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Catalytic wet oxidation of 2-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol in water with Mn(II)-MCM41

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Abstract

Chlorinated phenols are persistent and toxic organic compounds, harmful to organisms and humans even at low concentrations. Biological oxidation used for removing organics from industrial effluents is not suitable for these compounds and catalytic wet oxidation is one of the major alternatives for their destruction. In the present work, Mn(II)-incorporated MCM41 is used as catalyst for oxidation of 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP) and 2,4,6-trichlorophenol (2,4,6-TCP) in water with or without an oxidant (H_2O_2). Mn(II)-MCM41 is prepared by both direct hydrothermal synthesis and impregnation into MCM41 molecular sieve. The catalysts are characterized by XRD and FT-IR measurements for the structural features and by atomic adsorption spectrophotometry for the amount of Mn(II) entering into MCM41. The materials are calcined at 773 K for 5 h before use. The oxidation is carried out in a high-pressure stirred reactor at 353 K under various reaction conditions. The conversion achieved with directly synthesized Mn(II)-MCM41 for 2-CP, 2,4-DCP and 2,4,6-TCP is respectively 90.3, 55.1 and 50.8 % in 5 h for the reactant: H_2O_2 mole ratio 1:1, and 85.5, 60.6 and 60.2 % in absence of H_2O_2. The conversion with impregnated Mn(II)-MCM41 for 2-CP, 2,4-DCP and 2,4,6-TCP is respectively 90.3, 78.0 and 75.0% in 5 h with H_2O_2 and 91.1, 85.0 and 79.7% without H_2O_2. The oxidation follows first order kinetics. Effects of various reaction conditions and the probable mechanisms of oxidation have been discussed.

Keywords: 2-CP; 2,4-DCP; 2,4,6-TCP; Wet oxidation; Mn(II)-MCM41

1. Introduction

Phenols and their chlorinated derivatives represent one of the most abundant families of industrial toxic compounds which are resistant to biodegradation and persist in the environment for long periods [1,2]. These pollutants originate from a large number of different sources, the most important among them being the effluents of the petroleum and petrochemical industries, Kraft Mills, Olive Oil production, and various chemical manufacturing industries such as those making phenolic resins, herbicides, pesticides, solvents, paints, plastics and other chemicals [2–5].

2-Chlorophenol (2-CP) and 2,4-dichlorophenol (2,4-DCP) have both been recognised as priority pollutants by USEPA since 1976 [5]. Their use has been strictly restrained, but these compounds continue to be discharged into water from various industrial sources including pulp and paper industry effluents [6]. 2,4-Dichlorophenol (2,4-DCP) is a precursor to the manufacture of the widely used herbicide 2,4-dichlorophenoxy acetic acid (2,4-D) and is also the major transformation product of 2,4-D caused by solar photolysis and also microbial activities in soil or natural water. 2,4-DCP is also a water disinfection byproduct and is produced during incineration of municipal waste. 2,4,6-Trichlorophenol (2,4,6-TCP) is a toxic, mutagenic, and carcinogenic pollutant [7]. It is found in the emissions from fossil fuel combustion, municipal waste incineration, and chlorination of water containing phenol or certain aromatic acids with hypochlorite or during disinfection of water. Most uses of 2,4,6-TCP have been now discontinued because of its toxicity, but it continues to be used in the synthesis of several fungicides [8].

The toxic and bio-resistant organochlorine compounds in aqueous systems need to be transformed into harmless species. Biological oxidation requires longer retention time and is not suitable for high concentrations of pollutants or for persistent pollutants. The chemical methods are additive, requiring

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Nomenclature

C1	directly synthesized Mn(II)-MCM41
C2	impregnated Mn(II)-MCM41
CEC	cation exchange capacity (meq/g)
2-CP	2-chlorophenol
C_t	concentration at time t (mol L^{-1})
C_0	initial concentration (mol L^{-1})
2,4-DCP	2,4-dichlorophenol
k	first order rate coefficient (min^{-1})
2,4,6-TCP	2,4,6-trichlorophenol

high capital investment and creating problem of high dissolved solid content in the effluent [5]. Increasing amount of work has been devoted therefore to find an efficient, inexpensive, and green chemical degradation process for these persistent organic chemicals [4,9] and catalytic wet oxidation has become a favoured process. While transition metal complexes are widely used as oxidizing agents for organic compounds in homogeneous processes, their use is limited by durability constraints and difficulties in recovery after use. The homogeneous metal oxide catalyst is used in the form of fine particles, which aggregate into bigger ones resulting in a rapid loss of surface area and catalytic activity. 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) either by direct intercalation, ion exchange or encapsulation.

The mesoporous material, MCM-41, possessing a hexagonal array of pores with a large amount of surface SiOH groups and considerably weak acidity may be an ideal substrate for dispersing metal ions on it. MCM-41 has a broad spectrum of pore diameters from 15 to 100 Å, which is controlled by a suitable choice of the template or by changing the synthesis conditions. Attempts to insert transition metals, such as Cu [10], Ti, Cr, Mn or Fe into the MCM-41 framework have been reported recently. The oxidizing ability of MCM-41 synthesized hydrothermally and substituted with transition metal ions, either isomorphously or by impregnation has shown positive improvement [11]. It is to be noted that the synthesis and application of mesoporous MCM-41 materials, modified with an active species attached to the framework via host–guest interactions, creates discrete and uniform catalyst sites on the inner walls of the porous systems [12].

The present work evaluates the suitability and efficiency of catalysts obtained by incorporating Mn(II) into MCM41 by direct hydrothermal synthesis (C1) and by impregnation (C2) with respect to wet oxidation of 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP) and 2,4,6-trichlorophenol (2,4,6-TCP) in water with and without the presence of the oxidizing agent, H_2O_2. The reaction conditions were varied to investigate the effects of reaction time, catalyst load, feed concentration, mole ratio of the reactant and the oxidant, temperature and pH.

2. Materials and methods

2.1. Chemicals used

The following commercially available chemicals were used without further purification:

(i) Aluminium sulphate ($Al_2SO_4{\cdot}18H_2O$; Merck, India).
(ii) Fumed silica (Sigma, USA).
(iii) Tetraethyl orthosilicate (TEOS, 99%; Merck-Schuchardt, Germany).
(iv) Sodium hydroxide (Merck, India).
(v) Tetramethylammonium hydroxide pentahydrate ($TMAOH{\cdot}5H_2O$; Fluka, Switzerland).
(vi) Cetyltrimethylammonium bromide (CTMABr, 99%; B.D.H., England).
(vii) Ethyl amine (EA, 65%; Merck-Schuchardt, Germany).
(viii) Hexadecyltrimethylammonium chloride (HDTMACl; Fluka, Switzerland).
(ix) $MnCl_2{\cdot}4H_2O$ (Merck, India).

2.2. Hydrothermal synthesis of MCM41 and introduction of Mn(II) by impregnation

MCM-41 was synthesized [11] by mixing together aqueous solutions of aluminium sulphate (0.62 g) and sodium hydroxide (0.3 g) dissolved in minimum volume of water in a 250 mL Teflon-lined beaker and stirring the same continuously till a clear solution was obtained. Tetramethyl ammonium hydroxide (9.4 g) and fumed silica (9.26 g) were then added under stirring condition at room temperature. Hexadecyltrimethylammonium chloride (10.55 g) was added slowly and the pH of the mixture was maintained at 11.0 by adding sodium hydroxide pellets if necessary. Stirring was continued till a fine gel was obtained. The composition of the gel was: SiO_2:0.27 HDTMACl:0.06 $Al_2(SO_4)_3{\cdot}18H_2O$:0.03 Na_2O:0.33 TMAOH:20H_2O.

The gel was transferred into an autoclave and was kept at 373 K for 24 h. The crystals of MCM41 were recovered by filtration, washed with deionized water, dried in air and calcined at ~823 K in air for 5 h. Mn(II)-impregnated MCM-41 was prepared by mixing together equal amounts of MCM41 and $MnCl_2{\cdot}4H_2O$, using minimum volume of water for wetting, followed by evaporation of the solvent at 393 K for 5 h and calcination at 773 K for 6 h in air.

2.3. Hydrothermal synthesis of Mn(II)-MCM41

Mn(II)-MCM41 was synthesized hydrothermally following the method used for preparing Ti(IV)-MCM41 [13]. For this purpose, $MnCl_2{\cdot}4H_2O$ (0.2 g) was used as the Mn(II)-source and tetraethyl orthosilicate (TEOS) as the organic silicon source. In a Teflon vessel, Mn(II)-salt was dissolved in minimum amount of water (~5 mL) and to this solution, TEOS (8.96 mL), cetyltrimethylammonium bromide (2.9 g), ethylamine (1.33 mL) and tetramethylammonium hydroxide (1.5 g) were added one after another while continuously stirring the contents. The mixture was stirred mechanically at room temperature for 4 h to obtain a gel of composition 1.0 TEOS:0.2 CTMABr:0.02 Mn(II):0.6 EA:0.20 TMAOH:150 H_2O at pH 11.6. The gel was transferred into a teflon-lined stainless steel autoclave and kept at 373 K for 48 h under autogenous pressure. The resulting product was filtered, washed with distilled water and dried in air for 8 h, and calcined in air at ∼823 K for 24 h.

2.4. Characterization

MCM41 synthesis was confirmed by XRD measurements (Philips Analytical, PW 1710, Cu Kα radiation) and comparing the same with known XRD patterns of MCM41. The changes in surface topography of the Mn(II)-MCM41 catalysts were observed with SEM (LEO-1430 VP). The percentage of Mn(II) entering into MCM41 was determined with atomic absorption spectrophotometer (Varian SpectrAA 220). The catalysts were further characterized by FT-IR measurements (Perkin-Elmer Spectrum RXI, range 4400–440 cm^{-1}) using KBr self-supported pellet technique. The cation exchange capacity (CEC) of the catalysts was estimated by using copper bisethylenediamine complex method [14].

2.5. Wet oxidation of 2-CP, 2,4-DCP and 2,4,6-TCP

Catalytic oxidation was carried out in a high-pressure stirred reactor (Toshniwal Instruments, India) with equal volumes (25 mL each) of the reactant (2-CP, 2,4-DCP: 10^{-3} M, 2,4,6-TCP: 2×10^{-3} M) and H_2O_2 (10^{-3} M for 2-CP and 2,4-DCP; 2×10^{-3} M for 2,4,6-TCP), catalyst load of 2 g/L at 353 K under an autogenous pressure of 0.2 MPa and stirrer speed of 180 rpm for 5 h. The reactants were mixed together at room temperature, introduced into the reactor and then the heating was started to obtain the desired temperature. When evaluating the effects of a particular variable, appropriate changes were made in the values of the variable. When no H_2O_2 was used, the total volume was kept at 50 mL. The pH of the reactant solution was varied from 3.0 to 9.0 by adding a few drops of 0.1N HNO_3 or 0.1N NaOH.

The effects of pH and temperature were determined in a batch reactor under atmospheric pressure. After the reaction was over, the mixture was centrifuged (Remi Research Centrifuge, R24) and the unconverted reactant was estimated in the supernatant layer spectrophotometrically (Hitachi UV-visible U3210).

3. Results and discussion

3.1. Characterization of the catalysts

3.1.1. XRD study

The uncalcined MCM41 showed only one prominent diffraction peak at $2\theta = 2.7°$ followed by a broad band, while the calcined form showed three peaks at $2\theta = 2.38$, 4.1 and 4.8°. These results are in conformity with the literature values for MCM41. MCM41 materials are known to give three to five reflections between 2° and 5° indicating long range order in them, although samples with more reflections have also been reported. These reflections are assigned to the ordered hexagonal array of parallel silica tubes and can be indexed as (1 0 0), (1 1 0), (2 0 0), (2 1 0) and (3 0 0) reflections assuming a hexagonal unit cell. In the present work, the calcined MCM41 yielded three XRD peaks in the said region and the most prominent peak at $2\theta = 2.38°$ could be attributed to (1 0 0) reflection. The MCM41 materials are not crystalline at the atomic level, and therefore, no reflections at higher angles could be observed. The reflections at higher angles would any way be very weak because the structural features have very little influence at higher angles. In the metal impregnated MCM41 materials, the prominent (1 0 0) reflection ($2\theta = 2.38°$) appears to have been either masked or shifted. Thus, Mn(II)-MCM41 (both hydrothermally synthesized and impregnated) after calcination showed only two reasonably prominent peaks at 3.19° and 3.97° (2θ). The metal-impregnation thus affected the structural regularity of the materials as was observed by other workers [11]. The incorporation of metal ions into MCM41 lattice must have resulted in some amount of distortion of the hexagonal regularity manifesting itself in peak broadening and the observed shift (Fig. 1).

3.1.2. Scanning electron microscopy

The SEM micrographs (Fig. 2) indicate that compared to the parent MCM41, the surface topography has undergone significant changes in Mn(II)-MCM41 whether the sample was hydrothermally synthesized or obtained by impregnation technique. It is seen that in the directly synthesized Mn(II)-MCM41, the tendency was to form more of the small granules on the surface. This tendency increased further in the impregnated Mn(II)-MCM41 and the micrograph indicates that the bigger particles of MCM41 were now covered with small granules. In all the cases, the surface was not uniform and large number of faults and crevices could be clearly observed.

3.1.3. FT-IR study

Samples of uncalcined MCM41, calcined MCM41 and Mn(II)-MCM41 (hydrothermally synthesized) showed a characteristic FT-IR band at 960.0, 965.1 and 964.2 cm^{-1}, respectively (Fig. 3). This band may be assigned to lattice defects and is correlated to the presence of tetrahedral framework linkages of M–O–Si type. By carefully examining this band, it is seen that there was a slight red shift in Mn(II)-incorporated samples. Recent work suggests that this band can also be assigned to a Si–O vibration in a Si–OH group in siliceous MCM41 [15]. If this is the case, it is reasonable to attribute the red shift in Mn(II)-MCM41 to the replacement of an OH group by O–Mn(II) group. The broad absorption between 3650 and 3400 cm^{-1} in the FT-IR spectra (3430.1 cm^{-1} in uncalcined MCM41, 3434.7 cm^{-1} in calcined MCM41, 3480.0 cm^{-1} in hydrothermally synthesized Mn(II)-MCM41 and 3440.8 cm^{-1} in impregnated Mn(II)-MCM41) may be attributed to hydrogen-bonded vicinal pairs of silanol groups [16]. The broad band between 1000 and 1250 cm^{-1} of the MCM41 samples (1100 cm^{-1} and 1210.3 cm^{-1} in uncalcined MCM41, 1090.6 cm^{-1} and 1206.1 cm^{-1} in calcined MCM41, 1091.7 $cm^{-1}$and 1184.9 cm^{-1} in impregnated Mn(II)-MCM41 and 1092.7 and 1213.5 cm^{-1} in hydrothermally synthesized Mn(II)-MCM41) may be assigned to the asymmetric stretch-

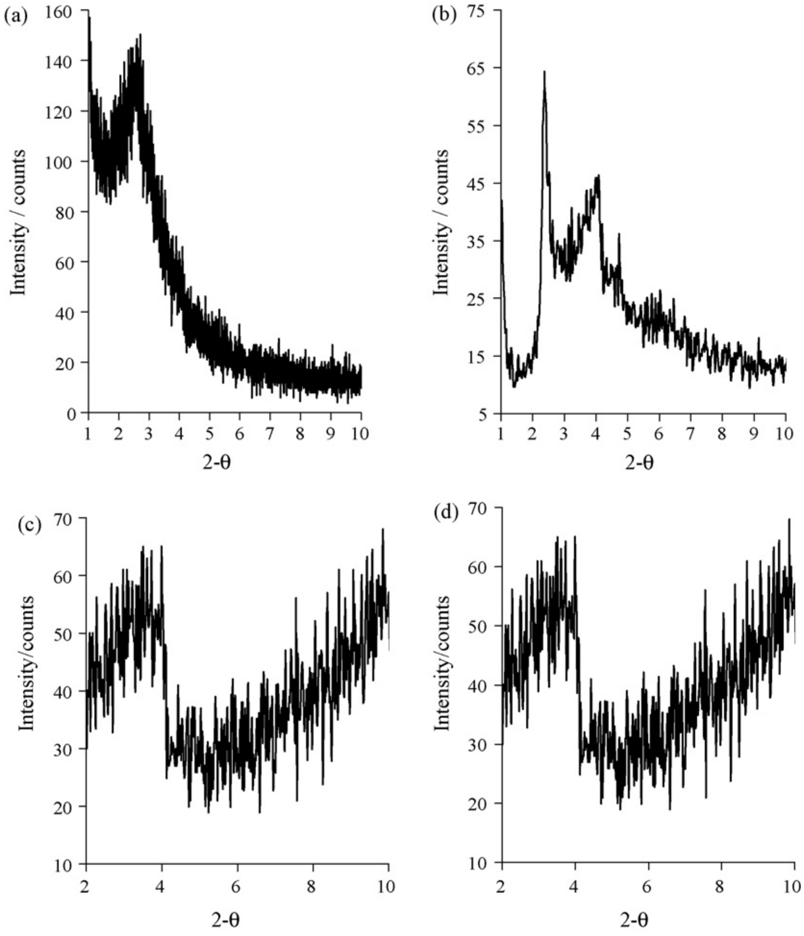


Fig. 1. XRD patterns for (a) uncalcined MCM41, (b) calcined MCM41, (c) hydrothermally synthesized Mn(II)-MCM41 and (d) Impregnated Mn(II)-MCM41.

ing of Si–O–Si bridges. The following FT-IR bands were also observed

(a) 799.4 and 1630.7 cm^{-1} in uncalcined MCM41,
(b) 794.4 and 1637.9 cm^{-1} in calcined MCM41,
(c) 669.8 and 1660.8 cm^{-1} in hydrothermally synthesized Mn(II)-MCM41
(d) 669.8 and 1626.4 cm^{-1} in impregnated Mn(II)-MCM41

These bands may be attributed to aliphatic C–H bending vibrations. Similarly, bands appearing at 2800–3100 cm^{-1} (2923.8 cm^{-1} in uncalcined MCM41, 2861.9 cm^{-1} in impregnated Mn(II)-MCM41 and 2930.3 cm^{-1} in hydrothermally synthesized Mn(II)-MCM41) may be assigned to aliphatic C–H stretching frequencies of the template in agreement with published results [17].

Introduction of Mn(II) into MCM41 has been seen to cause appreciable shift in IR bands. Further, OH-stretching vibrations corresponding to Brönsted OH groups could not be seen in accordance with very low Brönsted acidity of MCM41 materials.

3.1.4. AAS measurement

The impregnated Mn(II)-MCM41 sample, prepared with equal amounts of MCM41 and water soluble Mn(II) chloride (w/w), showed 1.1334% Mn(II) from AAS measurement. The hydrothermally synthesized Mn(II)-MCM41 with 0.02 mol Mn(II) showed only slightly different amount of 1.1248% of Mn (II) entering into MCM41. It is thus seen that impregnation can achieve entry of very similar amount of Mn(II) into MCM41.

3.1.5. Cation exchange capacity

The CECs of calcined MCM41, hydrothermally synthesized Mn(II)-MCM41 and impregnated Mn(II)-MCM41 were found to be 0.20, 0.21 and 0.26 meq/g. Although the differences are small, incorporation of Mn(II) by impregnation considerably enhanced the CEC. The CEC is normally attributed to structural defects and broken bonds on the material surface and is also assigned to structural hydroxyl transfers [18]. The wet impregnation was likely to increase the defects much more than direct hydrothermal synthesis along with an increase in the number of broken bonds, and the CEC increased.

3.2. Wet oxidation of 2-CP, 2,4-DCP and 2,4,6-TCP

3.2.1. Blank experiments

Before investigating the effectiveness of hydrothermally synthesized Mn(II)-MCM41 and impregnated Mn(II)-MCM41 as catalysts for wet oxidation of 2-CP, 2,4-DCP and 2,4,6-TCP

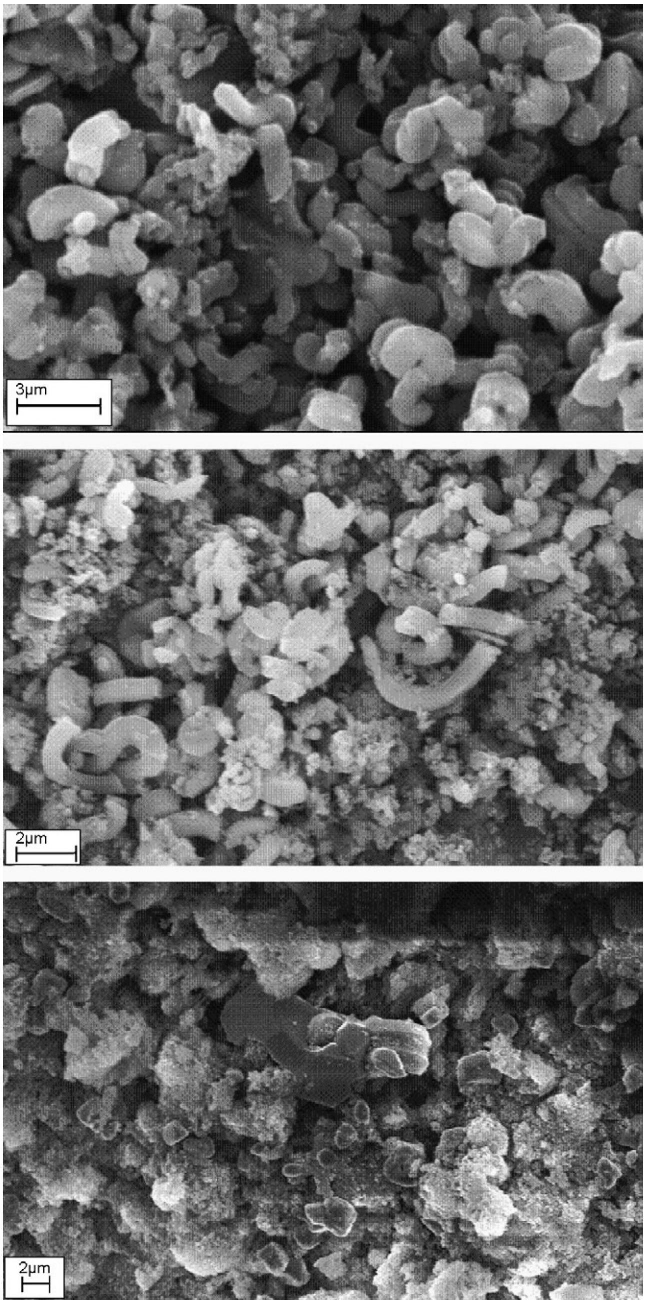


Fig. 2. SEM micrographs of MCM41 (top), Mn(II)-MCM41 (synthesized, middle), and Mn(II)-MCM41 (impregnated, bottom).

in water (1×10^{-3} M for 2-CP and 2,4-DCP and 2×10^{-3} for 2,4,6-TCP), a set of blank experiments were carried out for the following systems:

(i) 2-CP 2,4-DCP or 2,4,6-TCP alone without any catalyst and H_2O_2,
(ii) 2-CP 2,4-DCP or 2,4,6-TCP and H_2O_2 (1:1 molar ratio) without any catalyst,
(iii) 2-CP 2,4-DCP or 2,4,6-TCP with MCM41 as the catalyst (2 g/L), and
(iv) 2-CP 2,4-DCP or 2,4,6-TCP and H_2O_2 (1:1 molar ratio) with MCM41 as the catalyst (2 g/L)

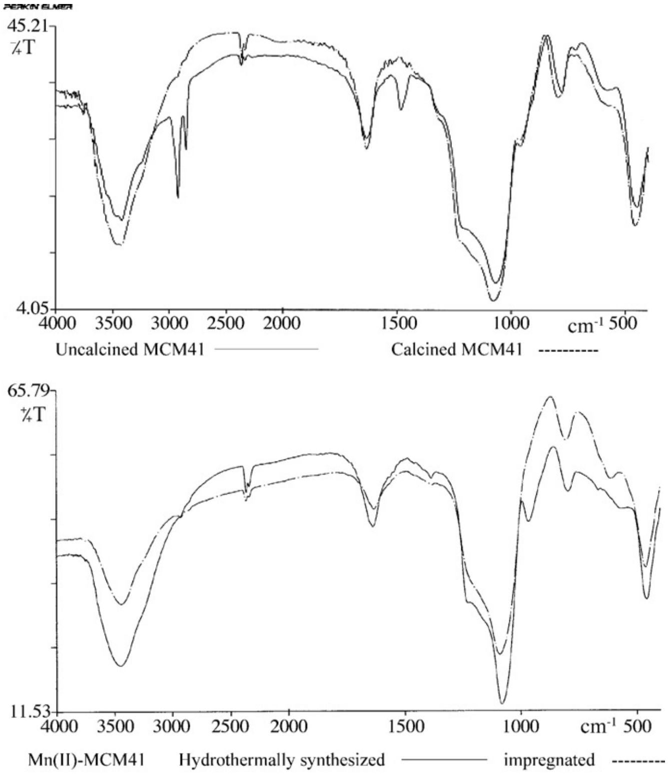


Fig. 3. FT-IR spectra of calcined and uncalcined MCM41 (above) and calcined samples of hydrothermally synthesized and impregnated Mn(II)-MCM41 (bottom).

under the same conditions of temperature (353 K), autogenous pressure (0.2 MPa), stirrer speed (180 rpm) and time interval (5 h). No measurable conversion could be recorded in (i) and (iii) while very low conversion could be observed in the set (ii) (2-CP 4.8 %, 2,4-DCP 4.6%, 2,4,6-TCP 3.5%) and the set (iv) (2-CP 8.0%, 2,4-DCP 6.4 %, 2,4,6-TCP 4.8%). It is clear from these blank experiments that 2-CP, 2,4-DCP and 2,4,6-TCP are very stable and show very little decomposition at 353 K as in (i), the mesoporous material MCM41 itself is a poor catalyst and could not bring about any decomposition of the three chlorophenols as in (iii), and the small amount of decomposition observed in (ii) and (iv) was due to some OH radicals produced from hydrogen peroxide at the temperature of reaction, 353 K.

The metal leaching was also studied in a set of blank experiments in which the catalysts were agitated in aqueous medium of pH 3.0–9.0 at 353 K for 5 h. The leaching increased with decrease in pH with maximum amount of Mn(II) coming out at pH below 3.0. The wet oxidation of 2-CP, 2,4-DCP, 2,4,6-TCP was carried out at the natural pH of their aqueous solutions, i.e. 4.3, 6.2 and 5.5, respectively and it was observed that at these pHs, the leaching did not create a situation of unacceptable Mn(II) concentration in water (the World Health Organization guideline value for Mn(II) in drinking water is 0.4 mg/L) [19].

3.2.2. Effect of pH

The pH of the medium has important influences on the wet oxidative destruction of the chlorophenols (Fig. 4). 90.3% of

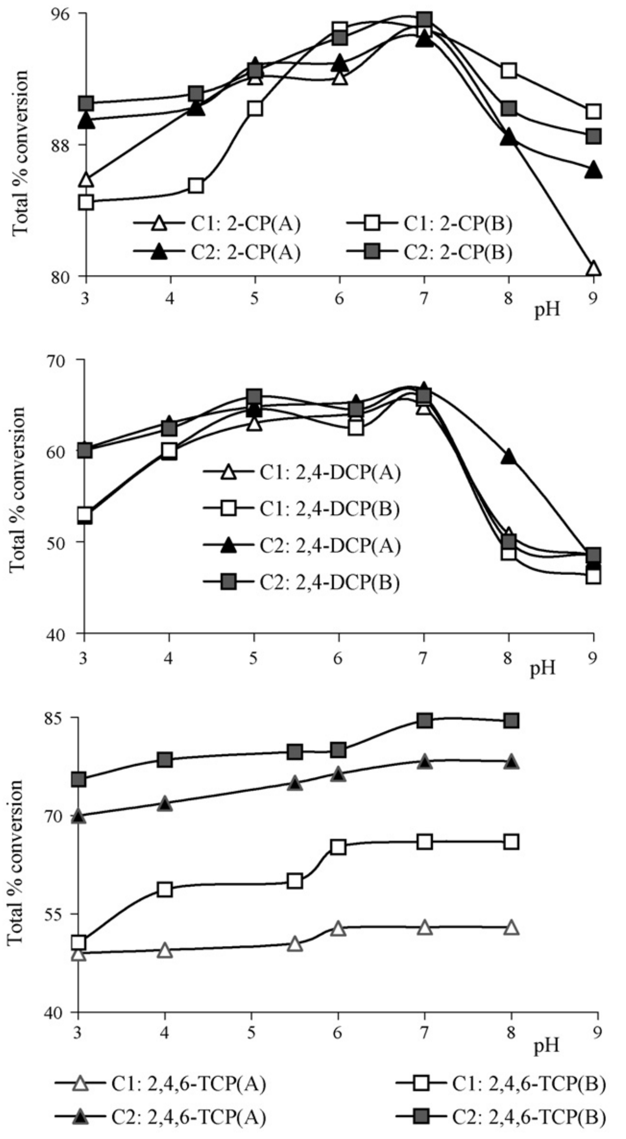


Fig. 4. Effects of pH on oxidation of 2-CP (top), 2,4-DCP (middle) and 2,4,6-TCP (bottom) with C1 and C2 (synthesized and impregnated Mn(II)-MCM41) as the catalysts with H_2O_2 (A) and without H_2O_2 (B) at 353 K (reaction time 300 min, catalyst load 2 g/L, 2-CP and 2,4-DCP 10^{-3} M, 2,4,6-TCP 2×10^{-3} M, reactant:H_2O_2 1:1).

2-chlorophenol was oxidized by H_2O_2 at the natural pH (4.3) of the aqueous solution with both directly synthesized and impregnated Mn(II)-MCM41. When no H_2O_2 was used, the conversion was 85.5% with directly synthesized Mn(II)-MCM41 and 91.1% with impregnated Mn(II)-MCM41 at the same pH. The conversion increased slowly till neutral conditions (pH 7.0) were obtained and then, decreased as the solution became alkaline.

The effects of increasing pH on 2,4-dichlorophenol oxidation were similar to that of 2-CP, but the conversion decreased much more rapidly (Fig. 4) after the alkaline conditions were reached. The aqueous solution of 2,4-DCP had a pH of 6.2 and it was seen that without adjusting the pH, 64.0 and 65.3 % conversion could be obtained with H_2O_2 over directly synthesized and impregnated Mn(II)-MCM41 catalysts, respectively. In absence of H_2O_2, the conversion was 62.5 and 64.5 % for directly synthesized and impregnated Mn(II)-MCM41, respectively.

For 2,4,6-trichlorophenol, the aqueous solution had a pH of 5.5 and oxidation up to 50.5 and 75.0 % could be obtained in presence of H_2O_2, and 60.0 and 79.7% conversion in absence of H_2O_2 (Fig. 4) over directly synthesized and impregnated Mn(II)-MCM41, respectively. However, the oxidation of 2,4,6-TCP increased almost continuously up to pH 8.0.

There are conflicting reports on effect of pH on wet catalytic oxidation. In oxidation of 2,4-dichlorophenol with Fenton's reagent, Oliveira et al. (2006) [20] have indicated the optimum pH to be around 3.5. On the other hand, Benitez et al. (1999) [21] have carried out oxidation of 2,4,6-TCP by ozone at pH 2.0 in presence of radical scavengers. Doong et al. (2000) [5] have shown that the photodegradation of 2-CP is favoured by higher pH. 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.

3.2.3. *Effect of reaction time and kinetics*

The increase in total conversion with reaction time (up to 300 min) for all the three reactants, 2-CP, 2,4-DCP and 2,4,6-TCP in the presence or absence of hydrogen peroxide for both directly synthesized (C1) and impregnated Mn(II)MCM41 (C2) catalysts is shown in Fig. 5.

The degradation of all three chlorophenols increased with the reaction time. When the reactant: H_2O_2 mole ratio is 1:1,

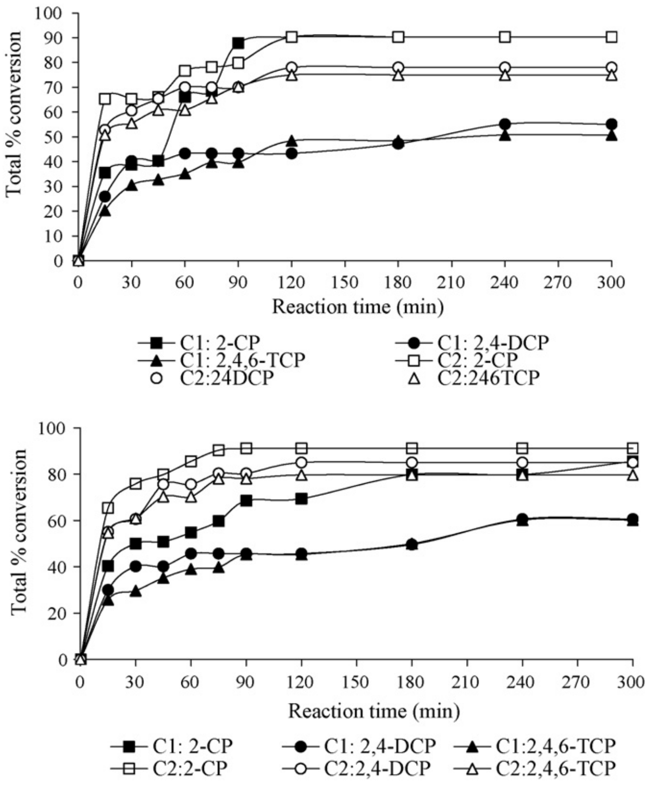


Fig. 5. Effects of reaction time on oxidation of 2-CP, 2,4-DCP and 2,4,6-TCP with C1 and C2 (synthesized and impregnated Mn(II)-MCM41) as the catalysts with H_2O_2 (reactant:H_2O_2 1:1, top) and without H_2O_2 (bottom) at 353 K (catalyst load 2 g/L, 2-CP and 2,4-DCP 10^{-3} M, 2,4,6-TCP 2×10^{-3} M).

conversion of 2-CP, 2,4-DCP and 2,4,6-TCP was enhanced from 35.5 to 90.3%, 25.9 to 55.1% and 20.3 to 50.8% for the catalyst C1 and from 65.3 to 90.3%, 52.8 to 78.0%, and 50.8 to 75.0% for C2 in the time interval of 15 to 300 min, the reaction being carried out at 353 K. The catalyst, C2, obtained by incorporating Mn(II) by wet impregnation is a more efficient catalyst than C1, which has Mn(II) introduced during the synthesis. It is possible that wet impregnation leaves much of Mn(II) on the accessible surface of MCM41 making it more effective in bringing about conversion of the chlorophenols. At a particular reaction time, the conversion is of the order of 2-CP > 2,4-DCP > 2,4,6-TCP. As the reactant molecules became more bulky, steric hindrance and other factors restricted their approach towards the active sites on the catalyst surface and conversion came down.

Significantly, the degradation reaction proceeded with almost the same efficiency even when no H_2O_2 was present in the reaction mixture. In the time interval of 15–300 min, the following conversions were recorded:

(a) 2-CP: C1 40.3–85.5% C2 65.3–91.1%
(b) 2,4-DCP: C1 30.0–60.6% C2 55.1–85.0%
(c) 2,4,6-TCP: C1 25.8–60.2% C2 54.7–79.7%

From these results, it appears that both the catalysts, C1 and C2, were almost equally effective in bringing about wet oxidation of 2-CP whether H_2O_2 was present or not in the reaction mixture. However, 2,4-DCP and 2,4,6-TCP oxidation was slightly more effective when there is no H_2O_2. The catalyst, C2 was more effective than C1 in all the conversions.

The reaction equilibrium was attained in a narrow range of time as shown below:

Reactant	Oxidant	Equilibrium time (min) for	
		Catalyst C1	Catalyst C2
2-CP	H_2O_2	120	120
2-CP	–	180	90
2,4-DCP	H_2O_2	240	120
2,4-DCP	–	240	120
2,4,6-TCP	H_2O_2	240	120
2,4,6-TCP	–	240	120

It is seen that the reaction equilibrium was reached twice as fast with impregnated Mn(II)-MCM41 as the catalyst compared to the hydrothermally prepared Mn(II)-MCM41 except in the case of 2-CP oxidation when the equilibrium time was the same for both the catalysts. Further, the equilibrium oxidation time does not seem to depend on whether an external oxidant (H_2O_2) is present or not, the exception was again 2-CP oxidation. Posada et al. (2005) [22] have claimed complete conversion of 2-chlorophenol (2CP) at 130 min when the reactions were carried out in aqueous medium at 433 K with Cu/CeO_2 catalyst. In the present work, the maximum conversion of 2-CP achieved was 91.1% with C2 (impregnated Mn(II)-MCM41) in 90 min (without any oxidant) at 353 K. The catalyst Mn(II)-MCM41 brought about the conversion at a much lower temperature and in a shorter duration of reaction time when compared to Cu/CeO_2.

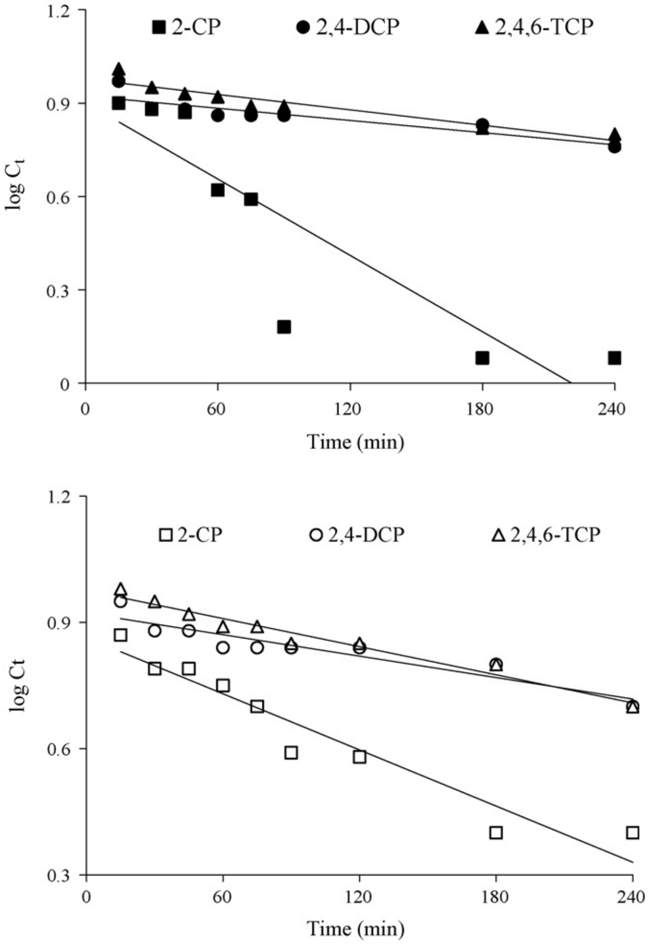


Fig. 6. First-order degradation of the reactants 2CP (10^{-3} M), 2,4-DCP (10^{-3} M) and 2,4,6-TCP (2×10^{-3} M) by wet oxidation over directly synthesized Mn(II)-MCM41(C1) at 353 K [catalyst load 2 g/L; reactant:H_2O_2 mole ratio 1:1 (top); without H_2O_2 (bottom)].

The reaction rates of the oxidative degradation have been tested for first order kinetics, by plotting $\log C_t$ versus time (Figs. 6 and 7) from the usual relation:

$$C_t = C_0 e^{-kt}$$

or,

$$\log C_t = \log C_0 - (k/2.303)t.$$

The plots are linear (regression coefficient, $R = 0.88$ to 0.97 in presence of H_2O_2, and = 0.94 to 0.98 in absence of H_2O_2) for both C1 and C2. The first order rate coefficient has the following values:

Reactant	Oxidant	First order rate coefficient (min^{-1}) for Catalyst C1	Catalyst C2
2-CP	H_2O_2	9.4×10^{-3}	6.4×10^{-3}
2-CP	–	4.8×10^{-3}	14×10^{-3}
2,4-DCP	H_2O_2	1.6×10^{-3}	3.0×10^{-3}
2,4-DCP	–	1.8×10^{-3}	10×10^{-3}
2,4,6-TCP	H_2O_2	1.8×10^{-3}	2.8×10^{-3}
2,4,6-TCP	–	2.3×10^{-3}	8.0×10^{-3}

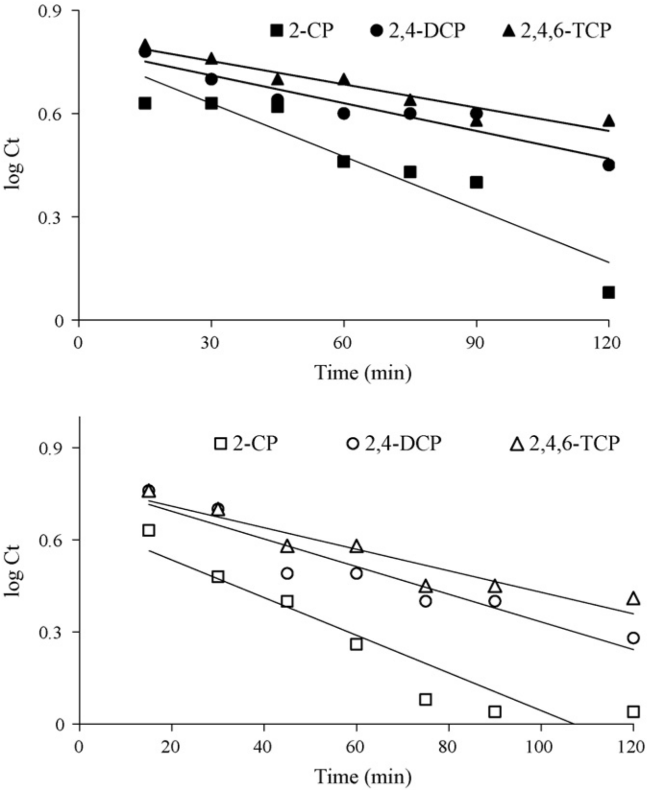


Fig. 7. First-order degradation of the reactants 2CP (10^{-3} M), 2,4-DCP (10^{-3} M) and 2,4,6-TCP (2×10^{-3} M) by wet oxidation over impregnated Mn(II)-MCM41(C2) at 353 K [catalyst load 2 g/L; reactant:H_2O_2 mole ratio 1:1 (top); without H_2O_2 (bottom)].

Significantly, the rate coefficient is almost 2–3 times higher with C2 when there is no external oxidant in the reactant mixture. These results are in conformity with the general observation that catalytic reactions usually follow first order kinetics. For example, Pera-Titus et al. (2004) [1] have reported first order kinetics for chlorophenol oxidation with Fenton's reagent. In the present work, compliance with second order kinetics was also tested by plotting the appropriate second order equation, but the plots showed very large deviations from linearity and were therefore, rejected.

Kinetics of catalytic oxidation of chlorophenols has not received much attention. Oliveira et al. (2006) [20] have shown that oxidation with Fenton's reagent is an efficient and fast process for 2,4-DCP degradation in conformity with pseudo-first-order model at least for the initial stage of the reaction when several competitive reactions are likely to consume the hydroxyl radicals through the formation of a number of intermediate products. The decomposition apparently involved several reactions with iron(II) and iron(III) species, hydrogen peroxide, hydroxyl radicals, and the organic substrate [1]. Benitez et al. (1999) [21] have studied the kinetics of the decomposition of 2,4,6-trichlorophenol by ozonation, Fenton's reaction, and also polychromatic UV irradiation. These authors have found that the oxidation by Fenton's reagent (Fe^{2+}/H_2O_2) follows a pseudo first order kinetics.

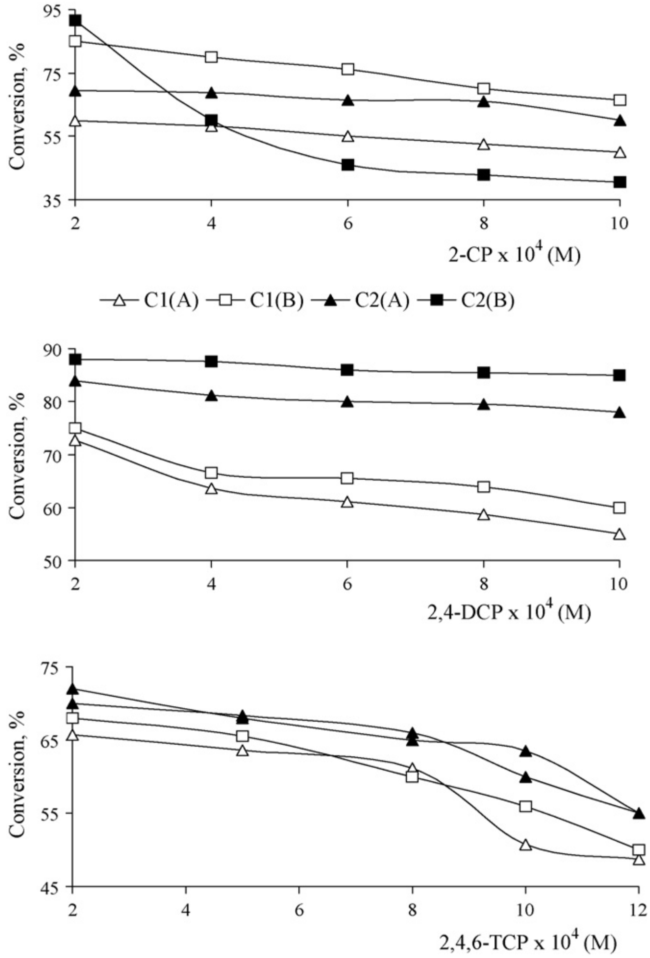


Fig. 8. Effects of reactant concentration on wet oxidation of 2CP (top), 2,4-DCP (middle) and 2,4,6-TCP (bottom) for the catalysts C1 and C2 (A with H_2O_2, reactant:H_2O_2 mole ratio 1:1) and (B without H_2O_2) at 353 K for reaction time of 300 min.

3.2.4. Effect of reactant concentration

The conversion at a constant catalyst load of 2 g/L for increasing concentrations of the chlorophenols had shown a decline (Fig. 8). Thus, when the concentration of 2-CP and 2,4-DCP was increased from 2×10^{-4} M to 4×10^{-4}, 6×10^{-4}, 8×10^{-4} and 10×10^{-4} M with a constant concentration of H_2O_2 (2×10^{-4} M) in the reaction mixture, 2-CP conversion decreased from 60.0 to 50.0% and 69.5 to 60.2%, 2,4-DCP conversion decreased from 72.7 to 55.0% and 84.0 to 78.0% for the catalysts C1 and C2, respectively in each case. Similar observation was recorded when no H_2O_2 was present in the reaction, the decrease now was from 85.0 to 66.4% and 91.7 to 40.5% for 2-CP, and 75.0 to 60.0% and 88.0 to 85.0% for 2,4-DCP for the catalysts C1 and C2, respectively in both cases.

Similarly, when the concentration of 2,4,6-TCP was increased from 2×10^{-4} M to 5×10^{-4}, 8×10^{-4}, 10×10^{-4} and 12×10^{-4} M keeping a constant concentration of H_2O_2 (5×10^{-4} M) in the reaction mixture, the conversion came down from 65.7 to 48.7% (C1) and 70.0 to 55.0% (C2). The decrease was almost identical for the same range of concentrations of 2,4,6-TCP when no H_2O_2 was used, the conversion going down from 68.0 to 50.0% (C1) and 72.0 to 55.0% (C2).

It was observed that the influence of chlorophenol concentration on wet oxidative destruction depends on the nature of the reactant, the catalyst and whether the external oxidant was present or not. For 2,4,6-TCP, for a sixfold increase in its concentration, the decrease in conversion remained between 15.0 and 18.0% for both C1 and C2 and whether H_2O_2 was added to the reaction mixture or not. The situation was different for 2-CP and 2,4-DCP. When H_2O_2 was present, the conversion of 2-CP came down almost by the same extent (10% for C1 and 9.3% for C2) for five times increase in 2-CP concentration, but without H_2O_2, the conversion of 2-CP in the same concentration range came down by 18.6% for C1 and 51.2% for C2. Increasing the concentration of 2,4-DCP by five times decreased the conversion almost similarly for C1 (decrease was 17.7% with H_2O_2 and 15.0% without H_2O_2), but the catalyst C2 behaved differently—the conversion being very little affected by the concentration increase (decrease was 6.0% with H_2O_2 and 3.0% without H_2O_2). The negative effect of increased concentration on the conversion was likely to be due to more and more reactant molecules flocking together to the catalyst surface competing for the active sites among themselves.

3.2.5. *Effect of catalyst load*

Five different catalyst loadings of 2, 4, 6, 8 and 10 g/L were used to carry out the oxidation reactions at constant reaction time of 300 min and reactant:H_2O_2 mole ratio of 1:1. The results (Fig. 9) show that the catalyst load did not have much influence on the conversions. Thus, 2-CP oxidation has remained constant at 95.9% (with H_2O_2) and at 85.5% (without H_2O_2) independent of the catalyst loading when the directly synthesized Mn(II)-MCM41 was used as the catalyst. The impregnated Mn(II)-MCM41 similarly gave an almost constant conversion of ~96.5% with H_2O_2 and 65.5 to 65.9% conversion without H_2O_2.

Similar observations were recorded with 2,4-DCP and 2,4,6-TCP. For the range of catalyst loadings, 2,4-DCP conversion was ~55.0 % and 78.0–78.5% (both in presence of H_2O_2), and 60.0–65.0% and ~85.0% (both in absence of H_2O_2) for directly synthesized and impregnated Mn(II)-MCM41, respectively. In case of 2,4,6-TCP, the oxidative conversion was 49.7–50.0% and ~75.0% (both in presence of H_2O_2) with directly synthesized and impregnated Mn(II)-MCM41, while the conversion was ~55.0 and ~79.0% (both in absence of H_2O_2), respectively for the two catalysts in the same order.

3.2.6. *Effect of mole ratio of the reactants*

To investigate the effects of increasing amount of H_2O_2, the mole ratio of hydrogen peroxide and the reactant was increased from 1:1 to 20:1 with respect to H_2O_2 for a constant reaction time of 300 min at catalyst load 2 g/L (Fig. 10). The catalyst, C1, brought about 60.0–89.5% conversion of 2-CP for the mole ratio range while the other catalyst, C2, converted 69.2–96.0% in the same range. For 2,4-DCP, 55.2–58.5% conversion was observed with C1 while the conversion remained constant at 78.0% for C2 independent of the mole ratio. 2,4,6-TCP oxidation varied from

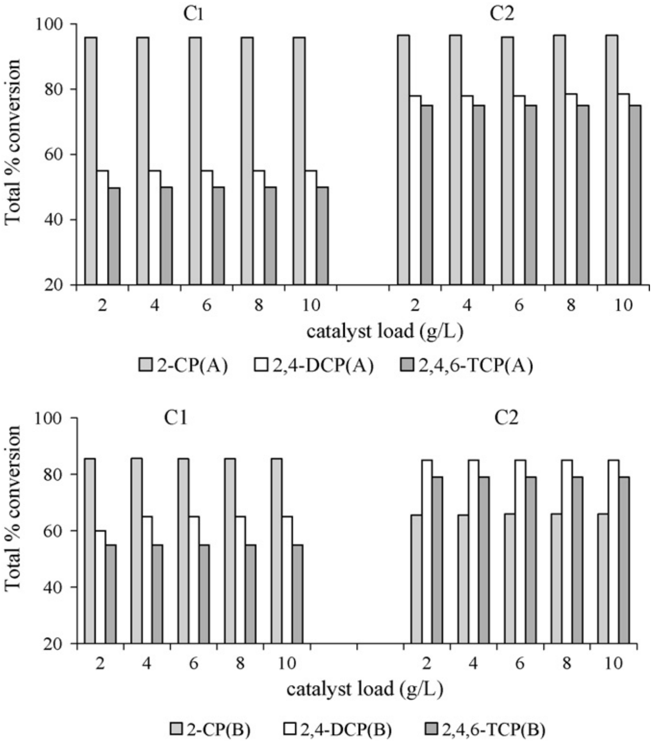


Fig. 9. Effects of catalyst load on wet oxidation of 2-CP (10^{-3} M), 2,4-DCP (10^{-3} M) and 2,4,6-TCP (2×10^{-3} M) using directly synthesized Mn(II)-MCM41, C1 and impregnated Mn(II)-MCM41, C2 as the catalysts with H_2O_2 [A: reactant:H_2O_2 mole ratio 1:1 (top) and B: without H_2O_2 (bottom) at 353 K, reaction time 300 min].

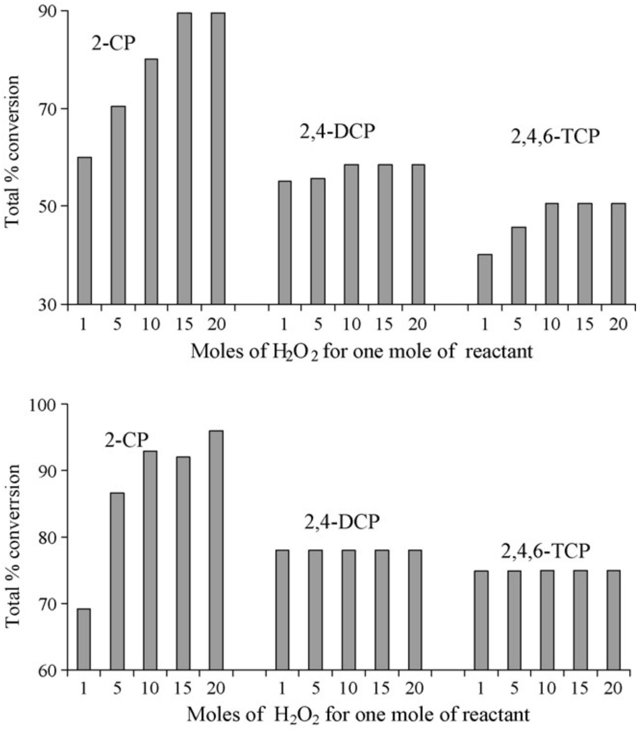


Fig. 10. Effects of mole ratio of feed on catalytic wet oxidation of 2-CP (10^{-3} M), 2,4-DCP (10^{-3} M) and 2,4,6-TCP (2×10^{-3} M) using C1 (top) and C2 (bottom) as the catalysts with H_2O_2 at 353 K (reaction time 300 min, catalyst load 2 g/L).

Table 1
Effect of temperature on wet oxidation of the reactants, 2-CP (10^{-3} M), 2,4-DCP (10^{-3} M) and 2,4,6- TCP (2×10^{-3} M) (reactant:H_2O_2 mole ratio 1:1, catalyst load 2 g/L, reaction time 300 min)

Catalyst	Temperature (K)	Total conversion (%) with H_2O_2			Total conversion (%) without H_2O_2		
		2-CP	2,4-DCP	2,4,6-TCP	2-CP	2,4-DCP	2,4,6-TCP
Mn(II)-MCM41 (synthesized)	333	95.0	54.9	45.9	85.0	60.0	58.5
	353	95.9	55.1	50.5	85.5	60.6	60.0
	373	96.0	60.0	55.9	87.0	65.3	65.0
	393	96.0	65.2	60.5	87.0	65.3	65.0
	413	96.0	65.2	60.5	87.0	65.3	65.0
Mn(II)-MCM41 (impregnated)	333	96.0	75.5	75.1	92.0	84.5	78.9
	353	96.5	78.0	75.0	92.5	85.0	79.7
	373	97.0	80.0	75.0	95.0	88.0	80.0
	393	97.0	85.0	77.2	97.6	88.0	82.5
	413	97.0	85.0	77.0	97.6	88.0	83.2

40.2 to 50.5% with C1 and 74.9 to 75.0% with C2. In general, 2-CP oxidation was much more affected by increasing proportion of H_2O_2 in the reaction mixture compared to 2,4-DCP and 2,4,6-TCP. Further the effects were more pronounced with C1 than with C2. The increase in H_2O_2 in the feed affected the oxidation of the three chlorophenols differently. It was obvious that a large excess of H_2O_2 did not particularly help the conversion, because at the comparatively high temperature of 353 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 [23].

The stoichiometric equations for the complete oxidation of 2-CP, 2,4-DCP and 2,4,6-TCP with H_2O_2 as given below indicate that the mole ratios of 1:13, 1:12 and 1:11 would be most suitable for bringing about complete oxidation of 2-CP, 2,4-DCP and 2,4,6-TCP, respectively.

2-CP :

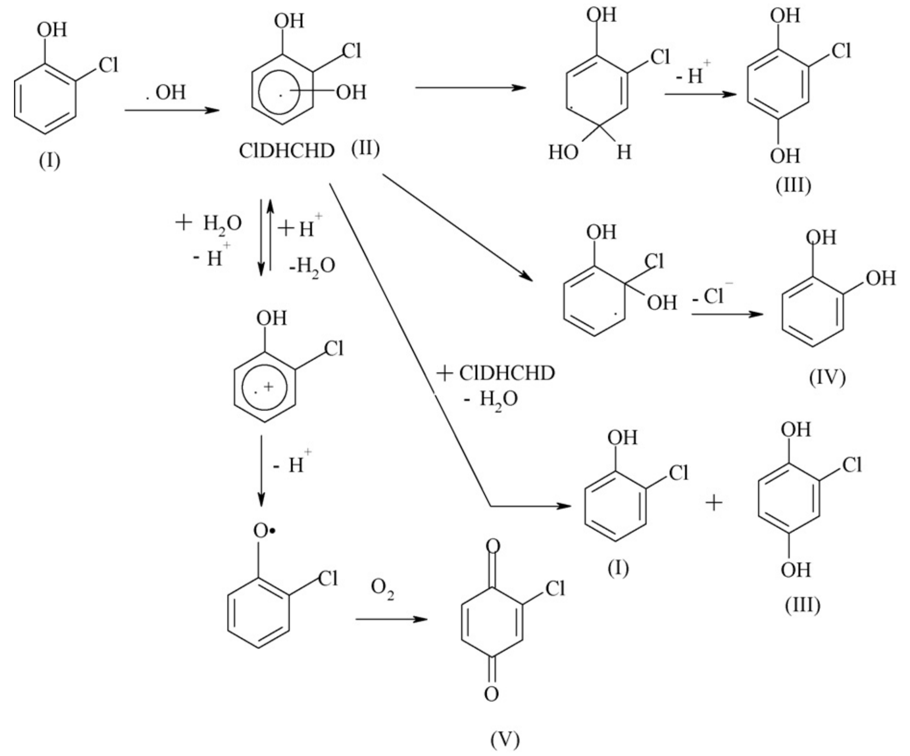
$$C_6H_4Cl(OH) + 13H_2O_2 \rightarrow 6CO_2 + 15H_2O + HCl$$

2, 4-DCP :

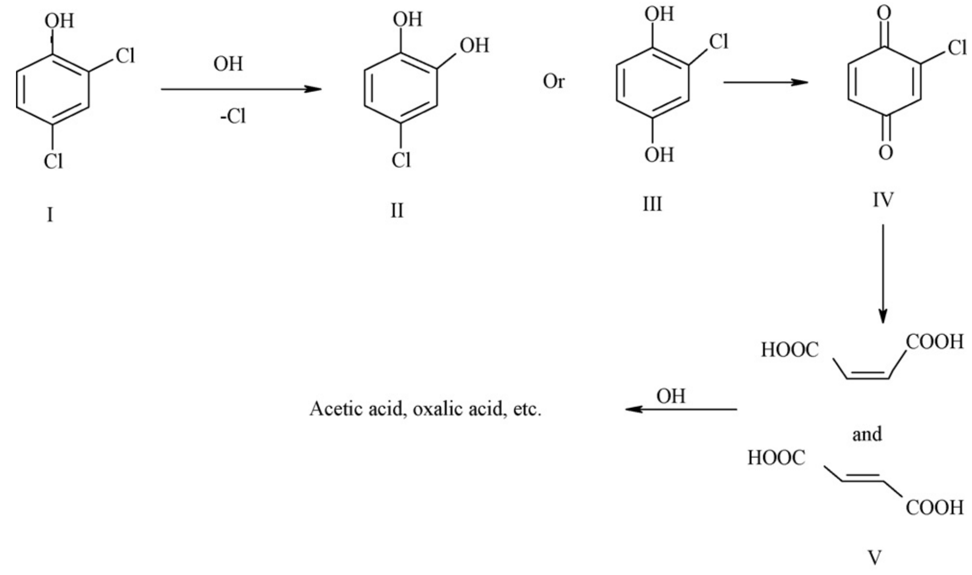
$$C_6H_3Cl_2(OH) + 12H_2O_2 \rightarrow 6CO_2 + 13H_2O + 2HCl$$

2, 4, 6-TCP :

$$C_6H_2Cl_3(OH) + 11H_2O_2 \rightarrow 6CO_2 + 11H_2O + 3HCl$$



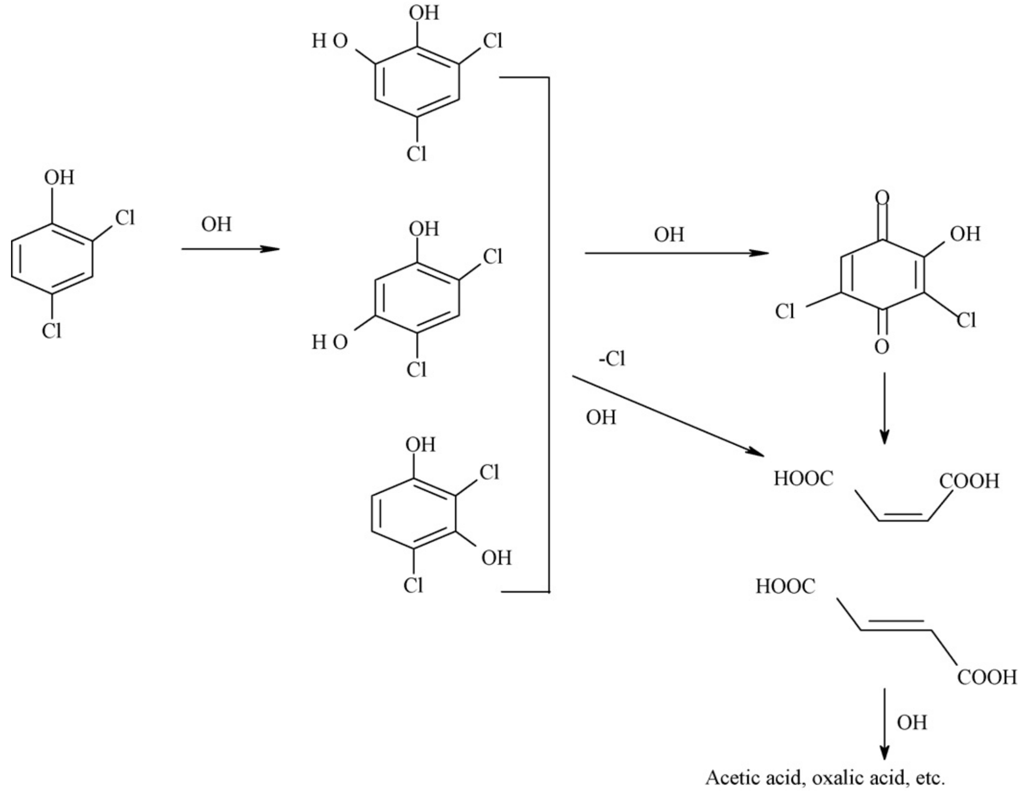
Scheme 1. Degradation pathway of 2-CP.



Scheme 2. Degradation pathway of 2,4-DCP.

For 2-CP oxidation, the results of influence of the mole ratio with respect to H_2O_2 are in almost conformity with the stoichiometric equation as the conversion settles down to a constant value at a mole ratio of about 1:15 for both the catalysts. A similar agreement is seen for 2,4-DCP and 2,4,6-TCP conversions over the catalyst C1 when the conversion reaches a constant value around the mole ratio of 1:10, but no such agreement could be seen for the catalyst C2. No satisfactory explanation could be found for the rather abnormal behaviour of the catalyst C2 for 2,4-DCP and 2,4,6-TCP oxidation unless it is assumed that the oxidation in this case does not go into completion stage.

In oxidation of anthracene to *tert*-butyl hydroperoxide (*t*-BHP), Srinivas et al. (2002) [11] have observed a conversion of >90% when the mole ratio of anthracene to *t*-BHP is increased from 1:2 to 1:10. Stoichiometrically they have found that 1:2 ratio with respect to the oxidant is sufficient to bring about the required oxidation, yet the requirement of higher

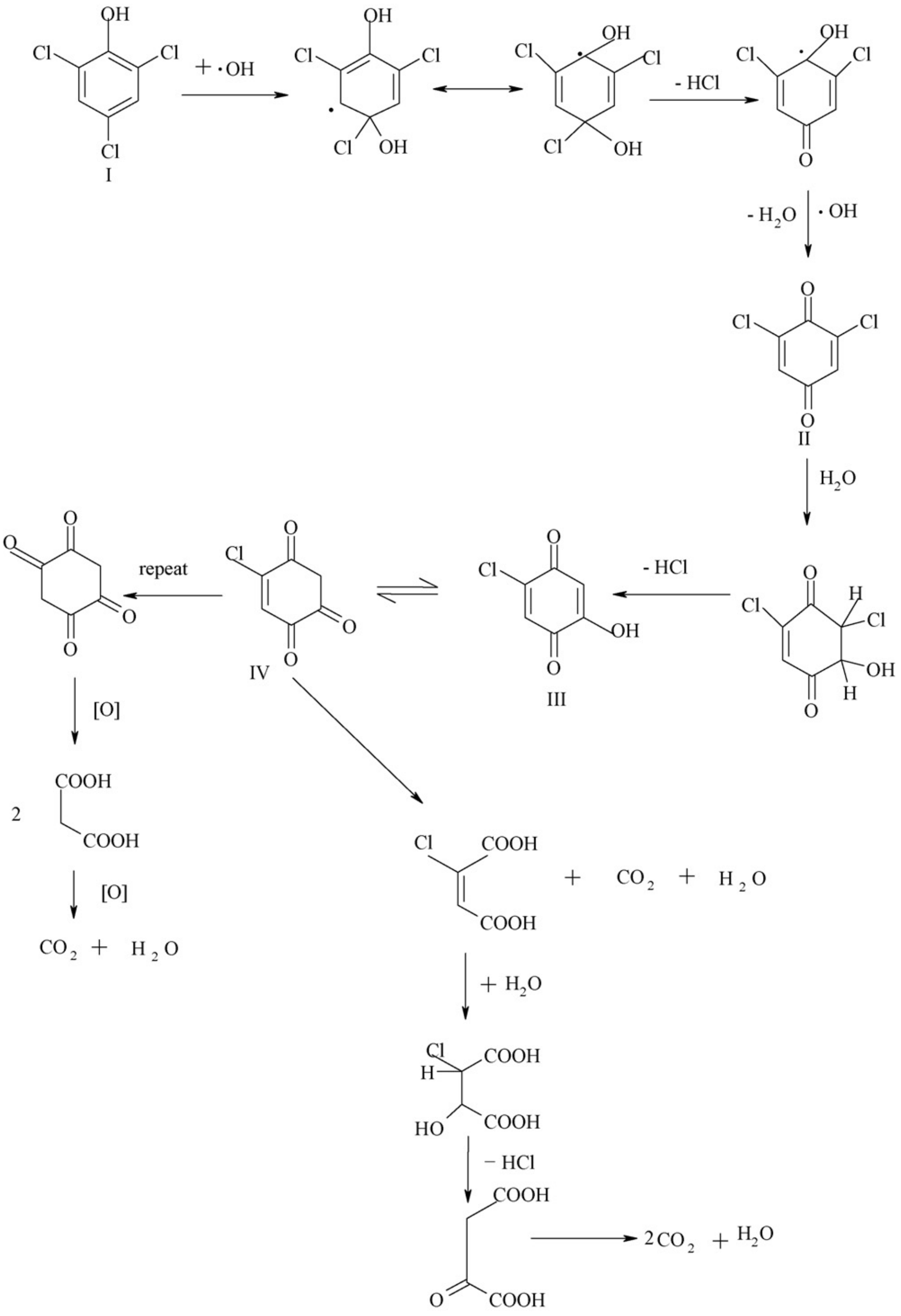


Scheme 3. Alternative degradation pathway of 2,4-DCP.

mole ratio with respect to *t*-BHP might have been necessary as the oxidant itself undergoes non-selective thermal decomposition.

3.2.7. Effect of temperature

The degradation of the chlorophenols was enhanced by carrying out the reactions at higher temperature (Table 1). The temperature was increased from 333 to 413 K in four steps of 20 K each. The conversion was found to be 95.0–96.0%, 54.9–65.2% and 45.9–60.5% for 2-CP, 2,4-DCP and 2,4,6-TCP in presence of H_2O_2 and 85.0–87.0%, 60.0–65.3% and 58.5–65.0% in absence of H_2O_2 for the directly synthesized Mn(II)-MCM41. The impregnated Mn(II)-MCM41 catalyst increased the conversion of 2-CP, 2,4-DCP and 2,4,6-TCP, respectively from 96.0 to 97.0%, 75.5 to 85.0% and 75.1 to 77.0% in presence of the oxidant and from 92.0 to 97.6%, 84.5 to 88.0% and 78.9 to 83.2% in absence of H_2O_2 in the temperature range of 333–413 K. It was seen that when the conversion was already sufficient (say, >75%), increasing the reaction temperature from 333 K by 80 K did not make much difference in



Scheme 4. Degradation pathway of 2,4,6-TCP.

the overall conversion. However, when the conversion was not very high at the lowest of the reaction temperature (333 K), the increase by 80 K made quite an impact on the conversion.

Such temperature-aided wet oxidation has also been observed by Parvulescu et al. (2004) [24] for oxidation of styrene over bimetallic Ru-(Cr, Ni, or Cu) supported on MCM-41 molecular sieves.

3.2.8. Mechanistic considerations

The oxidative decomposition of 2-CP, 2,4-DCP and 2,4,6-TCP is likely to proceed via hydroxyl radicals produced by either decomposition of hydrogen peroxide or by dissolution of atmospheric oxygen during stirring under the influence of the catalysts. The probable mechanism is based on OH radicals attacking and substituting the Cl-atoms. The following mechanisms are suggested based on (i) known products of degradation obtained through literature search, and (ii) possible products of degradation from the knowledge of degradation pathways likely to be followed by the chlorophenols.

The attack by ·OH radical converts 2-CP to a substituted hydroxycyclohexadienyl (HCHD) radical. In the simplified mechanism for the catalytic degradation of 2-CP (I), the addition of ·OH to the aromatic ring leads to the formation of chlorodihydroxycyclo-hexadienyl radical (ClDHCHD, II), which may disproportionate into 2-CP and chlorohydroquinone (III), or to simply chlorohydroquinone (III) if the addition is at *p*-position, or to pyrocatechol (IV) if the addition is at *o*-position (Scheme 1). In the alternative route, ClDHCHD (II) may be converted to 2-chloro-1,4-benzoquinone (V) through water elimination/H^+ abstraction. This may be aided by the presence of dissolved O_2. Further oxidation of the aromatic intermediates leads to ring opening and formation of carboxylic acids and hydroxylated carboxylic acids [25].

In case of 2,4-DCP, the OH groups are likely to replace the electron-withdrawing Cl-atoms successively by converting 2,4-DCP (I) to chlorocatechol (II, III), to 2-chloro-1,4-benzoquinone (IV) and finally to unsaturated dicarboxylic acids (V). OH groups also interact with the unsaturated dicarboxylic acids transforming them into simple acids like acetic acid, oxalic acid, etc., as the final products (Scheme 2). A similar scheme has been suggested in the photodegradation of 2,4-dichlorophenoxyacetic acid over titanium dioxide suspensions [26]. In another possible route, an electrophilic OH group adds onto the aromatic ring of the 2,4-DCP, leading to the formation of isomers 3,5-dichlorocatechol, 2,4-dichlororesorcinol and 4,6-dichlororesorcinol (Scheme 3). The last isomer was the hydroxylated product of 2,4-DCP. The three isomers undergo further hydroxylation and the intermediates thus produced rapidly dehydrogenate to their corresponding quinones, one of which has been identified as 3,5-dichloro-2-hydroxy-1,4-benzoquinone. The benzoquinones are converted to the simple organic acids by the same route.

The probable multistep pathway in oxidative destruction of 2,4,6-TCP (I) initiated by Mn(II)-MCM41 catalysts is also likely to proceed similarly as above (Scheme 4) with the OH groups successively replacing the electron-withdrawing Cl-atoms to give 2,6-dichloro-1,4-benzoquinone (II), which adds on more OH groups to give 5-chloro-2-hydroxy-1,4-benzoquinone (III). The product (III) converts to another product (IV) and undergoes further transformation in either of the two parallel pathways through ring cleavage and subsequent degradation to simple carboxylic acids, eventually mineralizing to CO_2 and H_2O. The photodegradation mechanism [27] by which 2,4,6-TCP undergoes conversion both in presence of H_2O_2 and in its absence has also been shown to involve similar intermediates such as 2,6-dichloro-1,4-benzoquinone (II).

The schemes of mechanism suggested have been supported by the fact that hydroxyl radicals have long been known as being capable of breaking aromatic rings of chlorobenzoquinone and other hydroxylated products, resulting in formation of maleic acids, fumaric acids, and simpler organic acids (via decarboxylation) including acetic acid, formic acid, glyoxylic acid, and oxalic acid. These low molecular weight organic acids gradually mineralize to carbon dioxide, the ultimate decomposition product of an organic compound.

When the oxidation proceeds without H_2O_2 in the reactant feed, the mechanisms are expected to be similar since the conversions will again be based on OH radicals. In this case, the OH radicals are likely to be formed from the metal oxides formed from the metal salts during calcination. The OH-radicals will originate from O on the catalytic system and H atom cleaved from the substrate (either the chlorophenol or water since the reactions were carried out in aqueous solution) as dissolved oxygen is not likely to take part in the oxidation process directly [28].

4. Conclusion

The results show that introduction of the transition metal, Mn(II) into MCM-41 through both hydrothermal and impregnation method could give very active and effective catalysts for wet oxidation of 2-CP, 2,4-DCP and 2,4,6-trichlorophenol. The catalyst brought about the maximum conversion in a shorter duration of reaction time (120 min). The final percentage of conversion was better without H_2O_2 than with H_2O_2 for the reactants except 2-CP with catalyst C1. The catalytic reactions followed first order reaction kinetics giving good linear plots with regression coefficients in the range of $R = 0.88–0.97$ in presence of H_2O_2, and = 0.94–0.98 in absence of H_2O_2 and the rate coefficient, $k_1 = 1.6 \times 10^{-3}$ to $9.4 \times 10^{-3}\ \text{min}^{-1}$ with H_2O_2 and $k_1 = 1.8 \times 10^{-3}$ to $14.0 \times 10^{-3}\ \text{min}^{-1}$ without H_2O_2 for both the catalysts taken together.

A small amount of catalyst (2 g/L) was sufficient for maximum oxidative destruction of all the three reactants in water. The influence of temperature was not uniform for all the catalytic reactions. The impregnated Mn(II)-MCM41 was found to give better results for destruction the organic pollutants than synthesized Mn(II)-MCM41.

The pH of the medium influences the oxidation and it was observed that oxidation of 2-CP and 2,4-DCP was not favoured by an alkaline pH, but 2,4,6-TCP oxidation showed an increasing trend at pH > 7.0.

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