ABSTRACT

This thesis consists of the following chapters:

Chapter 1: Introduction
Chapter 2: Experimental Methodology
Chapter 3: Characterization of the catalysts
Chapter 4: Wet oxidation of phenol
Chapter 5: Wet oxidation of 2-chlorophenol
Chapter 6: Wet oxidation of 4-chlorophenol
Chapter 7: Wet oxidation of 2,4-dichlorophenol
Chapter 8: Wet oxidation of 2,4,6-trichlorophenol
Chapter 9: Wet oxidation of 2-nitrophenol
Chapter 10: Wet oxidation of 4-nitrophenol
Chapter 11: Conclusion

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

Chapter 1 (Introduction) includes an introduction to the various sources of organic pollutants in the environment, particularly their harmful effects on humans and the ecosystem. Phenol and its analogous are the constituents of common industrial effluents particularly discharged by the petroleum, paper, agrochemical, pharmaceutical, rubber chemicals, dyes and pesticide industries. Almost all phenolic compounds under study are toxic, carcinogenic, nonbiodegradable and harmful in both aqueous system and the environment in general; imparting objectionable odour to drinking water and serious health problems to animals and humans. Therefore, removal of these pollutants from industrial waste water has become a major environmental concern. The chapter gives a brief description of various types of oxidative processes for the degradation of the organic pollutants, particularly Fenton and Fenton type processes and also reviews the oxidative treatment of phenolic water with particular reference to catalytic wet oxidation.
and wet peroxide oxidation. Various types of catalysts for wet oxidation with particular reference to transition metal, noble metal and mixed metal oxides and metals supported by clay or zeolite have also been described. The chapter also reviews the application of fly ash as an adsorbent and catalyst in various fields particularly for adsorption of heavy metals and phenolic contaminants from wastewater.

Chapter 2 (Experimental Methodology) includes the description of the methods used for modification of fly ash. 1.0 M sulphuric acid and 1.0 M NaOH were used separately to treat the water washed fly ash. After treatment, each type of fly ash material was refluxed with 1 M solution of Mn(II), Co(II), Ni(II) and Fe(III)-solution to obtain four water washed, four acid treated, four alkali treated catalysts. Thus, as a whole, 12 transition metal impregnated fly ash catalysts were obtained and tested for wet catalytic oxidation of the phenolic compounds.

A brief description of the techniques used for characterization of the catalysts is also given in this chapter. The techniques include Cation exchange capacity (CEC), atomic absorption spectrometry (AAS), X-ray fluorescence spectrophotometry (XRF), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and BET surface area and pore size measurement. The methodology for wet oxidation of the phenols, determination of conversion and mineralization (COD analysis), leachibility of the catalysts and product analysis (GC-MS) was also described.

Chapter 3 (Characterization of the catalysts) describes the physical properties of the catalysts obtained on the basis of the characterization techniques. The cation exchange capacity (CEC) of fly ash was enhanced after acid/alkali treatment and metal impregnation and this has been attributed to creation of defect sites and broken bonds on the oxide surfaces. Overall the order of increasing CEC is as follows:

F2 > N2 > C2 > M2 > F1 > N1 > C1 > M1 > F3 > C3 > N1 > M3 >> O

AAS measurements showed that the amount of Fe(III), Co(II), Ni(II) and Mn(II) entering into the fly ash material was different and follow the order of: Fe(III) > Co(II) > Ni(II) > Mn(II). XRF results confirm that silica is the major oxide and all the fly ash catalysts belong to Class F type fly ash. The LOI value (w/w %) also increased after metal impregnation.

The XRD spectra could show the differences in crystallinity and other properties in terms of the changes in the diffraction bands of the fly ash catalysts before and after acid/alkali or metal impregnation treatment. These results were supplemented with the FT-IR study. It was observed that the M–O stretching band shifted after acid and alkali treatment of the fly ash for all the eight catalysts. However, formation of new bonds was not observed in any of the cases, indicating little change in chemical properties of the metal oxides.

Scanning electron micrographs showed that the surfaces became rough and more porous after treatment of the fly ash with acid and alkali. After metal impregnation, the grains of salts over the surface of fly ash are clearly visible. BET adsorption-desorption isotherms of raw fly ash and the metal impregnated catalysts yielded Type II nitrogen adsorption isotherm with H3 hysteresis loop. The measurements indicated that both surface area and pore volume are higher for the acid treated fly ash catalysts than the
Chapter 4 (Wet oxidation of phenol) describes the results of wet oxidation of phenol and the substituted phenols (2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2-nitrophenol, 4-nitrophenol). The catalysts exhibited various levels of activity towards oxidation. The oxidation was carried out with reaction time, reactant concentration, catalyst load, pH, mole ratio of \( \text{H}_2\text{O}_2 \) and temperature of the medium as process variable and the conversions were recorded by varying one parameter at a time. The maximum conversions of phenol obtained in presence of \( \text{H}_2\text{O}_2 \) at equilibrium were: 59.1\% (90 min) for Mn(II)-water washed FA (M1), 63.2\% (90 min) for Mn(II)-acid treated FA (M2), 52.7\% (60 min) for Mn(II)-alkali treated FA (M3), 59.9\% (90 min) for Co(II)-water washed FA (C1), 63.1\% (90 min) for Co(II)-acid treated FA (C2), 49.1\% (60 min) for Co(II)-alkali treated FA (C3), 60.5\% (90 min) for Ni(II)-water washed FA (N1), 58.3\% (60 min) for Ni(II)-acid treated FA (N2), 50.6\% (90 min) for Ni(II)-alkali treated FA (N3) and 56.4\% (60 min) for Fe(III)-water washed FA (F1), 68.3\% (60 min) for Fe(III)-acid treated FA (F2), 56.4\% (90 min) for Fe(III)-alkali treated FA (F3). The reaction follows second order reaction kinetics with apparent kinetic constant of \((1.11 - 3.56) \times 10^2 \text{ L mol}^{-1} \text{ min}^{-1}\) with \( \text{H}_2\text{O}_2 \) (1:1 mole ratio). A catalyst load of 0.4 – 8.0 g L\(^{-1}\) was found to be sufficient for maximum destruction of phenol and the optimum reactant: \( \text{H}_2\text{O}_2 \) mole ratio varied from 1:1 to 1:20 depending on the catalyst. COD measurement showed that almost complete mineralization could be achieved with Fe(III)-acid treated FA (F2) (95.7\%) within 240 min. GC-MS analysis identified mainly biodegradable, low molecular weight carboxylic acids in the product mixture and a probable mechanism has been suggested.

Chapter 5 (Wet oxidation of 2-chlorophenol) describes the conversion of 53.4\% (90 min) for Mn(II)-water washed FA (M1), 60.7\% (60 min) for Mn(II)-acid treated FA (M2), 52.9\% (60 min) for Mn(II)-alkali treated FA (M3), 54.6\% (90 min) for Co(II)-water washed FA (C1), 58.4\% (60 min) for Co(II)-acid treated FA (C2), 51.4\% (90 min) for Co(II)-alkali treated FA (C3), 57.4\% (60 min) for Ni(II)-water washed FA (N1), 63.7\% (60 min) for Ni(II)-acid treated FA (N2), 49.9\% (60 min) for Ni(II)-alkali treated FA (N3) and 57.8\% (90 min) for Fe(III)-water washed FA (F1), 64.9\% (60 min) for Fe(III)-acid treated FA (F2), 53.1\% (90 min) for Fe(III)-alkali treated FA (F3) for 2-chlorophenol. The reaction follows second order reaction kinetics with apparent kinetic constant of \((0.66 - 3.51) \times 10^2 \text{ L mol}^{-1} \text{ min}^{-1}\) with \( \text{H}_2\text{O}_2 \) (1:1 mole ratio). A catalyst load of 0.4 – 8.0 g L\(^{-1}\) was found to be sufficient for maximum destruction of 2-chlorophenol and the optimum reactant: \( \text{H}_2\text{O}_2 \) mole ratio varied from 1:1 to 1:20 depending on the catalyst. COD measurement showed that almost complete mineralization could be achieved with Fe(III)-acid treated FA (F2) (95.6\%) within 240 min. GC-MS analysis identified (i) 1-butanoic acid, (ii) phenol and (iii) hydroquinone along with biodegradable low molecular weight acids in the product mixture and an appropriate mechanism has been suggested.

Chapter 6 (Wet oxidation of 4-chlorophenol) gives 4-chlorophenol \((5.0 \times 10^{-3} \text{ M})\) conversion of 50.7\% (30 min) for Mn(II)-water washed FA (M1), 62.1\% (90 min) for others (water washed and alkali treated fly ash based catalysts) and the maximum surface area was found in acid treated Fe(III)-catalyst (F2) (3.60 m\(^2\)/g).
Mn(II)-acid treated FA (M2), 50.0% (60 min) for Mn(II)-alkali treated FA (M3), 54.6% (60 min) for Co(II)-water washed FA (C1), 65.3% (90 min) for Co(II)-acid treated FA (C2), 45.4% (90 min) for Co(II)-alkali treated FA (C3), 60.6% (60 min) for Ni(II)-water washed FA (N1), 65.4% (120 min) for Ni(II)-acid treated FA (N2), 43.7% (45 min) for Ni(II)-alkali treated FA (N3) and 57.9% (60 min) for Fe(III)-water washed FA (F1), 68.8% (90 min) for Fe(III)-acid treated FA (F2), 53.4% (120 min) for Fe(III)-alkali treated FA (F3) at 323 K and 1:1 mole ratio of H$_2$O$_2$: 4-CP. The reaction follows second order reaction kinetics with apparent kinetic constant of $(0.97 - 3.26) \times 10^2$ L mol$^{-1}$ min$^{-1}$ with H$_2$O$_2$ (1:1 mole ratio). COD measurement showed that almost complete mineralization could be achieved with Fe(III)-acid treated FA (F2) (95.9%) within 240 min. GC-MS analysis identified (i) hydroquinone, (ii) phenol, (iii) malonic acid, (iv) oxalic acid, (v) acetic acid, (vi) acrylic acid in the product mixture and an appropriate mechanism has been suggested.

Chapter 7 (Wet oxidation of 2,4-dichlorophenol) describes the conversion of 2,4-dichlorophenol (1.0 x 10$^{-3}$ M) in presence of equimolar H$_2$O$_2$ was 60.2% for M1, 65.6% for M2, 57.2% for M3, 61.5% for C1, 67.1% C2, 57.1% C3, 64.9%N1, 67.4% N2, 53.1% N3 and 63.3% F1, 70.1% F2, 57.1% F3 at 323 K and equilibrium time (60 min). The reaction follows second order reaction kinetics with apparent kinetic constant of $(8.13 - 24.14) \times 10^2$ L mol$^{-1}$ min$^{-1}$. COD measurement showed that Fe(III)-acid treated FA (F2) (84.6%) could achieved maximum COD reduction within 240 min. GC-MS analysis identified (i) 1- butanoic acid, (ii) phenol, (iii) hydroquinone, (iv) 4-chlorocyclohexanone, (v) chlorocatechol, (vi) chlorobenzoquinone in the product mixture and an appropriate mechanism has been suggested.

Chapter 8 (Wet oxidation of 2,4,6-trichlorophenol) includes the wet oxidation of 2,4,6-trichlorophenol (1.0 x 10$^{-3}$ M) was from 54.0 to 62.0 % for Mn(II)-FA catalysts, 53.0 to 66.0 for Co(II)-FA catalysts, 52.0 to 67.0 for Ni(II)-FA catalyst and 55.0 to 66.8 % for Fe(III)-FA catalysts in presence of H$_2$O$_2$ (1:1 mole ratio) at 323 K, 1.0 g/L catalyst load and equilibrium time. The optimum pH for maximum conversion was around 6.0. Second order reaction kinetics gave apparent kinetic constant of $(5.72 - 12.16) \times 10^2$ L mol$^{-1}$ min$^{-1}$ with H$_2$O$_2$. Catalyst loads of 0.4 – 8.0 g L$^{-1}$ and reactant: H$_2$O$_2$ mole ratio of 1:1 to 1:20 could be used. COD reduction was maximum for Fe(III)-FA catalyst (F2) (93.5 %). The products (i) 2,6-dichloro-1,4-benzoquinone (ii) maleic acid (iii) fumeric acid (iv) oxalic acid and have been identified in GC-MS analysis and a possible mechanism for the oxidation is suggested.

Chapter 9 (Wet oxidation of 2-nitrophenol) explains the conversion of 2-nitrophenol (5.0 x 10$^{-3}$ M)in presence of equimolar H$_2$O$_2$ was 49.3% for M1, 54.6% for M2, 46.8% for M3, 49.4% for C1, 56.8% C2, 44.2% C3, 51.9% N1, 60.1% N2, 37.6 % N3 and 49.7% F1, 60.3% F2, 48.8% F3 at 323 K, 1.0 g/L catalyst load and equilibrium time. The reaction follows second order reaction kinetics with apparent kinetic constant of $(0.65 - 2.71) \times 10^2$ L mol$^{-1}$ min$^{-1}$. COD measurement showed that Fe(III)-acid treated FA (F2) (93.9 %) could achieve maximum COD reduction within 240 min. GC-MS analysis identified (i) 1- butanoic acid, (ii) phenol, (iii) hydroquinone, (iv) 4-chloro-
cyclohexanone, (v) chlorocatechol in the product mixture and an appropriate mechanism has been suggested.

**Chapter 10 (Wet oxidation of 4-nitrophenol)** describes the conversion of 4-nitrophenol (5.0 x 10^{-3} M) in presence of equimolar H_2O_2 was 48.6% for M1, 57.9% for M2, 47.8% for M3, 48.4% for C1, 61.6% C2, 45.7% C3, 55.9% N1, 61.4% N2, 39.6% N3 and 53.8% F1, 63.3% F2, 47.1% F3 at 323 K, 1.0 g/L catalyst load and equilibrium time. The reaction follows second order reaction kinetics with apparent kinetic constant of (0.98 – 3.26) x 10^2 L mol^{-1} min^{-1}. COD measurement showed that Fe(III)-acid treated FA (F2) (92.9 %) could achieve maximum COD reduction within 240 min. GC-MS analysis identified (i) 1-butanolic acid, (ii) phenol, (iii) hydroquinone, in the product mixture and an appropriate mechanism has been suggested.

**Chapter 11 (Conclusion)** summarizes the oxidation abilities of the catalysts for oxidation of phenol, 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2-nitrophenol and 4-nitrophenol. It also suggests a list of works for further investigation.

The thesis concludes with a complete list of the references, consulted during the work.