaction mixture increases, adsorption of nitrophenolate ions on the catalyst surface
decreases due to competition with other ions (released from H₂O₂ and H₂O) and a small
decrease in 2-NP oxidation results.

9.3. Effects of reaction time on the oxidation of 2-nitrophenol

The oxidation reactions were carried out with water washed, acid treated and alkali
treated metal incorporated fly ash materials as catalysts at different reaction times that
varied from 5 to 240 min. All the reactions were carried out with aqueous solution of 2-
nitrophenol of concentration 5.0 × 10⁻³ M at a temperature of 323K and under
atmospheric pressure. 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 3 – 8 %. The detailed results are discussed below:

(i) Mn(II)-FA catalysts

The conversion of 2-NP increased with reaction time (5 – 240 min) till equilibrium
conditions were reached (Figure 9.5). The conversion of 2-NP in presence of H₂O₂ in
1:1 molar ratio was 39.5, 42.9 and 36.7 % 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 50.9, 57.5, and 48.8 % after 240 min. For all the
three catalysts, the reaction almost attained its equilibrium at 60 min. The conversion was rapid and the major part of the conversion was completed within 15 min.

![Graph showing conversion vs. reaction time for M1, M2, and M3 catalysts](image)

**Figure 9.5.** Effects of reaction time on oxidation of 2-nitrophenol (5.0 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) at 323 K (2-NP: H_2O_2 mole ratio 1:1, catalyst load 1.0 g/L).

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

The conversion of 2-NP increased with reaction time (5 – 240 min) (Figure 9.6) till equilibrium conditions were reached. The conversion was 44.3, 48.4 and 35.8 % 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 (2-NP/H_2O_2 mole ratio 1:1), which increased to 51.2, 58.4 and 45.3 % after 240 min. For C1 and C2, the reaction attained equilibrium after 60 min showing almost constant conversion afterwards. For C3, the reaction attained its equilibrium at 45 min. It is observed that the oxidation between 15 min and 240 min was only marginal.

(iii) **Ni(II) FA catalysts**

The conversion of 2-NP increased with reaction time (5 – 240 min) as shown in Figure 9.7 till equilibrium was reached. The conversion was 42.8, 47.8, and 31.5 % respectively for Ni(II)-water washed FA (N1), Ni(II)-acid treated FA (N2), Ni(II)-alkali treated FA (N3) after 15 min and slowly increased to 54.9, 61.3, and 41.7 % after 240 min (phenol: H_2O_2 mole ratio 1:1). For all the three catalysts, the equilibrium was attained after 60 min.

(iv) **Fe(III)-FA catalysts**

For this group of catalysts, the conversion of 2-NP increased with reaction time (5 – 240 min) from 28.5 – 53.8 %, 48.3 – 63.7 % and 39.1 – 50.4 % respectively (Figure 9.8) for Fe(III)-water washed FA (F1), Fe(III)-acid treated FA (F2), and Fe(III)-alkali treated FA (F3) in the reaction time interval of 5 to 240 min. The reaction reached equilibrium after 60 min for F1 and F2, and 45 min for F3.
Figure 9.6. Effects of reaction time on oxidation of 2-nitrophenol (5.0 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-NP: H\(_2\)O\(_2\) mole ratio 1:1, catalyst load 1.0 g/L).

Figure 9.7. Effects of reaction time on oxidation of 2-nitrophenol (5.0 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-NP: H\(_2\)O\(_2\) mole ratio 1:1, catalyst load 1.0 g/L, pH as prepared).
Maximum conversion (63.7%) was observed at 240 min (2-NP concentration 5.0 x 10^{-3} M) with catalyst Fe(III)-acid treated FA catalyst (F2) in presence of H_2O_2 (1:1) at 323 K showing its equilibrium at 60 min. It is to be noted that the 2-nitrophenol oxidation in the present work was carried out at a much higher concentration with lower catalyst load and temperature than what was used by Chaliha et al. (2012). Asha et al. (2013), have reported similar results in the photocatalytic degradation reaction of 2-NP over Ag-based TiO_2 (2-NP 50 mg/L, catalyst dose 1.5 g/L, pH 6.22, temperature 30 ± 2 °C) showing a faster rate of degradation at the initial 200 min after which the rate became slow. This behavior of degradation was explained on the basis of less availability of the active sites on the photocatalyst surface. Chaliha et al. (2012) had also reported similar pattern of results in the oxidation of 2-NP (1.0 x 10^{-3} M) in a high pressure stirred reactor (temperature 353 K, catalyst load 2.0 g/L, pH 5.2, pressure 0.2 MPa, stirred speed 180 rpm) that showed an increased trend of conversion (> 78%) with time (5 to 300 min). Interestingly, no H_2O_2 was used in the reactions and both synthesized and impregnated Mn- MCM41 gave > 35% conversion at the early stage of the reaction (5 min) and showed equilibrium at 240 min.

9.4. Kinetic study for wet oxidation of 2-nitrophenol

Kinetic study of the wet oxidation of 2-NP, the reaction was carried out starting from 5 min to the equilibrium time for each catalyst with the same reaction conditions (reaction temperature 323 K, pressure 1.0 atm, 2-NP concentration 5.0 x 10^{-3} M, 2-NP: H_2O_2 mole ratio: 1:1, catalyst loading 1.0 g/L, pH 5.2 as prepared solution). The rates of the oxidative degradation reaction 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:
\[ \log C_t = \log C_0 - \left(\frac{k}{2.303}\right) t \]  

(1)

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:

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

(2)

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 coefficient (Atkins et al., 2010). The results are summarized below:

**Mn(II)-FA catalysts.** The first order kinetic plots for Mn(II)-water washed FA (M1), Mn(II)-acid treated FA (M2) and Mn(II)-alkali treated FA (M3) catalysts are linear (Figure 9.9 top) and the values of the first-order rate coefficients (\(k_1\)) and regression coefficients are given in Table 9.1. The second order plots for Mn(II)-FA catalysts (Figure 9.9 bottom) are also linear up to the equilibrium time. The second order rate coefficient (\(k_2\)) along with the regression coefficients are shown in Table 9.1. Among the three catalysts, the acid treated catalyst (M2) gave a higher rate coefficient (both first order and second order), indicating that the active sites on M2 had comparatively higher affinity for 2-nitrophenolate ions for their eventual oxidation.

**Table 9.1.** First order and second order rate coefficients for oxidation of 2-nitrophenol over Mn(II)-FA catalysts, M1, M2, M3 (reaction temperature 323 K, 2-NP: 5.0 x 10^{-3} M, catalyst loading 1.0 g/L, pH as prepared, \(k_1\) in min^{-1}, \(k_2\) in L mol^{-1} min^{-1})

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**Co(II)-FA catalysts.** For Co(II)-water washed FA (C1), Co(II)-acid treated FA (C2) and Co(II)-alkali treated FA (C3), both first and second order kinetic plots are shown in Figure 9.10 and the plots are linear (R= 0.99) up to the reaction time of 60 min for both C1 and C2 and up to 45 min for C3. The values of the rate coefficients (both \(k_1\) and \(k_2\)) shown in Table 9.2 indicate that the Co(II)-FA catalysts follow second order kinetics more effectively than the first order kinetics and among all the three catalysts the acid treated catalyst (C2) give the better results indicating that after acid treatment, the nature and affinity of the 2-nitrophenol adsorption sites of the material changes. In general, the second order rate coefficients follow the order: C2 > C3 > C1 indicating that the acid treated Co(II)-FA had a faster rate of conversion of 2-nitrophenol in aqueous medium. However, it is observed that for the first order kinetic modal, the alkali treated catalyst (C3) showed better result and the order of the first rate coefficient was C3 > C2 > C1.
Table 9.2. First order and second order rate coefficients for oxidation of 2-NP over Co(II)-FA catalysts, C1, C2, C3 (reaction temperature: 323 K, 2-NP: 5.0 x 10^{-3} M, catalyst loading 1.0 g/L, pH as prepared, $k_1$ in min$^{-1}$ and $k_2$ in L mol$^{-1}$ min$^{-1}$)

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Figure 9.9. First order (Top) and Second order (Bottom) kinetic plots for wet oxidation of 2-nitrophenol with H$_2$O$_2$ at 323 K over Mn(II)-FA (M1,M2,M3) respectively (Catalyst 1.0 g/L, 2-NP: H$_2$O$_2$ mole ratio 1:1, pH as prepared).
Figure 9.10. First order (Top) and Second order (Bottom) kinetic plots for wet oxidation of 2-nitrophenol with H₂O₂ 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-NP: H₂O₂ mole ratio 1:1, pH as prepared).

Ni(II)-FA catalysts. Both first order and second order kinetic plots were also plotted for the Ni(II)-FA catalysts (N1, N2, N3) in Figure 9.11. In both cases, the plots are linear with regression coefficient, R= 0.99 up to the reaction time of 60 min for all the three catalysts (Table 9.3). From the values of regression coefficients, it is difficult to ascertain whether first order or second order mechanism is followed in 2-nitrophenol oxidation over Ni(II)-FA catalysts. In both cases, the rate coefficient has higher values for the acid treated catalyst (N2). In general, the rate coefficients (both first and second
order) follow the following order: N2 > N1 > N3 indicating that the alkali treated Ni(II)-FA has the slowest rate of conversion of 2-nitrophenol in aqueous medium.

**Table 9.3.** First order and second order rate coefficients for catalytic oxidation of 2-nitrophenol over Ni(II)-FA catalysts, N1, N2, N3 (reaction temperature: 323 K, 2-NP: 5.0 x 10^{-3} M, catalyst loading 1.0 g/L, pH as prepared, k_1 in min^{-1} and k_2 in L mol^{-1} min^{-1})

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**Fe(III)-FA catalysts.** For these catalysts also, very good linear plots (Figure 9.12) were obtained for first (Top) order as well as second (Bottom) order kinetics with high regression coefficients. Table 9.4 shows that the rate coefficients (both first and second order) follow the order, F1 > F2 ≈ F3 indicating that the oxidation of aqueous 2-NP takes place with a faster rate on water washed Fe(III)-FA (F1).

**Table 9.4.** First order and second order rate coefficients for oxidation of 2-nitrophenol over Fe(III)-FA catalysts, F1, F2, F3 (reaction temperature: 323 K, 2-NP: 5.0 x 10^{-3} M, catalyst loading 1.0 g/L, pH as prepared, k_1 in min^{-1} and k_2 in L mol^{-1} min^{-1})

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The results of kinetic study indicate that incorporation of Mn(II), Co(II), Ni(II) and Fe(III) into fly ash yields catalysts with slightly different properties for 2-nitrophenol oxidation in aqueous medium. Among all the twelve catalysts, Fe(III)-water washed fly ash (F1) gives higher rate coefficients for first order and whereas Ni(II)-acid treated fly ash (N2) gives the higher rate coefficients for second order kinetics. It is however not possible from the present work to definitely establish the order of the reaction.

In an earlier work, Wang et al. (1999) have reported that 2-NP photo degradation with catalyst TiO_2 (2.0 g/L) carried out in a batch reactor (2-NP concentration 0.1 mM, light intensity 2.25 mW/cm^2) follows Langmuir- Hinshelwood mechanism and follow first order kinetics with rate constant of 0.027 min^{-1} at pH 7.0 (R^2 0.99). Chaliha et al. (2012) have reported that wet air oxidation of aqueous 2-nitrophenol (1.0 x 10^{-3} M) at 353 K and 0.2 MPa with Mn(II)-MCM41 (either synthesized or impregnated) as the catalysts (2.0 g/L) in a stirred reactor follows first order kinetics with a rate constant of
3.7 and 5.8 \times 10^{-3} \text{ L g}^{-1}\text{min}^{-1}) \text{ for synthesized and impregnated catalysts respectively. Testing for second order kinetics did not yield good results.}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{kinetic_plots.png}
\caption{First order (Top) and Second order (Bottom) kinetic plots for wet oxidation of 2-nitrophenol with H$_2$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-NP: H$_2$O$_2$ mole ratio 1:1).}
\end{figure}
Figure 9.12. First order (Top) and Second order (Bottom) kinetic plots for wet oxidation of 2-nitrophenol with $\text{H}_2\text{O}_2$ 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-NP: $\text{H}_2\text{O}_2$ mole ratio 1:1)

In the present work, good linearity was observed with both first and second order kinetics, and it is very difficult to identify the exact order of the oxidative reaction of 2-nitrophenol. It is however true that the kinetics of a catalytic reaction is extremely complex and depends on several mutually-dependent factors such as catalyst type and loading, concentration of reactant and other parameters.
9.5. Effects of catalyst load on wet oxidation of 2-nitrophenol

To study the effects of catalyst loadings on 2-NP oxidation, five different catalyst loads of 0.4, 1.0, 2.0, 4.0, 8.0 g/L were taken (2-NP 5.0 x 10^{-3} M, temperature 323 K, pressure 1 atm, hydrogen peroxide 5.0 x 10^{-3} M, mole ratio 1:1). The results obtained with the different catalysts are discussed below.

(i) Mn(II)-FA catalysts

When the catalyst loading was increased from 0.4 to 8.0 g/L, 2-NP oxidation increased from 50.3 – 53.3 % only for Mn(II)-water washed FA (M1), 56.3 – 59.2 % for Mn(II)-acid treated FA (M2) and 48.1 – 51.3 % for Mn(II)-alkali treated FA (M3) as shown in Table 9.5. The increase of 2 to 3 % in 2-NP oxidation was much less when compared to the actual increase in the catalyst loading. Thus, the oxidation has no apparent dependence on catalyst loading.

Table 9.5. Effects of catalyst load on 2-nitrophenol oxidation with Mn(II)-FA catalysts, M1, M2, M3 at 323 K (2-NP 5.0 x 10^{-3} M, 2-NP: H_2O_2 mole ratio 1:1, time 240 min, pH as prepared)

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>2-nitrophenol oxidation (%) at catalyst load (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.4</td>
</tr>
<tr>
<td>M1</td>
<td>50.3</td>
</tr>
<tr>
<td>M2</td>
<td>56.3</td>
</tr>
<tr>
<td>M3</td>
<td>48.1</td>
</tr>
</tbody>
</table>

(ii) Co(II)-FA catalysts

Table 9.6 shows the effects of increasing catalyst load (0.4 to 8.0 g/L) on 2-NP oxidation with Co(II)-FA catalysts. The oxidation increased from 49.6 – 53.7 % for Co(II)-water washed FA (C1), 57.5 – 61.8 % for Co(II)-acid treated FA (C2) and 44.8 – 58.7 % for Co(II)-alkali treated FA (C3). The increase was confined to about 3 - 4 % in each case indicating that increasing the catalyst load has only marginal influence on 2-nitrophenol oxidation.

Table 9.6. Effects of catalyst load on 2-nitrophenol oxidation with Co(II)-water washed FA (C1), Co(II)-acid treated FA (C2), Co(II)-alkali treated FA (C3) respectively at 323 K (2-NP 5.0 x 10^{-3} M, 2-NP: H_2O_2 mole ratio 1:1, reaction time 240 min)

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>2-nitrophenol oxidation (%) at catalyst load (g/L)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>0.4</td>
</tr>
<tr>
<td>C1</td>
<td>49.6</td>
</tr>
<tr>
<td>C2</td>
<td>57.5</td>
</tr>
<tr>
<td>C3</td>
<td>44.8</td>
</tr>
</tbody>
</table>

(iii) Ni(II)-FA catalysts

With Ni(II)-FA catalysts, 2-NP oxidation increased from 53.5 – 57.2 % for Ni(II)-water washed FA (N1), 59.4 – 63.8 % for Ni(II)-acid treated FA (N2) and 41.1 – 44.9 % for Ni(II)-alkali treated FA (N3) for increase in catalyst loading from 0.4 to 8.0 g/L (Table 9.7). The increase was ~ 3 % for N1, ~ 4 % for N2 and ~ 4 % for N3.
Table 9.7. Effects of catalyst load on 2-nitrophenol oxidation with Ni(II)-water washed FA (N1), Ni(II)-acid treated FA (N2), Ni(II)-alkali treated FA (N3) respectively at 323 K (2-NP $5.0 \times 10^{-3}$ M, 2-NP: $H_2O_2$ mole ratio 1:1, reaction time 240 min)

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>2-nitrophenol oxidation (%) at catalyst load (g/L)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>0.4</td>
</tr>
<tr>
<td>N1</td>
<td>53.5</td>
</tr>
<tr>
<td>N2</td>
<td>59.4</td>
</tr>
<tr>
<td>N3</td>
<td>41.1</td>
</tr>
</tbody>
</table>

(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-NP oxidation (Table 9.8). The oxidation increased from 51.3 – 56.7 % for Fe(III)-water washed FA (F1), 62.8 – 66.3 % for Fe(III)-acid treated FA (F2) and 50.4 – 54.6 % for Fe(III)-alkali treated FA (F3). The increase was only ~3 to ~ 4 % as the catalyst loading was increased by 20 times.

Table 9.8. Effects of catalyst load on 2-nitrophenol oxidation with Fe(III)-water washed FA (F1), Fe(III)-acid treated FA (F2), Fe(III)-alkali treated FA (F3) respectively at 323 K (2-NP $5.0 \times 10^{-3}$ M, 2-NP: $H_2O_2$ mole ratio 1:1, reaction time 240 min)

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>2-nitrophenol oxidation (%) at catalyst load (g/L)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>0.4</td>
</tr>
<tr>
<td>F1</td>
<td>51.3</td>
</tr>
<tr>
<td>F2</td>
<td>62.8</td>
</tr>
<tr>
<td>F3</td>
<td>47.3</td>
</tr>
</tbody>
</table>

From these results, it can be inferred that variations in catalyst loadings (0.4 – 8.0 g/L), keeping the other parameters constant, have only minor impacts on 2-nitrophenol oxidation. The increase in conversion of 2-nitrophenol was not comparable with the increase in catalyst load. For example, with 20 times increase in load of Fe(III)-acid treated FA catalyst (from 0.4 to 8.0 g/L), only 3% increase in conversion was observed. Chaliha et al. (2012) have reported similar effects showing that with increase in catalyst load from 2.0 to 10.0 g/L, the conversion of 2-NP ($10^{-3}$ M) was not influenced much at 353 K (reaction time 300 min) over both synthesized and impregnated Mn(II)-MCM41 catalysts indicating that the amount of active O* species present in the catalyst was nearly the same and thus the minimum catalyst loading (2.0 g/L) was just as effective in almost 78 % conversion. Such a view is not tenable in the present work since the increase in 2-NP oxidation did not reach a peak within the considerably wide range of catalyst loadings, but showed only a small continuous increase in conversion in the whole range of loadings. It is possible that the catalysis by the fly ash-based materials also proceed by a free radical mechanism involving OH radicals, generated by interactions of active O-species on the catalyst surface with molecules like $H_2O_2$ and $H_2O$. It is to be noted that the FA-based catalysts are not pure oxides, yet some limited amount of oxide formation is likely during the calcination process in air. Therefore,
whether the catalyst amount is 0.4 g L\(^{-1}\) or 8.0 g L\(^{-1}\), the amount of oxide or more precisely, the number of active species per unit mass remains the same. Hence the conversion was not likely to change much with increase in catalyst loading and therefore a small amount of catalyst load (0.4 g/L) is as good as any higher loading and may be sufficient for initiation of free radical mechanism for conversion of phenol. This brings about almost 40 – 60 % conversion under moderate conditions. It is also likely that under the conditions, the oxidation might have been controlled, not by surface chemical reactions, but by the rate at which phenol molecules are transported from the liquid phase to the catalyst surface in which case catalyst loading will not have much effect on conversion.

9.6. Effects of mole ratio on wet oxidation of 2-nitrophenol

With an increase in the mole ratio of hydrogen peroxide and 2-NP from 1:1 to 20:1 for a reaction time of 240 min (catalyst load 1.0 g L\(^{-1}\)), the wet oxidative reaction has shown better conversion (Table 9.9). Six different mole ratios of H\(_2\)O\(_2\) to 2-nitrophenol (0, 1.0, 2.0, 5.0, 10.0, 20.0) were taken (5.0 \(\times\) 10\(^{-3}\) M) with fixed reaction time (240 min), temperature (323 K) and pressure (1.0 atm).

Table 9.9: Effects of increasing mole ratio of feed (H\(_2\)O\(_2\): 2-NP) on oxidation of 2-NP (5.0 \(\times\) 10\(^{-3}\) M) with metal impregnated fly ash (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 as prepared)

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Conversion (%) of 2-nitrophenol at different mole ratio of (H(_2)O(_2)/2-NP)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>M1</td>
<td>6.7</td>
</tr>
<tr>
<td>M2</td>
<td>12.3</td>
</tr>
<tr>
<td>M3</td>
<td>3.1</td>
</tr>
<tr>
<td>C1</td>
<td>8.8</td>
</tr>
<tr>
<td>C2</td>
<td>14.7</td>
</tr>
<tr>
<td>C3</td>
<td>5.1</td>
</tr>
<tr>
<td>N1</td>
<td>10.7</td>
</tr>
<tr>
<td>N2</td>
<td>17.3</td>
</tr>
<tr>
<td>N3</td>
<td>3.4</td>
</tr>
<tr>
<td>F1</td>
<td>10.1</td>
</tr>
<tr>
<td>F2</td>
<td>16.8</td>
</tr>
<tr>
<td>F3</td>
<td>7.8</td>
</tr>
</tbody>
</table>

(i) Mn(II)-FA catalysts

When the mole ratio of hydrogen peroxide and 2-NP was increased from 0:1 to 20:1, phenol oxidation increased from 6.7 – 91.9 % for Mn(II)-water washed FA (M1), 12.3 – 93.7 % for Mn(II)-acid treated FA (M2) and 3.1 – 89.5 % for Mn(II)-alkali treated FA (M3). This huge increase in 2-nitrophenol oxidation as a result of increasing the number of moles of the oxidant (H\(_2\)O\(_2\)) is shown in Figure 9.13.
Figure 9.13. Effects of mole ratio of H$_2$O$_2$ on oxidation of 2-nitrophenol (5.0 x 10$^{-3}$ M) with Mn(II)-FA catalysts (M1, M2, M3) at 323 K (reaction time 240 min, catalyst load 1.0 g/L, pH as prepared)

(ii) Co(II)-FA catalysts

Figure 9.14 shows the effects of increasing mole ratio of H$_2$O$_2$: 2-NP from 0:1 to 20:1, when conversion of 2-nitrophenol increased from 8.8 – 91.1 % for Co(II)-water washed FA (C1), 14.7 – 94.1 % for Co(II)-acid treated FA (C2) and 5.1 – 86.5 % for Co(II)-alkali treated FA (C3).

Figure 9.14. Effects of mole ratio of H$_2$O$_2$ on oxidation of 2-nitrophenol (5.0 x 10$^{-3}$ M) with Co(II)-FA catalysts (C1, C2, C3) at 323 K (time 240 min, catalyst load 1.0 g/L, pH as prepared)

(iii) Ni(II)-FA catalysts

With Ni(II)-FA catalysts, 2-NP oxidation increased from 54.9 – 94.7 % for Ni(II)-water washed FA (N1), 61.3 – 95.7 % for Ni(II)-acid treated FA (N2) and 41.7 – 83.7 % for Ni(II)-alkali treated FA (N3) when the mole ratio of H$_2$O$_2$: 2-NP was increased from
1.1 to 20.1 (Figure 9.15). With no H₂O₂ in the reaction mixture, the conversion was very low, i.e., 10.7, 17.3 and 3.4 % respectively for Ni(II)-water washed FA (N1), Ni(II)-acid treated FA (N2), and Ni(II)-alkali treated FA (N3) at the similar reaction condition.

![Figure 9.15](image)

**Figure 9.15.** Effects of mole ratio of H₂O₂ on oxidation of 2-nitrophenol (5.0 x 10⁻³ M) with Ni(II)-FA catalysts (N1, N2, N3) at 323 K (reaction time 240 min, catalyst load 1.0 g/L, pH as prepared)

(iv) Fe(III)-FA catalysts

In the case of Fe(III)-FA catalysts, increase in mole ratio of H₂O₂: 2-NP from 1.1 to 20.1 had similar effects on 2-NP oxidation with that of the other three metal incorporated catalysts (Figure 9.16). The oxidation increased from 53.8 – 93.3 % for Fe(III)-water washed FA (F1), 63.7 – 97.7 % for Fe(III)-acid treated FA (F2) and 50.4 – 87.4 % for Fe(III)-alkali treated FA (F3). If the reaction was carried out with the same set of conditions as above but without taking H₂O₂ in the reactant mixture, the catalyst, F1, F2 and F3 could convert 10.1 %, 16.8 %, 7.8 % of 2-nitrophenol.

The stoichiometric equation for the complete oxidation of 2-nitrophenol with H₂O₂ (Equation 4) shows that for bringing about complete oxidation of 1 mole of 2-NP, 13.5 moles of H₂O₂ are required:

\[
2C_6H_4(NO_2)(OH) + 27 H_2O_2 \rightarrow 12 CO_2 + 31 H_2O + HNO_3 + HNO_2
\] (3)

Thus, the results obtained in this work, showing enhancement in oxidation of 2-nitrophenol with increasing amount of H₂O₂ in the feed, are in agreement with the stoichiometric equation. Thus, significantly large conversion could be obtained with increasing concentration of H₂O₂.
In the catalytic wet peroxide oxidation of 2-NP (10^{-3} M) with two catalysts viz. Fe_{2}O_{3} (70 g/L, 60 min) and MnO_{2} (10 g/L, 120 min), Chaliha et al. (2006) have observed that with increase in H_{2}O_{2} mole ratio 1:1 to 1:10, the conversion of 2-NP increased and showed highest conversion (above 89.0 %) with 1:10 mole ratio at 305 K. The amount of hydrogen peroxide was shown to play a very important role on oxidation of 2-NP. Stoichiometrically, it was found that a ratio of almost 1:10 with respect to the oxidant was sufficient to bring a significant amount of oxidation of 2-NP. Compared to these results, it was found in the present work that all the twelve catalysts showed more than 80 % conversion with a very low catalyst load and comparatively high reactant concentration.

9.7 Effects of reactant concentration on 2-nitrophenol oxidation
The reactant (2-NP) was used in six different concentrations of 4.0, 6.0, 8.0, 10.0, 20.0 and 50.0 x 10^{-4} mol/L to evaluate the role of 2-NP concentration on the wet oxidation process at temperature 323 K and at atmospheric pressure.

(i) Mn(II)-FA catalysts. The reactions were carried out with a fixed catalyst load of 1.0 g/L. With increase in concentration of phenol from 4.0 x10^{-4} – 50.0 x 10^{-4} M, the conversion decreased in the following order:

- 67.9 –50.9 % for Mn(II)-water washed fly ash (M1),
- 73.4 – 57.5 % for Mn(II)-acid treated fly ash (M2) and
- 67.9 – 48.8 % for Mn(II)-alkali treated fly ash (M3).

Increasing 2-NP concentration (at fixed catalyst load, reaction time and reaction temperature) is equivalent to an increase in the number of the reactant molecules that compete among themselves for the available adsorption sites on the catalyst surface where the conversion takes place. Since the number of adsorption sites on the catalyst
surface is constant for a particular catalyst load, the conversion is bound to come down drastically with increased reactant concentrations.

The decrease in 2-NP oxidation with Mn(II)-FA catalysts with increase in 2-NP concentration (4.0 x 10^{-4} to 50.0 x 10^{-4} M) is represented graphically in Figure 9.17.

![Figure 9.17](image)

**Figure 9.17.** Oxidation of 2-nitrophenol at different concentrations with M1, M2 and M3 catalysts (catalyst load 1.0 g/L, reaction time 240 min, 2-NP: H_2O_2 mole ratio 1:1, reaction temperature 323 K and atmospheric pressure)

(ii) **Co(II)-FA catalysts.** The catalyst load taken was 1.0 g/L while 2-NP concentration was varied from 4.0 x 10^{-4} to 50.0 x 10^{-4} mol/L). The decrease in conversion with increased concentration of phenol was (i) 69.1 – 51.2 % for Co(II)-water washed fly ash (C1), (ii) 74.1 – 58.4 % for Co(II)-acid-treated fly ash (C2) and (iii) 65.1 – 45.3 % for Co(II)-alkali treated fly ash (C3). The detailed results and a comparison of the performance of the three catalysts with increasing 2-NP concentration are shown graphically in Figure 9.18.

![Figure 9.18](image)

**Figure 9.18.** Oxidation of 2-nitrophenol at different concentrations (catalyst load 1.0 g/L for C1, C2 and C3, reaction time 240 min, 2-NP: H_2O_2 mole ratio 1:1, reaction temperature 323 K and atmospheric pressure, pH as prepared)
(iii) Ni(II)-FA catalyst. In this case, the decrease in conversion of the wet oxidation with increased concentration of 2-NP was observed as (i) 74.1 – 54.9 % for Ni(II)-water washed fly ash N11), (ii) 78.7 – 61.3 % for Ni(II)-acid-treated fly ash (N2) and (iii) 60.2 – 41.7 % for Ni(II)-treated fly ash (N3). A comparison of the performance of the three Ni(II)-catalysts with increasing 2-NP concentration is shown in Figure 9.19.

![Graph showing % Conversion vs 2-NP concentration (x 10^-4 M)](image)

Figure 9.19. Oxidation of 2-nitrophenol at different concentrations (catalyst load 1.0 g/L for N1, N2 and N3, reaction time 240 min, 2-NP: H_2O_2 mole ratio 1:1, reaction temperature 323 K and atmospheric pressure, pH as prepared)

(iv) Fe(III)-FA catalysts. The decrease in conversion in the wet oxidation of 2-nitrophenol with increase in reactant concentration was as follows:

(i) 74.4 – 53.8 % for Fe(III)-water washed fly ash (F1),
(ii) 83.2 – 63.7 % for Fe(III)-acid-treated fly ash (F2) and
(iii) 69.1 – 50.4 % for Fe(III)-alkali treated fly ash (F3).

These results and a comparison of the performance of the Fe(III)-catalysts with increasing 2-NP concentration are shown in Figure 9.20.

Thus, from the above results, it can be summarized that when 2-nitrophenol concentration was varied from 4.0 x 10^{-4} to 50 x 10^{-4} mole L^{-1} with constant reaction time (300 min), catalyst load (1.0 g L^{-1}) and constant amount of the oxidant H_2O_2 (50.0 x 10^{-4} mole L^{-1}), the conversion of the reactant came down. The decrease in conversion was observed to follow almost similar pattern in all the twelve cases.

The decreased conversion of 2-nitrophenol with increase in its concentration can be attributed to stiff competition for active sites on the catalyst surface that the reactant molecules had to face. However, it was observed that the decrease was not to the same extent for all the catalysts and therefore, the type of the catalyst also played an important role in deciding the oxidative conversion.
In the present case, Fe(III)-acid treated catalyst (F3) showed maximum conversion of 83.2% at the lowest phenol concentration of $4.0 \times 10^{-4}$ mol/L. These results were supported by Chaliha et al. (2012). They also showed similar trends of results with 2-NP over Mn(II)-MCM 41 (temperature 353 K, catalyst load 2.0 g/L, reaction time 300 min) with variation of the concentration of the reactant from 2.0 to 10.0 ($x \times 10^{-4}$ M). A large number of reactant molecules flocking together over the catalyst surface competing amongst themselves for the active sites is the reason for lower oxidation at higher concentration.

Zaggout et al. (2008) have reported similar pattern of results for electrochemical degradation of 2-nitrophenol over PbO$_2$/Ti modified electrode (current density 40 mA cm$^{-2}$, pH 2.47, temperature 303 K, NaCl 4.0 g/L). They have reported that as 2-NP concentration increased from 10 to 300 mg/L, the conversion in terms of COD removal efficiency was reduced. There was however little effect if the concentration is < 100 mg/L.

### 9.8 Effects of the reaction temperature on 2-nitrophenol oxidation

To observe the influence of reaction temperature on the catalytic wet oxidation reactions of 2-NP, 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-NP concentration of $5.0 \times 10^{-3}$ M, catalyst load of 1.0 g/L and a reaction time of 240 min in the presence of equimolar H$_2$O$_2$. It was found that the reaction temperature had positive influence on 2-nitrophenol 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 300 min, 2-NP oxidation varied from 48.1 – 54.9 % for Mn(II)-water washed FA (M1), 55.1 – 63.8 % for Mn(II)-acid treated FA (M2) and 46.6 – 53.6 % for Mn(II)-alkali treated FA (M3) as shown in Figure 9.21. It is observed from the trends that the
conversion was still increasing at 343 K and might reach higher values at higher temperatures.

**Figure 9.21.** Effects of reaction temperature on oxidation of 2-nitrophenol (5.0 x 10^{-3} M) with Mn(II)-FA catalysts (M1, M2, M3) (reaction time 240 min, 2-NP: H₂O₂ mole ratio 1:1, catalyst load 1.0 g/L)

(ii) Co(II)-FA catalysts

Figure 9.22 shows the effects of increasing reaction temperature on the conversion of 2-NP over Co(II)-FA catalysts. As the reaction temperature was increased from 303 to 343 K, 2-NP oxidation also increased from 46.2 – 55.7 % for Co(II)-water washed FA (C1), 55.7 – 61.2 % for Co(II)-acid treated FA (C2), 42.4 – 48.3 % for Co(II)-alkali treated FA (C3). While the conversion over C1 was continuously increasing over the whole temperature range, it reached a plateau for C2 and C3 after the reaction temperature exceeded ~ 323 K.

**Figure 9.22.** Effects of reaction temperature on oxidation of 2-nitrophenol (5.0 x 10^{-3} M) with Co(II)-FA catalysts (C1, C2, C3) (reaction time 240 min, 2-NP: H₂O₂ mole ratio 1:1, catalyst load 1.0 g/L)
(iii) Ni(II)-FA catalysts

With Ni(II)-FA catalysts, 2-NP oxidation varied from 51.7 – 56.9 % for Ni(II)-water washed FA (N1), 57.1 – 66.8 % for Ni(II)-acid treated FA (N2) and 37.6 – 45.6 % for Ni(II)-alkali treated FA (N3) in the temperature range of 303 to 343 K (Figure 9.23). For all the three Ni(II)-FA catalysts, there was a continuous increasing trend in conversion, however, the rate was somewhat slow for N1 and N3 after 333 K in comparison to N2.

![Graph showing conversion vs reaction temperature for Ni(II)-FA catalysts](image)

**Figure 9.23.** Effects of reaction temperature on oxidation of 2-nitrophenol (5.0 x 10^{-3} M) with Ni(II)-FA catalysts (N1, N2, N3) (reaction time 240 min, 2-NP: H_2O_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 the reaction temperature from 303 to 343 K had similar effects on 2-NP oxidation with that of the other metal impregnated catalysts (Figure 9.24). The oxidation increased from 50.7 – 57.8 % for Fe(III)-water washed FA (F1), 61.1 – 68.3 % for Fe(III)-acid treated FA (F2) and 46.1 – 56.7 % for Fe(III)-alkali treated FA (F3). It is observed that the conversion of 2-NP continued to increase even after a reaction temperature of 343 K for all the three catalysts and thus expected to increase continuously with increase in temperature.

General observations on the basis of the above results are that at a higher reaction temperature, the oxidation of 2-nitrophenol showed an enhanced trend for all the metal incorporated catalysts, although there are differences for each individual catalyst. With increase in temperature, the mobility of the reactant molecules improves and they can reach the catalyst surface without the transport limitation and undergo transformation. The influence of temperature in case of all the catalysts is almost a linear increase in conversion. Out of the catalysts, Fe(III)-acid treated FA (F2) gives the maximum conversion (68.3 %) at 343 K under equivalent conditions.
Tian et al. (2007) have carried out electrochemical oxidation of 2-NP (initial concentration 0.35 mM) on Ti/IrO\textsubscript{2}-SnO\textsubscript{2}-Sb\textsubscript{2}O\textsubscript{3} electrode in 0.5 M NaOH and varied the temperature from 275 to 313 K and found that the rate of electrochemical removal of 2-nitrophenol increased indicating an endothermic oxidation process. Similar results were reported earlier by Jain et al. (2004). Extensive hydrogen bonding between water and NP molecules was suggested by these authors who showed that with increase in the temperature, the two processes of (a) diffusion of 2-NP molecules to the catalyst surface and (b) the breaking of hydrogen bonds, were enhanced promoting formation of hydroxyl radicals which govern oxidation of 2-NP. According to Chaliha at el. (2012), oxidation of 2-NP (10\textsuperscript{-3} M) with both synthesized and impregnated Mn(II)-MCM 41, the effect of temperature was not much. They reported that, as the temperature increased from 333 to 413 K, the conversion of 2-NP was enhanced only a little indicating that the oxidation process did not require a large energy input and a temperature of just 333 K could bring about 75.8 % and 87.9% conversion for both the catalysts after 300 min with a catalyst load of 2.0 g/L.

9.9 Monitoring of 2-nitrophenol oxidation with COD measurement

Reduction in COD load of the reaction mixture was another clear indication of 2-nitrophenol mineralization. For Mn(II)-FA catalysts, it was observed that the initial COD load of the reaction mixture (2-NP: 5.0 x 10\textsuperscript{-3} M, H\textsubscript{2}O\textsubscript{2}: 5.0 x 10\textsuperscript{-3} M, catalyst load: 1.0 g L\textsuperscript{-1}, temperature 323 K, reaction time 0 – 240 min) decreased from 980 to 240, 140 and 300 mg/L respectively for Mn(II)-water washed FA, Mn(II)-acid treated FA and Mn(II)-alkali treated FA (Figure 9.25) (The same results can be expressed in terms of COD reduction of 20.4 to 75.5%, 36.7 to 85.7% and 14.3 to 69.4 % for M1, M2, M3 in the reaction time interval of 15 to 240 min).
The COD reduction does not truly conform to the extent of increase in oxidation of 2-NP (Figure 9.25) which showed comparatively large oxidation (39.5, 42.9 and 36.7 % for M1, M2 and M3 respectively) within the first 15 min of reaction time. This indicates that COD reduction and 2-NP oxidation do not follow identical rates and at the initial stage of reaction, COD reduction is much slower in comparison 2-NP oxidation. However, as the reaction proceeds further, COD reduction becomes larger and eventually it is more than 2-NP oxidation. Thus, after 240 min of reaction, COD reduction was 75.5, 85.7 and 69.4 % for the catalysts, M1, M2 and M3 respectively while 2-NP oxidation was 50.9, 57.5, and 48.8 % under identical reaction conditions. It was observed that M2 and M3 showed the maximum (28.2) and minimum (20.6) difference between the COD reduction and 2-NP conversion. Large decrease in COD loading pointed to an approach towards complete mineralization.

For Co(II)-FA catalysts, the COD load of the reaction mixture (Figure 9.26) decreased from 980 to 220, 120, 340 mg/L for reaction time of 0 to 240 min for Co(II)-water washed FA, Co(II)-acid treated FA and Co(II)-alkali treated FA (COD reduction increased from 26.5 to 77.6 %, 30.6 to 87.8 % and 10.2 to 65.3 % for C1, C2, C3 as reaction time increased from 15 to 240 min). At 240 min, the oxidation of 2-NP was 51.2, 58.4, 45.3 % for C1, C2 and C3 respectively showing a significant difference between COD reduction and conversion of 2-NP.

In case of Ni(II)-catalysts, the COD load of the reaction mixture (Figure 9.27) decreased from 980 to 200, 80, 400 mg L\(^{-1}\) for reaction time of 0 to 240 min for Ni(II)-water washed FA, Ni(II)-acid treated FA and Ni(II)-alkali treated FA respectively (COD reduction increased from 36.7 to 79.6 %, 36.7 to 91.8 % and 18.4 to 59.2 % for N1, N2, N3 as the reaction time increased from 15 to 240 min).
Figure. 9.26. COD reduction in 2-nitrophenol 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-NP $5.0 \times 10^{-3}$ M, catalyst loading 1.0 g/L, pH as prepared, 2-NP: H$_2$O$_2$ mole ratio 1:1).

Figure. 9.27. COD reduction in 2-nitrophenol 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-NP $5.0 \times 10^{-3}$ M, catalyst loading 1.0 g/L, pH as prepared, 2-NP: H$_2$O$_2$ mole ratio 1:1).

For Fe(III)-catalysts, the COD load of the reaction mixture (Figure. 9.28) decreased from 980 to 220, 60, 360 mg L$^{-1}$ for reaction time of 0 to 240 min for Fe(III)-water washed FA, Fe(III)-acid treated FA and Fe(III)-alkali treated FA respectively (COD reduction increased from 20.4 to 77.6 %, 24.5 to 93.9 % and 14.3 to 71.4 % for F1, F2, F3 as the reaction time increased from 15 to 240 min).
The present work demonstrated 93.9% COD removal in CWAO process of 2-NP at 323 K with Fe(III)-acid-treated FA catalyst (F2). From Table 9.10, it was observed that the difference between 2-NP conversion and COD removal was the largest for the catalyst N2 (30.5) and it could be inferred that N2 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. The order of the catalysts showing higher mineralization was given below:

\[ \text{N2} \approx \text{F2} > \text{C2} > \text{M2} > \text{C1} > \text{N1} \approx \text{M1} > \text{F1} > \text{F3} > \text{M3} > \text{C3} > \text{N3} \]

Zaggout et al. (2008) have reported that in electrochemical degradation of aqueous 2-nitrophenol solution (100 mg/L) over PbO$_2$/Ti modified electrode (current density 40 mA cm$^{-2}$, pH 2.47, NaCl 4.0 g/L), the COD reduction came down with increase in time and at the saturation time (60 min), maximum COD reduction (almost 95 %) was observed at 303 K. Sankara Narayanan et al. (2003) had reported that for the electro Fenton process of 2-CP, with increase in reaction time, both oxidation and COD removal increased, but the rate at which COD reduction takes place was somewhat less compared to the rate of oxidation of 2-CP.

9.10. Mechanism of oxidative destruction

A mechanism for the oxidation of 2-NP is suggested below based on (i) GC-MS identification of some products after the reaction, (ii) known products of degradation obtained from literature, and (ii) possible products of degradation from the knowledge of degradation pathways likely to be followed by the reactants.

In GC-MS analysis, (i) 2-nitrohydroquinone and (ii) 2-nitro-1,4-benzoquinone were found in the product mixture of 2-NP oxidation.

The probable pathway for oxidative destruction of 2-NP (I) initiated by the catalysts could be proposed to have proceeded via the hydroxyl radicals (Scheme 7) as follows:

1) The radicals will add to 2-NP (I) at the para-position of the cyclic ring to give 2-nitrohydroquinone (II),
2) This product (II) is converted by more hydroxyl radicals to 2-nitro-1,4-benzoquinone (III),
3) 2-nitro-1,4-benzoquinone (III) undergoes further transformation through ring cleavage and subsequent degradation to simple aliphatic compounds, which will eventually decompose to CO$_2$, H$_2$O, HNO$_2$, and HNO$_3$.

Najjar et al. (2001) have suggested an identical scheme for degradation of 2-NP by photodegradation on Al-pillared montmorillonite doped with copper.
Figure. 9.29 GC-MS of the product mixture of 2-nitrophenol ($5.0 \times 10^{-2}$ M) oxidation over Mn(II)-water washed fly ash (M1, load 1.0 g/L, reaction time 240 min, temperature 323 K, 2-NP/H$_2$O$_2$ mole ratio 1:5)
Figure. 9.30. Reaction scheme showing the pathways for product formation in catalytic wet oxidation of 2-NP with H$_2$O$_2$ over Mn(II), Co(II), Ni(II) and Fe(III)-fly ash as the catalyst.

9.11. 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-nitrophenol. 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-NP) in the reaction mixture, more than 90% conversion could be achieved. The results showed that the total conversion of 2,4,6-TCP 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 give linear agreement with first and 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 (5.5) of the as prepared 2-nitrophenol aqueous solution.