Removing Phenol from Water: A Case Study in Catalytic Oxidation with Mn(II)-Impregnated Fly Ash

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Abstract—*Phenol is a persistent and toxic organic compound, entering water mainly from the effluents of chemical industries. It is known to be carcinogenic and harmful to all organisms, including humans, even at low concentration. Any effluent containing phenol or its derivatives should be treated for their removal before the same can be discharged into a natural water body. Among the methods for phenol removal, catalytic wet oxidation has turned out to be to be one of the most effective processes. In the present work, water washed, acid treated and alkali treated Mn(II)-impregnated fly ash was used as the catalyst for oxidative removal of phenol from water in the presence of an oxidant (H_2O_2). Fly ash, which was obtained as a useless waste from a coal-based thermal power plant, was first washed thoroughly with water and then treated with dilute acid (1.0 M H_2SO_4) and alkali (1.0 M NaOH) separately. The material was washed till it was free of acid and alkali and then refluxed with an aqueous solution of 1.0 M $MnCl_2$. $4H_2O$ for 6 h, washed again several times, and was calcined at 773 K for 5 h to obtain the catalyst. The structural and compositional features of the catalyst were determined with BET, SEM, FT-IR, CEC and AAS measurements. The phenol oxidation was carried out in a water bath shaker at 323 K under various reaction conditions at natural pH of the aqueous phenol solution and atmospheric pressure. The percentage conversion achieved was 59.8, 65.2 and 54.6% respectively with Mn (II) impregnated water washed, acid treated and alkali treated fly ash respectively in 300 min for the reactant: H_2O_2 mole ratio of 1:1. Effects of various reaction conditions on oxidative destruction of phenol in water have been highlighted.*

Keywords: *Phenol; catalytic wet oxidation; water washed and acid treated Mn (II)- impregnated fly ash, water treatment.*

1. INTRODUCTION

Phenol has been identified by the US EPA (Environmental Protection Agency) as major organic pollutants due to their toxic nature towards the ecosystem and humans at very low concentrations [1-2]. This prompted to set a discharge limit of 10^{-4} g/L in waste water [3]. Yang et al. [4] have reported that the concentration of phenol in drinking water should be < 0.5 pg/L. According to Indian EPR (1986), the permissible limit of phenol in inland water must was set as 10^{-3} g/L and in public sewer and marine coastal areas the limit was 5.0 x 10^{-3} g/L which was also reported by Gupta et al. [5]. The main source of phenol is industrial wastewater such as those from petroleum refineries, textile, dyes, chemical industries like pharmaceuticals, resin, fertilizer [6-7].

Different strategies such as "clean" technology, improvement of existing technologies, or development of new, innovative technologies (advanced oxidation) have been developed to satisfactory reach the requested objectives. Among these, the catalytic wet air oxidation (CWAO process) using air or pure oxygen as oxidant 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 [8-12]. By contrast, the use of hydrogen peroxide (CWPO process) allows performing oxidation reaction at ambient conditions, limiting the investment costs, even if the low reaction rates compare to those of CWAO process needs high volume reactors. Hydrogen peroxide appears to be an appropriate and potential oxidant due to high oxygen content and yielding water as the only byproduct. Again heterogeneous catalysts are found to be more desirable because homogeneous catalysts require an additional separation step for the soluble species leading to high treatment costs. Among various catalysts, transition metal oxides and supported noble metals have been reported to be widely applied in CWAO [13-15]. 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 [3]. Therefore, in this wet oxidation process, the organic contaminants are not fully oxidized, but converted to biodegradable intermediates with less toxicity and low COD [15]. The biodegradable end products mostly consist of low molecular weight alcohols like ethanol, carboxylic acids, like acetic and propionic acids, etc., that can be ultimately converted to CO_2 and H_2O [16].

In the present work, Mn (II) was incorporated into fly ash was used as the catalyst for oxidation of phenol in water in presence of H_2O_2 and the activity of the catalysts were studied under different reaction variables like reaction time, reaction kinetics and reactant mole ratio etc.

2. EXPERIMENTAL METHODOLOGY

2.1 Coal Fly Ash and its Treatment

The coal fly ash, in fine powder form, was collected from Thermal Power Station, Kokrajhar, India.

10.0 g of the fly ash was mixed with 100 mL of (i) distilled water, (ii) 1.0 M H_2SO_4 and (iii) 1.0 M NaOH separately in 250 mL corked Erlenmeyer flasks and shaken for 6 h continuously. The mixtures were allowed to settle down and filtered with Whatman 40 filter paper, washed repeatedly with double-distilled water till the washings were acid or alkali free. The materials were dried at 373 K and preserved for further use.

Mn(II)-impregnated fly ash materials were prepared by refluxing with 10.0 g of the thoroughly washed fly ash with 40 ml of 1.0 M metal solution [$MnCl_2.4H_2O$] 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 for use as catalysts. Altogether three different catalysts were obtained:

Mn(II)– water washed fly ash (M1)
Mn(II)– 1.0 N acid treated fly ash (M2)
Mn(II)– 1.0 N base treated fly ash (M3)

3. CHARACTERIZATION OF THE CATALYSTS

3.1 Measuring Mn(II) in the Catalysts

The amount of Mn(II) entering into the fly ash material was determined with atomic absorption spectrometric measurement. From AAS analysis, it is found that catalyst M1, M2 and M3 have 45.0, 21.61 and 37.65 mg of Mn(II) per 1.0 kg of fly ash.

The amount of Mn present in the calcined raw fly ash (O) was 12.52 mg/kg.

3.2 FT-IR Spectroscopy

The FT-IR measurements of the raw fly ash and the catalysts are shown in Fig. 1. The assignments of all the major FT-IR bands are discussed below:

(i) The material showed a prominent IR band at around 1099.4 cm^{-1} which may be attributed to the Si–O–Si asymmetric stretching. Two other bands around 798 and 470 cm^{-1} were also observed. These bands are typical for Si-O bending vibrations of quartz present in the fly ash as

a major constituent. Absorption around 1103 cm^{-1} could be assigned to Fe-O vibrations arising from the considerable amount of iron present in the fly ash as Fe_2O_3.
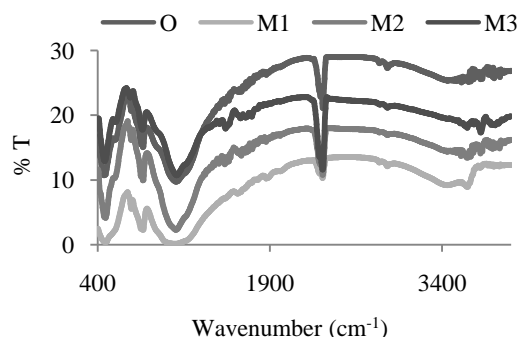

Fig. 1: FT-IR spectra of the calcined samples of Mn(II)-impregnated fly ash M1, M2 and M3.

The band observed between 2931 and 2862 cm^{-1} could be assigned to the asymmetric and symmetric stretching of – CH_2 groups from residual carbon compounds in the fly ash.

(i) The broad absorption band between 3650–3400 cm^{-1} (Fig. 3.6) was attributed to the presence of hydrogen bond between the vicinal pairs of surface – OH groups of Si-OH and adsorbed water molecules on the surface [17-18].

3.3 CEC determination of Catalysts

The cation exchange capacities (CEC) of the materials were determined with copper bisethylenediamine complex method [19]. The values are 22.6, 48.7, 63.7 and 37.5 meq/kg for raw fly ash, M1, M2 and M3 respectively. It is observed that, the CEC increases after treatment (either acid or alkali). However it is observed that the effect is more in the acid treated fly ash

Koukouzas et al. [20] have reported that the CEC of coal fly ash was 1.4 to 17.4 meq/kg. These values are much lower than the values obtained in the present work. In earlier work, Woolard et al. [21] had reported that on hydrothermal treatment of coal fly ash with NaOH, the CEC of the material was increases. This result was supported by [22]. In the present work, the cation exchange capacity of the alkali treated fly ash was higher than raw FA (O), which is in agreement with the result obtained by [21-22]. But the rate of increases was not same in the present case. This might be due to the strength of the NaOH (1.0 M) which is much lower than that used by [21-22]. According to [3], the CEC of a material increases due to the increase in the number of cation exchangeable sites. Thus, it may be inferred that in the present case, after acid or alkali or metal impregnation processes, the number of such exchangeable sites increases. Rodrigues et al. [23] have suggested that the increase in the exchangeable sites of a material might be due to the creation of defect sites and broken bonds present on the surface of the materials.

3.4 Surface Area and Pore Size Measurement

The BET isotherm for the fly ash in this work is shown in Fig. 2 and it is observed that the isotherm belonged to type II according to the IUPAC classification.

The isotherm has a hysteresis loop of type H3, normally attributed to porous solids with capillary condensation occurring inside the micropores.
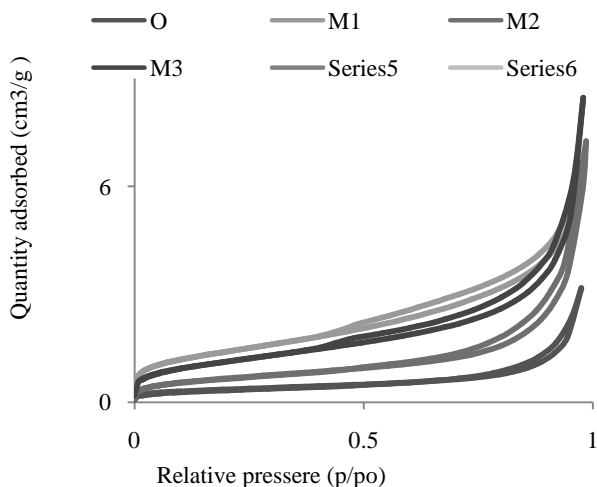

Fig. 2: The BET adsorption-desorption isotherms of raw fly ash (O) and Mn(II)-impregnated fly ash (M1, M2, M3).

3.5 Scanning Electron Microscopy

Scanning electron micrographs of the raw fly ash (O) along with Mn(II)- impregnated forms are presented in Fig. 3. Changes in topography are distinctly visible after treatment with acid/alkali making the surface rough due to uneven acid or alkali action.
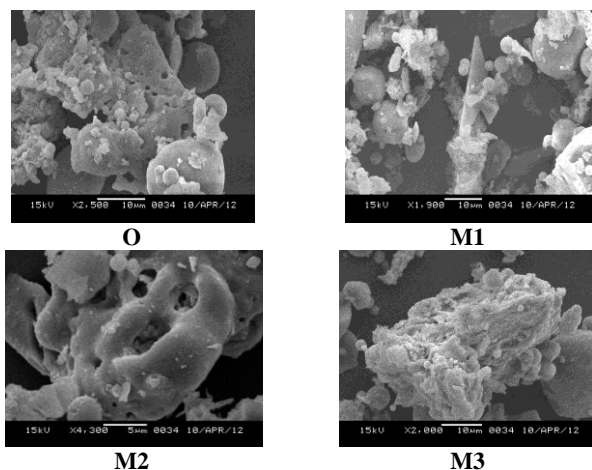

Fig. 3: SEM image of calcined raw fly ash (O, top left), Mn(II)-water washed fly ash (M1, top right), Mn(II)-acid treated fly ash (M2, bottom left) and Mn(II)-alkali treated fly ash (M3, bottom right).

Changes in topography are distinctly visible after treatment with acid and alkali making the surface rough due to uneven acid or alkali action. The acid treatment appeared to have damaged the surface of fly ash much more than the simple washing with water or treatment with the alkali. Acid treatment has also been seen as creating additional intra-particular space, possibly through corrosive action.

H_2SO_4 being a very corrosive acid, treatment of the materials with this acid is likely to erode the surface and create a porous structure with uneven topography. The acid-treated surface may, therefore, function as an agglomeration of active sites that would promote adsorption and consequently, catalytic reaction process.

4. WET OXIDATION OF PHENOL

4.1 Blank Experiments

The following blank experiments were carried out on wet oxidation of phenol:

(i)   Aqueous phenol alone

(ii) Aqueous phenol and H_2O_2 (1:1 molar ratio)

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

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

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

No measurable conversion could be recorded in (i) and (iii) while the conversion observed in (ii) and in (iv) was about ~ 9.2 and 20.4 % respectively. From these blank experiments it can be concluded that phenol is normally very stable and fly ash itself is a poor catalyst which itself could not give any significant decomposition of phenol as found in experiment (i) and (iii). While some amount of decomposition observed in experiment (ii) and (iv) may be due to the .OH radicals that produced from H_2O_2 at 323 K and also fly ash itself had some adsorption property which provide an appreciable amount of oxidation.

4.2 Effects of Reaction Time

The conversion of phenol increased with reaction time (5 – 300 min) till equilibrium conditions were reached (Fig. 4.). The conversion of phenol in presence of H_2O_2 in 1:1 molar ratio was 59.8, 65.2, and 54.6 % respectively after 300 min. For M1 and M2, the reaction attained equilibrium after 90 min showing almost constant conversion afterwards. For M3, the reaction attained its equilibrium at 60 min. The results showed that the conversion was very fast and the major part of the conversion was completed within 15 min.
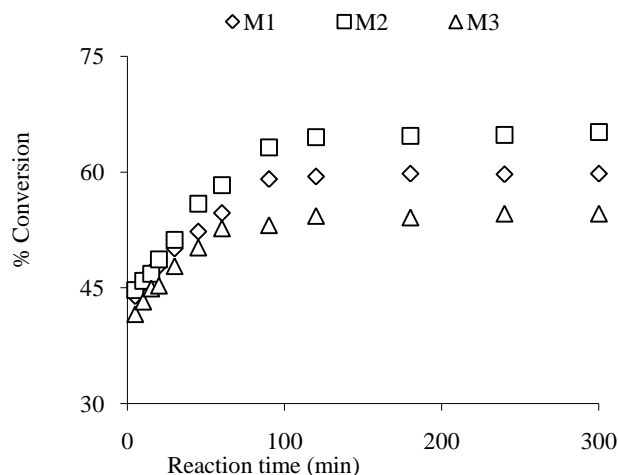
Fig. 4: Effects of reaction time on catalytic wet oxidation of phenol (5.0 x 10⁻³ M) with M1, M2 and M3 at 323 K (phenol: H₂O₂ mole ratio 1:1, catalyst load 1.0 g/L).

4.3 Kinetics of Wet Oxidation of Phenol

The rates of the oxidative degradation reaction were tested for conformity with both first and second order kinetics, however good results were observed with second order kinetics (Fig. 5.) by plotting $1/C_t$ versus time (min) according to the second order kinetic equation:

$$1/C_t = k_2t + 1/C_0 \qquad (1)$$

where C_0 and C_t represent the initial concentration and any concentration at time 't' of the reactant, k_2 is the second order rate coefficient [24].

Among the three catalysts, the acid treated catalyst (M2) gave a higher rate coefficient, indicating that the active sites on M2 had a comparatively higher affinity for phenolate ions for their eventual oxidation.
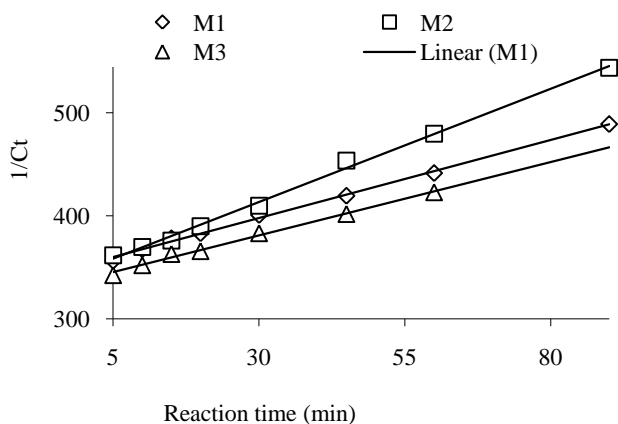

Fig. 5: Second order kinetic plots for wet oxidation of phenol with H₂O₂ over M1, M2 and M3 respectively (catalyst 1.0 g/L, phenol: H₂O₂ mole ratio 1:1, pH as prepared).

4.4 Effects of Mole Ratio

With an increase in the mole ratio of H_2O_2 and phenol from 1:1 to 20:1, the wet oxidative reaction has shown better conversion (Table 1.).

The stoichiometric equation for the complete oxidation of phenol with H_2O_2 (Equation 4) shows that for bringing about complete oxidation of 1 mole of phenol, 14 moles of H_2O_2 are required:

$$C_6H_5(OH) + 14H_2O_2 \rightarrow 6CO_2 + 17H_2O \qquad (2)$$
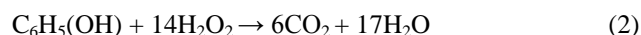
Thus, the results obtained in this work, showing enhancement in oxidation of phenol with increasing amount of H_2O_2 in the feed, are in agreement with the stoichiometric equation.

In the catalytic wet peroxide oxidation of phenol with CuO impregnated activated carbon, Liou et al. [25] have observed that with increase in H_2O_2 concentration, the conversion of phenol also increased and showed almost complete conversion at 353 K, when the mole ratio of phenol to H_2O_2 was increased to 1:9.4 or more at 180 min (1.0 g/L catalyst load, [phenol] 1000 mg/L, [H_2O_2] 0.1 mole/L). Stoichiometrically, they have found that almost 1:10 ratio with respect to the oxidant is sufficient to bring complete oxidation of phenol. Compared to the above results, in the present work, all three catalysts showed more than 80 % conversion at a lower temperature.

Table 1: Effects of increasing mole ratio of feed (H₂O₂: phenol) on catalytic wet oxidation of phenol (5.0 x 10⁻³ M) with M1, M2, M3 at 323 K

Conversion (%) of phenol at different mole ratio of H2O2		Catalysts		
		M1	**M2**	**M3**
	0	9.8	12.6	6.1
	1	59.8	65.2	54.6
	2	67.6	71.6	65.7
	5	81.1	83.4	78.5
	10	87.6	89.4	84.7
	20	93.3	96.3	91.9

5. CONCLUSION

From the above results, it can be concluded that Mn(II)-impregnated fly ash produce active oxidation catalysts for the treatment of water contaminated with phenol. In presence of sufficient quantity of H_2O_2 (10:1 mole ratio with phenol) in the reaction mixture, more than 80 % conversion could be achieved. A significant amount of conversion is observed at a very short time (15 min) for all the catalysts. The reactions were found to give linear agreement with second order kinetics. The reactions were found to give linear agreement with second order kinetics and with respect to the rate of conversion; the catalysts are in the order

M2 > M1 > M3.

As phenol is one of the toxic pollutant, the present work shows that catalytic wet oxidative treatment of the effluent with Mn(II)- impregnated fly ash may be a viable tertiary treatment technique for the removal of phenol from water or effluent.

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