WET OXIDATIVE METHOD FOR THE REMOVAL OF 2, 4, 6-TRICHLOROPHENOL IN WATER USING CO(II), MN(II), NI(II)-INCORPORATED FLY ASH CATALYSTS

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Abstract: 2, 4, 6-trichlorophenol is a persistent and carcinogenic water pollutant generated by various industries and is resistant to biological oxidation. The presence and removal of 2, 4, 6-trichlorophenol and other chlorophenols from the environment has received wide attention in recent times. In the present work, Mn(II), Co(II) and Ni(II) were incorporated separately into fly ash from a coal-based power plant and the materials were used as catalysts for oxidation of 2, 4, 6-trichlorophenol in water with the oxidant, H_2O_2. The catalysts were characterized by XRD and FTIR measurements. Before use, the materials were calcined at 773-823 K for 5 h. The oxidation reactions were carried out in a high pressure stirred reactor at 323 K under various reaction conditions. The conversion achieved with Mn(II), Co(II) and Ni(II) incorporated fly ash in 3 h was respectively 63.4, 61.9 and 68.9 % with 2, 4, 6-TCP : H_2O_2 molar ratio of 1:1. The oxidation followed second order kinetics having rate coefficient of 13.7 − 16.1 L mol^{-1} min^{-1}. The results show that introduction of Mn(II), Co(II) and Ni(II) into fly ash through impregnation produces very effective catalysts for wet oxidation of 2, 4, 6-trichlorophenol.

Keywords: 2, 4, 6-TCP; wet oxidation; Mn(II)-fly ash; Co(II)-fly ash; Ni(II)-fly ash

1. Introduction:

Chlorophenol (CP) has been classified as first degree toxic pollutants by the US Environmental Protection Agency (EPA) and EC Environmental Directive (2455/2001/EC) [1]. Chlorophenols containing one or more chlorine atoms are non-colored, poorly acidic and toxic compounds that show low biodegradability and have long half-lives [2]. They are mainly released into the environment in water as wastes generated by various sources like the plastic, pesticide, and other organochemical industries [3]. 2, 4, 6- trichlorophenol (2, 4, 6-TCP) is a potential water pollutant used as a wood and glue preservative, in pesticide formulations (herbicides, fungicides, bactericides) [4], and in leather tanning and finishing. 2, 4, 6-TCP has also been detected in the emissions from fossil fuel combustion, municipal waste incineration, and chlorination of water containing phenol or certain aromatic acids with hypochlorite or during the disinfection of drinking water sources [5]. The increased availability of these compounds in water and their known toxic and carcinogenic effects have been of great environmental concern in recent times and continued use of these compounds in numerous applications and the resultant wastewaters have been responsible for contaminating the surrounding soil and water courses affecting public health [6–10].

Different strategies such as "clean" technology or development of new, innovative technologies (advanced oxidation) have been developed. The main purpose behind such technologies has been to convert the toxic and bioresistant organochlorine compounds in aqueous systems into harmless species. This is carried out by decomposing or oxidizing the compounds by chemical, photochemical and biological processes. Among these, the wet air oxidation (WAO process) could appear to be very promising to achieve high conversion of organic pollutants, but unfortunately this process need high pressure and temperature implying increasing the investment costs [11-14]. By contrast, the use of hydrogen peroxide allows performing oxidation reaction at ambient conditions, limiting the investment costs. Hydrogen peroxide appears to be an appropriate and potential oxidant due to high oxygen content and yielding water as the only byproduct. Among various catalysts, transition metal oxides and supported noble metals have been reported to be widely applied in CWAO [15-17]. But their use is limited by durability constraints and difficulties in recovery after use. This problem is usually overcome by dispersing the catalyst components on a porous support such as charcoal, polymers, zeolites and layered structures (pillared clays and hydrotalcites) by direct intercalation, ion exchange and encapsulation [18].

In the present work, metal ions, viz., Mn(II), Co(II) and Ni(II) was incorporated into fly ash and utilize these materials as the catalyst for oxidation of 2, 4, 6-trichlorophenol in water in the presence of a common oxidizing agent, H_2O_2, under various conditions to evaluate the effects of reaction time, feed concentration, mole ratio of reactant and oxidant and pH.

2. Materials and methods:

2.1. Chemicals used:

The following commercially available chemicals were used without further purification:

- o Manganese(II) chloride tetrahydrate (E. Merck, Mumbai, India), Cobalt(II) nitrate hexahydrate (E. Merck, India) and Nickel(II) nitrate hexahydrate (E. Merck, India)
- o H_2O_2 (E. Merck, Mumbai, India) was used as the oxidant;
- o 2, 4, 6-trichlorophenol (TCP) (Merck-Schuchardt, Honenbrunn, Germany).
- o Fly ash was collected from the Bongaigaon Thermal Power Station, Assam, India.

2.2. Catalyst preparation:

The fly ash sample was thoroughly washed with distilled water and was refluxed with 40 ml of 1.0 M metal solution at 373 K for 6 h. After refluxing, the materials were washed with distilled water several times and were dried in an air oven at 373 K. The material was then calcined at 773 K for 5 h and was preserved as catalysts as shown below:

- o Catalyst A : Mn (II) incorporated into fly ash
- o Catalyst B : Co (II) incorporated into fly ash
- o Catalyst C: Ni (II) incorporated into fly ash.

2.3. Characterization of the catalysts:

The catalysts were characterized with FT-IR (Shimadzu IR Affinity-1 FT-IR Model range 4400 to 440 cm^{-1}, KBr pellet technique) and powder XRD (Phillips Analytical PW 1710, Cu Kα radiations) measurements. The metal content in parent fly ash and in the catalysts was determined with atomic absorption spectrometry (Perkin Elmer AAnalyst 220).

2.4. Wet oxidation of 2, 4, 6-trichlorophenol (2, 4, 6-TCP):

2.4.1. Stock solutions:

Stock solutions of 2, 4, 6-trichlorophenol (concentration 1.0×10^{-3} M) and equimolar H_2O_2 were prepared in double distilled water. Other solutions were prepared by appropriate dilution whenever necessary. The reactions were carried out in 100 ml capped Erlenmeyer flasks taking equal volumes of TCP and H_2O_2 (25 ml each) with catalyst load of 1.0 g/L and the flasks were agitated in a constant temperature water bath shaker (NSW, New Delhi, India) at 323 K for 300 min.

For studying the effects of different reaction parameters, appropriate changes were made as given in Table 1.

Table 1: Process variables for the wet catalytic oxidation of 2, 4, 6-trichlorophenol.

Sl. no	Process variable	Value/range
1	Volume of reactant	25.0 mL
2	Volume of H_2O_2	25.0 mL
3	TCP concentration	1.0×10^{-3} M
4	Catalyst loading	1.0 g/L
5	Temperature	323 K
6	Reaction time	5 – 300 min

7	TCP/H_2O_2 (mole ratio)	1:1- 1:20
8	pH	3 – 9

The variation of pH was achieved through addition of a few drops of either 0.1 N HNO_3 or 0.1 N NaOH as the case may be.

The rate of the catalytic reaction with respect to the TCP was tested for first order and second order kinetics using the following equations [19]:

(a) First order rate equation:

$$C_t = C_o \exp (-k_1 t) \tag{1}$$

Or, the linear form,

$$\log C_t = \log C_o - (k_1/2.303)\, t \tag{2}$$

(b) Second order rate equation:

$$dC/dt = k_2 (C_0 - C_t)^2 \tag{3}$$

Or, the linear form

$$1/C_t = k_2 t + 1/C_0 \tag{4}$$

where C_o and C_t represent the initial concentration and any concentration at time 't' of the reactant, k_1 and k_2 are respectively first order and second order rate coefficients. The linear plots obtained from the linear forms of the rate equations were used for obtaining the values of the rate coefficients. After the reaction is over, the mixture is filtered and the unconverted reactant is estimated in the supernatant layer spectrophotometrically (Hitachi UV-visible U3210).

3. Results and discussion:

3.1 Characterization of the catalysts:

The XRD spectra of calcined fly ash, and Mn(II)-, Co(II)- and Ni(II)- incorporated fly ash is given, respectively, in Fig. 1. The fly ash samples yielded mainly 3 peaks in the range of 4 - 30° which were in accordance with the literature [20, 21]. All the fly ash samples had similar X-ray diffraction patterns indicating similarity in their mineralogical compositions. The major peak at $2\theta = 26.65^o$ (d = 3.34 Å), 26.69^o (d = 3.34 Å), 26.53^o (d = 3.36 Å) and 26.42^o (d = 3.37 Å) respectively for parent fly ash, Mn(II)-, Co(II)- and Ni(II)- incorporated fly ash, corresponds to that of quartz, indicating that quartz or silica is a major constituent of fly ash. Another mineral, mullite, was also found in the fly ash samples indicated by strong peaks at $2\theta = 16.54^o$, 17.80^o and 16.33^o (d: 5.36, 4.98 and 5.43 Å).
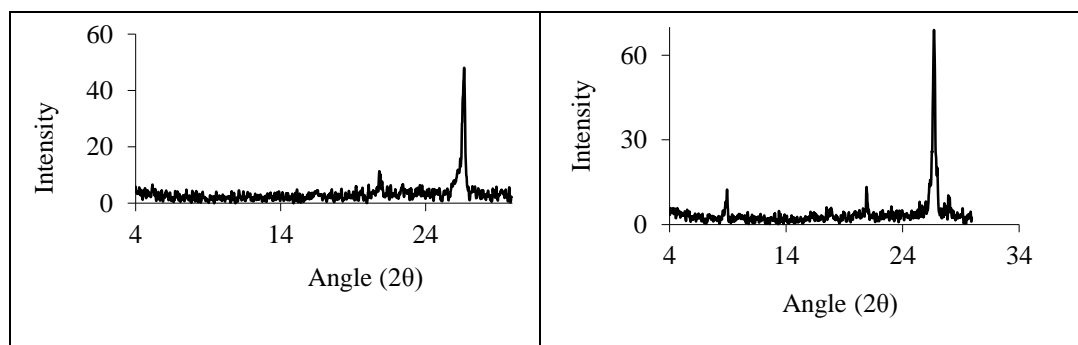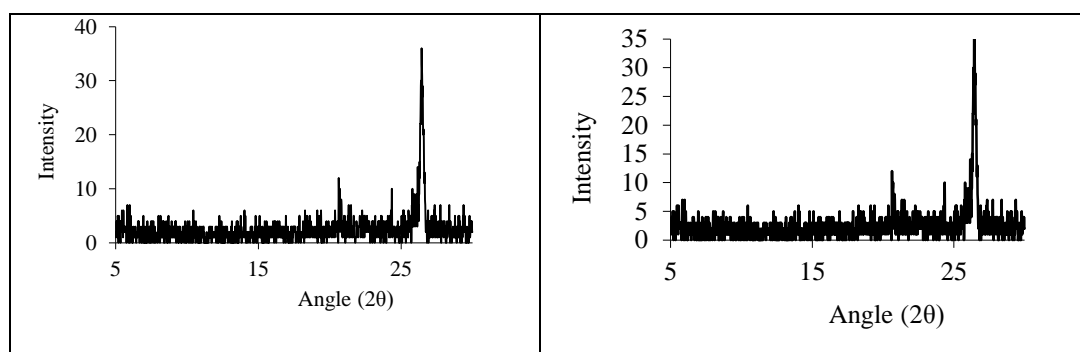
Figure 1: XRD patterns of the calcined sample of parent raw fly ash (O, top left), Mn(II)-fly ash (A, top right), Co(II)- fly ash (B, bottom left) and Ni(II)- fly ash (C, bottom right) respectively.

Sarkar et al. [20] have found that fly ash collected from thermal power plant, eastern India, have quartz as the priority mineral. Some peaks of Mullite, magnetite and kaolinite are also observed. It is found that the mineral peaks are highly dependent on particle size of the component. Li et al. [21] have also reported that the main mineral peak in fly ash was quartz.

IR spectra of calcined samples of Mn(II), Co(II) and Ni(II) impregnated fly ash show the same prominent bands as found in the calcined parent fly ash Fig. 2. The following assignment of FT-IR bands can be made:

o   Calcined fly ash, Mn(II)-, Co(II)-, and Ni(II)-incorporated fly ash show a prominent IR band at 1099.4, 1099.4, 1114.9, and 1103.3 cm -1, respectively. This band around 1055 cm^{-1} to 1100 cm^{-1} is normally assigned to Si–O–Si asymmetric stretching[20].
o   The band between 2920 and 2850 cm^{-1} could be assigned to asymmetric and symmetric stretching of –CH$_2$ groups from residual carbon compounds in fly ash [20].
o   IR bands in the regions, 800-795 cm^{-1} corresponded to aromatic C–H bending vibrations.
o   The broad band between 3400-3000 cm^{-1} was attributed to surface – OH groups of Si-OH and adsorbed water molecules on the surface [20].
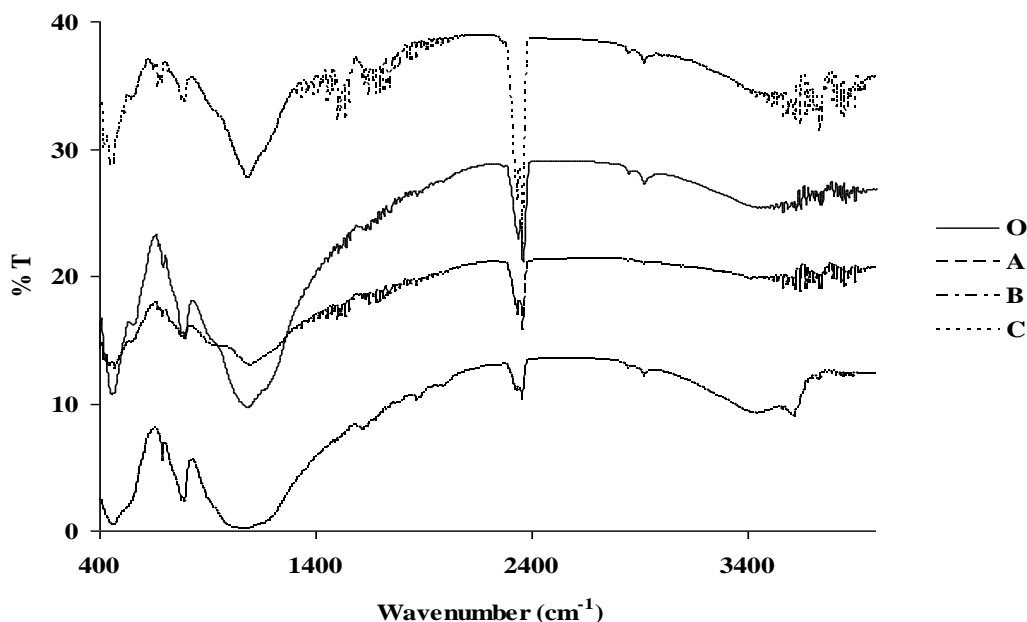

Figure 2: FT-IR spectra of calcined raw fly ash (O) and of calcined samples of Mn(II)-, Co(II)- and Ni(II)-impregnated fly ash (A, B and C respectively).

AAS measurement of the calcined metal-impregnated fly ash catalysts shows that 45.05, 608.9 and 704.6 mg/kg of Mn(II), Co(II) and Ni(II), respectively, have entered into the parent fly ash. The actual amount of metal present in the parent fly ash was Mn (II): 12.52 mg/kg, Co (II): 74.4 mg/kg and Ni (II): 83.9 mg/kg respectively.

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

3.2.1. Blank experiments:

Before investigating the effectiveness of Mn(II), Co(II) and Ni(II)- impregnated fly ash as catalysts for wet oxidation of 2, 4, 6-trichlorophenol in water, a set of blank experiments were carried out for the systems

- o   2, 4, 6-TCP alone without any catalyst and H_2O_2,
- o   2, 4, 6-TCP and H_2O_2 (1:1 molar ratio) without any catalyst,
- o   2, 4, 6-TCP with parent fly ash as the catalyst, and
- o   2, 4, 6-TCP and H_2O_2 (1:1 molar ratio) with parent fly ash as the catalyst

under the same conditions of temperature and pressure as used with the metal impregnated fly ash catalysts. No measurable conversion could be recorded in (i) and (iii) while negligible conversion (<10%) could be observed in both (ii) and (iv).

3.2.2. Effect of reaction time and kinetics:

The degradation of 2, 4, 6-TCP is enhanced if the reaction time is increased from 5 to 300 min (2, 4, 6-TCP: H_2O_2 mole ratio 1:1) during which the conversion increased from 35.6–63.4% for Mn(II)-fly ash, 44.6–61.9% for Co(II)- fly ash and 48.0–69.1% for Ni(II)- fly ash (Fig. 3.) Interestingly, even with a reaction time of 15 min, Ni(II)- impregnated fly ash can bring about 53.0% transformation of 2, 4, 6-TCP. Comparing these results in presence of the oxidizing agent (H_2O_2), it is seen that when the reaction time is 300 min, out of all the three catalysts Ni (II)-fly ash con convert more 2, 4, 6-TCP than the other two.
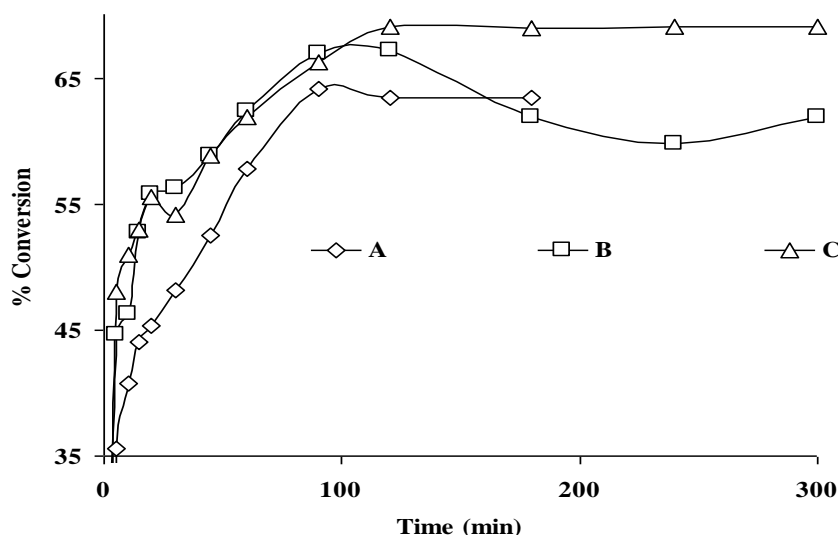

Figure 3: Effects of reaction time on the wet oxidation of TCP with Mn(II)-, Co(II)-, Ni(II)- impregnated catalyst (temperature 323 K, catalyst load 1.0 g/L, TCP and H_2O_2 concentration 1.0 x 10^{-3} M).

The reaction rates of the oxidative degradation have been tested for both first and second order kinetics. For all the cases, second order kinetics obtained by plotting $1/ C_t$ (averages of three different sets of measurements under identical conditions) versus time (Fig.4.) showed better fit with the experimental results (regression coefficient, R> 0.99). The second order rate coefficient was 13.84, 13.6 and 11.1 L mol^{-1} min^{-1} respectively for Mn(II), Co(II) and Ni(II)- fly ash.
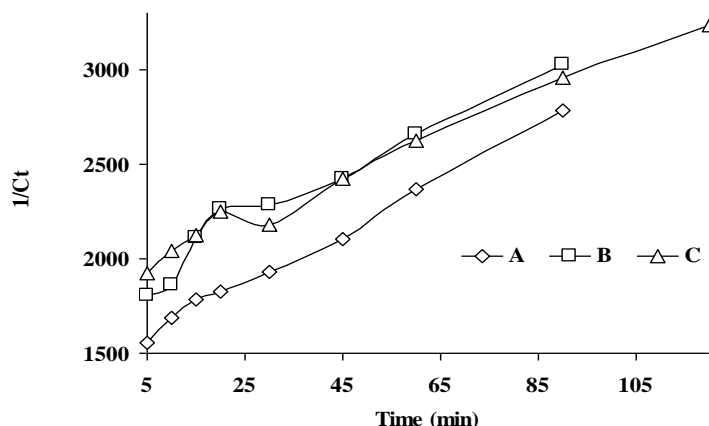
Figure 4: The second-order degradation of 2, 4, 6-trichlorophenol (1.0×10^{-3} mol L^{-1}) by wet oxidation at 323 K (catalyst load 1.0 gL^{-1} and TCP : H$_2$O$_2$ mole ratio 1:1).

Kinetics of catalytic oxidation of TCP has not received much attention. Literature shows that all the reactants mostly follow first or pseudo first order kinetics. Oliveira et al. [22] have reported that with Fenton reagent, DCP and TCP showed pseudo first order kinetics. Wolfovich et al. [23] have also found that 2, 4, 6-trichlorophenol in catalytic wet oxidation with nanocasted Mn–Ce-oxide catalyst showed first order kinetics at 353 K. In the present work, the results did not yield good first order plots and the oxidation process appeared to be in agreement with second order mechanism. In this case significant decrease in 2, 4, 6-TCP concentration was noticed within a few minutes of the commencement of the reaction. The rate of decrease gradually comes down till it is observed that after about 90 min, $1/C_t$ becomes nearly constant implying attainment of equilibrium.

3.2.3. Effects of concentration:

The activity of the catalysts with respect to 2, 4, 6-TCP conversion is likely to decline if the concentration of the reactant is increased. This is what is observed when the concentration of 2, 4, 6-TCP is increased from 2×10^{-4} M to 4.0, 6.0, 8.0, 10.0×10^{-4} M keeping a constant concentration of H$_2$O$_2$ (1×10^{-3} M) in the reaction mixture. The conversion has declined from 92.2–63.4 % for Mn(II)-fly ash, 98.0–61.9 % for Co(II)- fly ash and 89.4–69.1 % for Ni(II)- fly ash (Fig. 5.) in the concentration range of 2, 4, 6-TCP used.
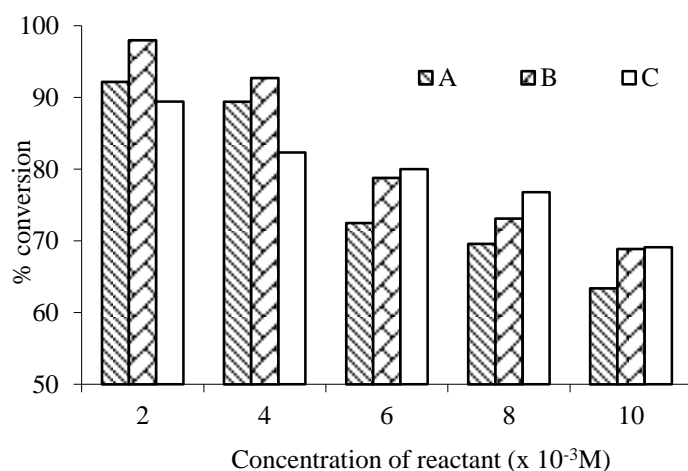

Figure 5: Effects of concentration of 2, 4, 6-TCP on its wet oxidation at 323 K (reaction time 300 min, catalyst load 1.0 g/L).

3.2.4. Effects of mole ratio:

An increase in the mole ratio of hydrogen peroxide and 2, 4, 6-TCP from 1:1 to 20:1 for a reaction time of 300 min (catalyst load 1.0 g/L) has show significant effect on the conversion, which changes from 63.4 to 100 % for Mn(II)- fly ash, 61.9 to 100 % for Co(II)- fly ash and from 69.1 to 100 % for Ni(II)- impregnated fly ash (Fig. 6.). It is found that 1:1 molar ratio of the reactant to oxidant can bring sufficient amount of destruction of the pollutant, because at the reaction temperature of 323 K, H_2O_2 itself may undergo some amount of decomposition aided by the presence of the catalyst and such decomposition has been recognized as a factor determining the overall rate of the reaction as well as the product yield [18]. The stoichiometric equation for the complete oxidation of 2, 4, 6-TCP with H_2O_2 was given below indicate that the mole ratios of 1:11 would be most suitable for bringing about complete oxidation of 2, 4, 6-TCP.

$$C_6H_2Cl_3(OH) + 11\ H_2O_2 \rightarrow 6\ CO_2 + 11\ H_2O + 3\ HCl \tag{5}$$
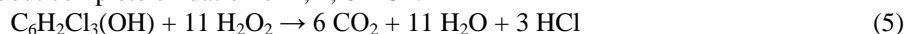
3.2.5. Effects of pH:

The pH of the reaction medium influences the catalytic reactions of 2, 4, 6-TCP in a positive manner (Fig. 7.). As the pH was increased from 3.0 to 9.0, the conversion had an upward trend: 56.5–100 % for Mn(II)-, 55.4–100 % for Co(II)- and 52.2–100 % for Ni(II)-impregnated fly ash respectively. At the natural pH of 2, 4, 6-TCP aqueous solution (pH 5.5), the conversion is: 63.4 for Mn(II)- 61.9 for Co(II)- and 69.1 for Ni(II)- fly ash. The results show that with all the three catalysts, the conversion does not increase appreciably from pH 3.0 to the natural pH of 2, 4, 6-TCP aqueous solution (5.5). However, if the pH is increased above this value, the conversion increases giving 100 % conversion up to pH 7.0 and above. This is important to note that H and OH ions play a significant role in the mechanism of oxidative decomposition of 2, 4, 6-TCP.

There are conflicting reports on the effects of pH on wet catalytic oxidation of chlorophenols. Tang et al. [24] have shown that 2,4-dichlorophenol oxidation increased with pH up to pH 5.0 and then the oxidation decreased. On the other hand, Tai et al. [25] have shown that 2, 4, 6-TCP destruction by molybdate ions in the presence of hydrogen peroxide under basic conditions (9.0-11.0) showed good degradation efficiency. It is likely that the effect of pH is determined by several factors, viz., the reactant, the catalyst, the mechanism of oxidation and the general environment in which the reaction is carried out.
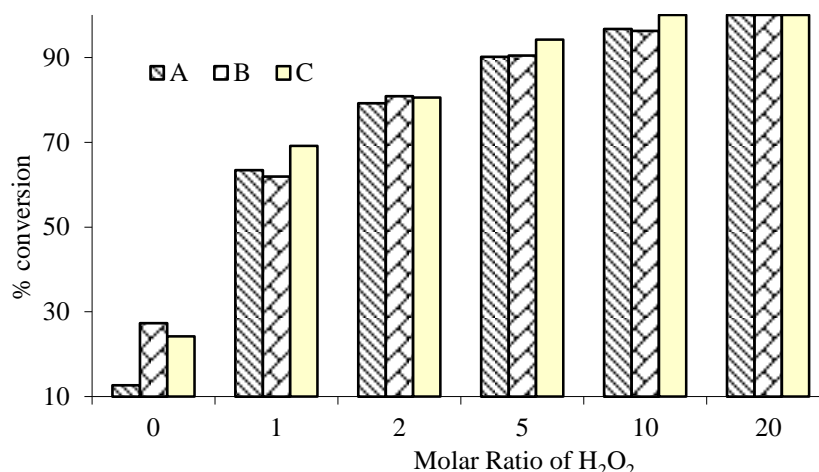

Figure 6: Effects of mole ratio of feed on catalytic wet oxidation of 2, 4, 6-TCP (1.0×10^{-3}M) with H_2O_2 at 323 K (reaction time, 300 min; catalyst load, 1.0 g/L).
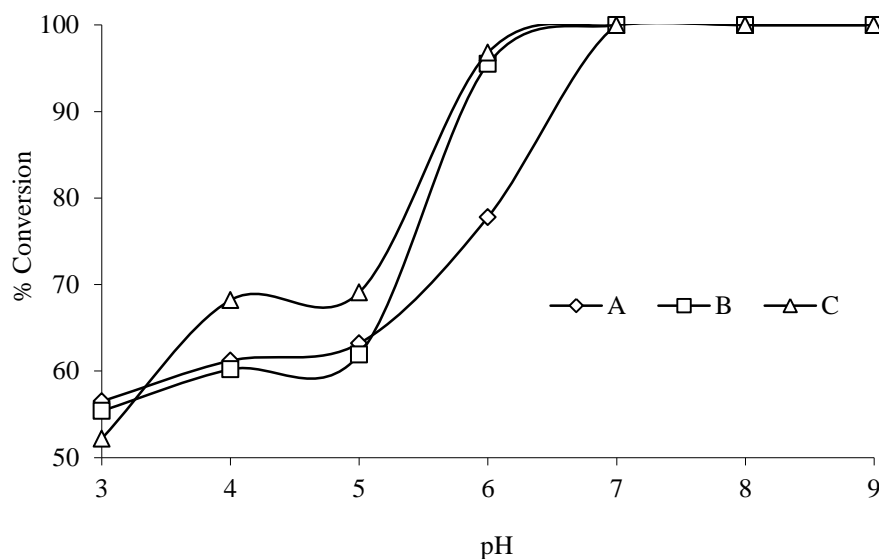
Figure 7. Effects of pH on wet oxidation of trichlorophenol with Mn(II)-, Co(II)-, Ni(II)-impregnated catalyst at 323 K (reaction time 300 min, catalyst load 1.0 gL^{-1}).

4. Conclusion:

The results show that introduction of the transition metals, Mn(II), Co(II) and Ni(II) into fly ash through the simple process of impregnation could give very active and effective catalysts for wet oxidation of 2, 4, 6-trichlorophenol. The following general observations summarize the results:

(i) The conversion is not much dependent on the catalyst load and small amount of catalyst (1.0 g/L) has been found to be sufficient for giving significant destruction of 2, 4, 6-TCP.

(ii) Full conversion is achieved when the pH is near 7.0 and above and at the natural pH of aqueous 2, 4, 6-TCP solution (5.5), considerable destruction of the target pollutant is achieved.

Of the different reaction variables, it was observed that reactant mole ratio (2, 4, 6-TCP/H_2O_2), 2, 4, 6-TCP concentration and pH had the maximum influence on the conversion while the effects of reaction time were not very significant.

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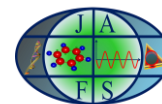
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