

# Wet oxidative method for removal of 2,4,6-trichlorophenol in water using Fe(III), Co(II), Ni(II) supported MCM41 catalysts

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Received 10 February 2007; received in revised form 7 May 2007; accepted 8 May 2007

Available online 16 May 2007

## Abstract

Chlorophenols in water are resistant to biological oxidation and they have to be destroyed by chemical oxidation. In the present work, Fe(III), Co(II) and Ni(II) incorporated MCM41 mesoporous solids were used as catalysts for oxidation of 2,4,6-trichlorophenol in water with or without the oxidant, H<sub>2</sub>O<sub>2</sub>. The catalysts were prepared by impregnation and were characterized by XRD and FTIR measurements. The parent MCM41, Fe(III), Co(II) and Ni(II) impregnated MCM41 had cation exchange capacity of 20.5, 25.5, 24.2, 26.0 mequiv./100 g, respectively. The catalysts were used after calcination at 773–873 K for 5 h. The reactions were carried out in a high pressure stirred reactor at 0.2 MPa (autogenous) and 353 K under various reaction conditions. The conversion achieved with Fe(III), Co(II) and Ni(II) incorporated MCM41 in 5 h is respectively 59.4, 50.0 and 65.6% with 2,4,6-TCP:H<sub>2</sub>O<sub>2</sub> molar ratio of 1:1, and 60.2, 60.9 and 68.8% in absence of H<sub>2</sub>O<sub>2</sub>. The oxidation has a first order rate coefficient of  $(1.2\text{--}4.8) \times 10^{-3} \text{ min}^{-1}$ . The results show that introduction of Fe(III), Co(II) and Ni(II) into MCM-41 through impregnation produces very effective catalysts for wet oxidation of 2,4,6-trichlorophenol.

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**Keywords:** 2,4,6-TCP; Wet oxidation; Fe(III)-MCM41; Co(II)-MCM41; Ni(II)-MCM41

## 1. Introduction

Chlorophenols are persistent and toxic organic compounds released into water as wastes from the plastic, pesticide, and other organochemical industries and research centers [1]. These compounds together represent the most abundant family of industrial toxic compounds with their origin in a large number of different sources [2]. 2,4,6-Trichlorophenol (2,4,6-TCP) is used as a wood and glue preservative, as an antimildew agent for textiles [3], in pesticide formulations (herbicides, fungicides, bactericides), and in leather tanning and finishing. 2,4,6-TCP has 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. Most uses of 2,4,6-TCP have been now discontinued in the United States because of its toxicity, but it continues to be used in the synthesis of

some fungicides [4]. Investigators have detected trichlorophenol (unspecified isomers) in river water samples, landfill leachate samples, chemical plant effluent water samples, sewage treatment plant effluent samples, tap water samples, and in ambient air [4,5]. 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 [6–11].

Wet oxidation (WO) is a well-known process for the purification of concentrated municipal and industrial wastewaters [12]. Chlorinated phenols and other persistent organic compounds are usually not destroyed during the biological effluent treatment processes and catalyst-based oxidation technologies have been in demand for their elimination. The main purpose behind such technologies has been to convert the toxic and bio-resistant organochlorine compounds in aqueous systems into harmless species. This is carried out by decomposing or oxidizing the compounds by chemical, photochemical and biological processes. However, the biological processes need longer retention time and are not applicable to high concentrations of pollutants.

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The chemical methods are additive processes, which are not only expensive but also increase the dissolved solid load of the effluent [13].

Mesoporous molecular sieve material, MCM-41, has the potential to be used as a supports for catalysts. By incorporating various transition metal species isomorphously into the mesoporous framework, it has been found that redox molecular sieves are effective in the selective oxidation of bulky organic compounds [14]. Current research focuses on the synthesis and application of modified mesoporous MCM-41 materials which have an active species attached to the framework via host–guest interactions, creating discrete and uniform catalyst sites on the inner walls of the porous systems [15]. MCM-41 has been synthesized by hydrothermal process using a surfactant as an organic template. Various oxidation reactions in liquid phase have been reported on heterogeneous catalysts [16]. The strong demand in the chemical industry for phenolic compounds has led to the development of improved catalyst-based technologies for partial oxidation reactions.

MCM-41 with high surface area and porosity offers the possibility to directly incorporate the transition metal ions inside the mesoporous framework by substitution of Si atoms in regular tetrahedral positions. A large series of transition metal ions such as Ti, V, Cr, Fe, Co, Ni, Mn, Cu, La and Ru have been used to modify the MCM-41 silica framework. The modified materials have shown remarkable catalytic activity for partial oxidation of hydrocarbons under mild conditions [17].

The purpose of the present work is to incorporate metal ions of group VIII, viz., Fe(III), Co(II) and Ni(II) into MCM41 and utilize these mesoporous materials for wet oxidation of 2,4,6-trichlorophenol in water with and without the presence of a common oxidizing agent, H<sub>2</sub>O<sub>2</sub>, under various conditions to evaluate the effects of reaction time, catalyst load, feed concentration, mole ratio of reactant and oxidant, temperature and pH.

## 2. Materials and methods

### 2.1. Synthesis of Fe(III), Co(II) and Ni(II) incorporated MCM41

Commercially available aluminum sulphate (E. Merck, India), sodium hydroxide (E. Merck, India), tetramethylammonium hydroxide pentahydrate (Fluka, Switzerland), silica fumed (Sigma, USA), hexadecyltrimethylammonium chloride (Fluka, Switzerland) are used for synthesizing the support, MCM41. Iron(III) nitrate nonahydrate (E. Merck, India), cobalt(II) nitrate hexahydrate (E. Merck, India) and nickel(II) nitrate (E. Merck, India) are used for incorporation of metals into MCM41. 2,4,6-Trichlorophenol (2,4,6-TCP) for the reactions is procured from Fluka, Switzerland. All other chemicals used are of analytical grade.

MCM-41 is synthesized [18] 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 is obtained. Tetramethyl ammonium hydroxide

(9.4 g) and fumed silica (9.26 g) are then added under stirring condition at room temperature. Hexadecyltrimethylammonium chloride (10.55 g) is added slowly and the pH of the mixture is maintained at 11.0 by adding sodium hydroxide pellets if necessary. Stirring is continued till a fine gel is obtained. The composition of the gel is 1.0SiO<sub>2</sub>:0.27HDTMACl:0.06Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O:0.03Na<sub>2</sub>O:0.33TMAOH:20H<sub>2</sub>O. The gel is transferred into an autoclave and is kept at 373 K for 24 h. The crystals of MCM41 are recovered by filtration, washed with deionized water, dried in air and calcined at ~823 K in air for 5 h. Fe(III), Co(II) and Ni(II) impregnated MCM41 is prepared by mixing together equal amounts of MCM41 and iron(III) nitrate nonahydrate or cobalt(II) nitrate hexahydrate or nickel(II) nitrate, using minimum volume of water for wetting, followed by evaporation of the solvent at 393 K for 5 h and calcination at 773–873 K for 5 h in air.

### 2.2. Catalyst characterization

Metal supported MCM41 synthesis is confirmed by XRD measurements (Philips Analytical X-Ray Spectrophotometer, PW 1710, Cu K $\alpha$  radiation). The percentage of Fe(III), Co(II) and Ni(II) entering into MCM41 is determined with Atomic Absorption Spectrophotometer (Varian SpectraAA220). The catalysts are further characterized by FTIR measurements (Perkin-Elmer Spectrum RXI, range 4400–440 cm<sup>-1</sup>) using KBr self-supported pellet technique. The cation exchange capacity (CEC) of the catalysts is estimated using the copper bisethylenediamine complex method [19].

### 2.3. Wet oxidation of 2,4,6-TCP

Catalytic oxidation is carried out in a high-pressure stirred reactor (Toshniwal Instruments, India) under the following conditions:

2,4,6-TCP	2 mM (except when monitoring concentration effects)
H <sub>2</sub> O <sub>2</sub>	2 mM or as stated
Catalyst load	2 g/L or as stated
Temperature	353 K (except when monitoring temperature effects)
Pressure	0.2 (autogenous)
Stirrer speed	180
Time	5 h or as stated

The effects of temperature and pH are studied in a batch reactor. After the reaction is over, the mixture is centrifuged 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 uncalcined and calcined MCM41, and Fe(III)-MCM41, Co(II)-MCM41 and Ni(II)-MCM41 are given, respectively, in Figs. 1 and 2. The calcined MCM41 gives three XRD peaks corresponding to  $2\theta$  values of 2.37° ( $d = 37.32 \text{ \AA}$ ), 4.10° ( $d = 21.81 \text{ \AA}$ ) and 4.74° ( $d = 18.63 \text{ \AA}$ ), but the uncalcined

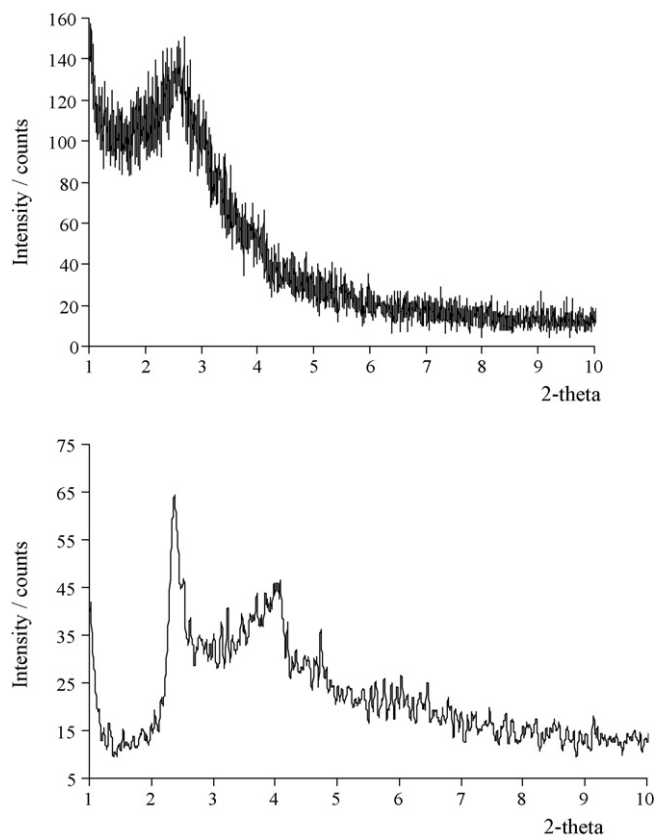


Fig. 1. XRD of uncalcined (top) and calcined (bottom) MCM41.

MCM41 has only one prominent peak at  $2\theta = 2.57^\circ$  ( $d = 34.33 \text{ \AA}$ ) followed by a broad band [20] have shown that MCM41 gives three to five reflections between  $2^\circ$  and  $5^\circ$ . The materials are thus expected to have long range order due to hexagonal arrays of parallel silica tubes and are indexed as (1 0 0), (1 1 0), (2 0 0), (2 1 0) and (3 0 0) reflections. In the present work, the calcined MCM41 yields the most prominent diffraction peak at  $2\theta = 2.37^\circ$ , which could therefore be attributed to (1 0 0) reflection. It is known that the MCM41 materials are not crystalline at the atomic level, and therefore, reflections at higher angles are not expected. The structural features have minimum influence on reflections at higher angles and therefore, such reflections are likely to be very weak to the point of almost complete exclusion. In MCM41 materials, the prominent (1 0 0) reflection ( $2\theta = 2.37^\circ$ ) appears to have been either masked or shifted. The calcined samples of MCM41 impregnated with Fe(III), Co(II) and Ni(II) show the following prominent XRD peaks:

- (a) Fe(III)-MCM41:  $3.39^\circ$  ( $d = 26.05 \text{ \AA}$ ) and  $3.92^\circ$  ( $d = 22.49 \text{ \AA}$ ),
- (b) Co(II)-MCM41:  $3.96^\circ$  ( $d = 22.31 \text{ \AA}$ ), and
- (c) Ni(II)-MCM41:  $2.99^\circ$  ( $d = 29.46 \text{ \AA}$ ) and  $4.04^\circ$  ( $d = 21.84 \text{ \AA}$ ).

The hexagonal unit cell length ( $a_0$ ) obtained from the XRD measurements are 39.6, 43.1, 30.1, 25.8 and  $34 \text{ \AA}$ , respectively, for uncalcined and calcined MCM41, Fe(III)-MCM41, Co(II)-MCM41 and Ni(II)-MCM41. The shift in the (1 0 0) reflection

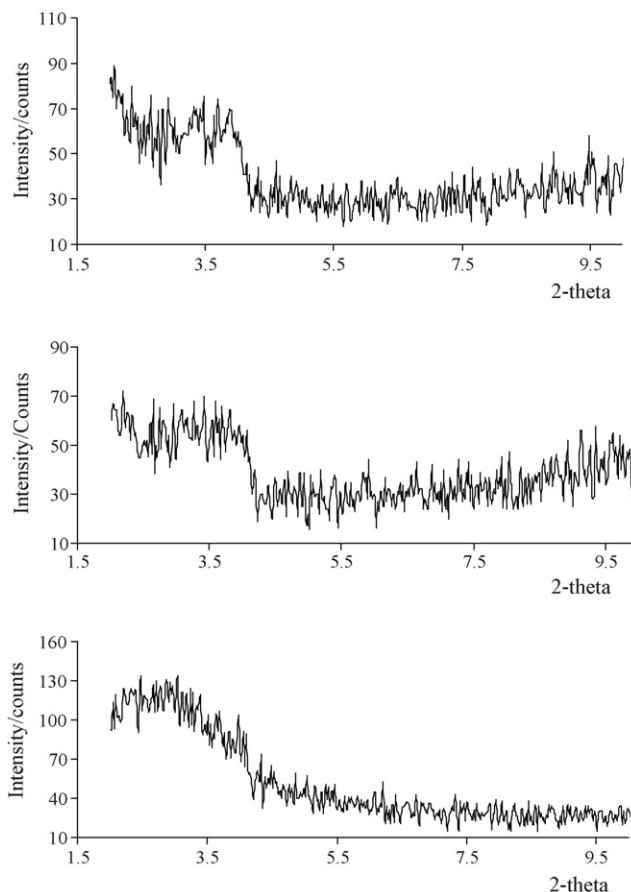


Fig. 2. XRD of calcined Fe(III)-MCM41 (Top), Co(II)-MCM41 (middle) and Ni(II)-MCM41 (bottom).

band and changes in the other characteristics of the materials show that metal-impregnation has considerable influence on the structural regularity of the impregnated MCM41 materials although the influence may not be uniform as is found by other workers [16]. The metal ions enter into MCM41 lattice distorting the hexagonal regularity of the materials which results in peak broadening and the observed shift. On comparing the XRD patterns of the calcined MCM41 and the calcined metal ion-impregnated MCM41 materials, it is seen that Co(II) causes the highest distortion in the regular hexagonal structure followed by Fe(III) and Ni(II). The  $d$ -spacing due to (1 0 0) reflection also changes in the same order, i.e.  $\text{Co(II)} > \text{Fe(III)} > \text{Ni(II)}$ . It is also the impregnation of Co(II) into MCM41 that brings about the largest decrease in the hexagonal unit cell length followed by Fe(III) and Ni(II). The tip width of the (1 0 0) peak also exhibits some significant changes in the order of calcined  $\text{MCM41} < \text{Fe(III)} < \text{Co(II)} < \text{Ni(II)}$  which may be related to the peak broadening.

IR spectra of calcined samples of Fe(III), Co(II) and Ni(II) impregnated MCM41 show the same prominent bands as found in the calcined MCM41 (Fig. 3). The following assignment of FTIR bands can be made:

- (i) Uncalcined MCM41, calcined MCM41, Fe(III)-MCM41, Co(II)-MCM41, and Ni(II)-MCM41 show a prominent IR

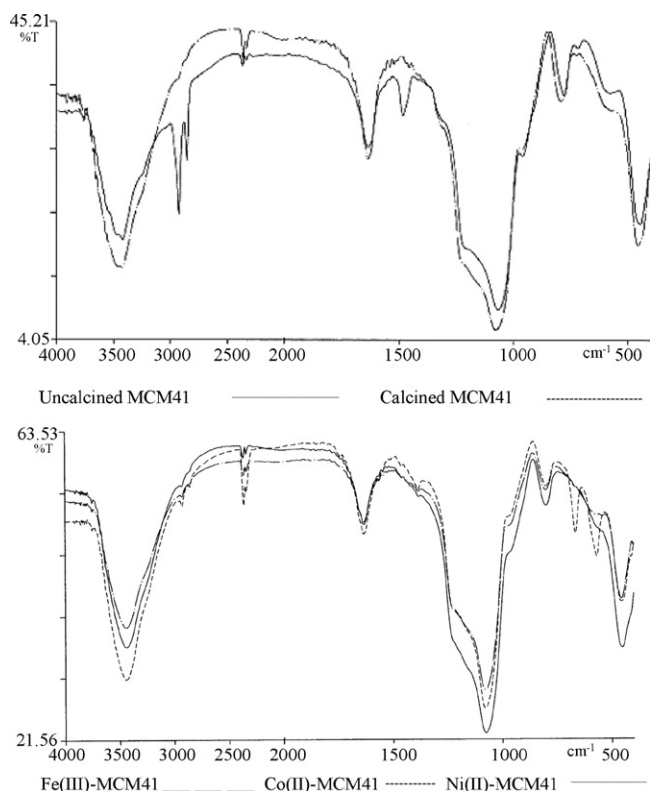


Fig. 3. FT-IR spectra of uncalcined and calcined MCM41 (top) and of calcined samples of Fe(III), Co(II) and Ni(II) supported MCM41 (bottom).

band at 960.0, 965.1, 967.0, 966.0, and 964.2  $\text{cm}^{-1}$ , respectively. This band around 960  $\text{cm}^{-1}$  is normally assigned to lattice defect correlated with the presence of tetrahedral framework linkages of the type M–O–Si [16,21] and is known to undergo slight red shift on metal-incorporation. This shift is visible in all the cases in the present work. Assignment of this band to a Si–O vibration in Si–OH groups in siliceous MCM41 has also been suggested [22]. If this is the case, it is reasonable to attribute the red shift in metal incorporated MCM41 to the replacement of H from an OH group by a metal ion to form O–M type of linkage.

- (ii) The broad absorption band between 3650 and 3400  $\text{cm}^{-1}$  in the FTIR spectra (3430.1  $\text{cm}^{-1}$  in uncalcined MCM41, 3434.7  $\text{cm}^{-1}$  in calcined MCM41, 3447.3  $\text{cm}^{-1}$  in Fe(III)-MCM41, 3450.6  $\text{cm}^{-1}$  in Co(II)-MCM41 and 3460.4  $\text{cm}^{-1}$  in Ni(II)-MCM41) may be attributed to hydrogen-bonded vicinal pairs of silanol groups [20].
- (iii) The broad band between 1000 and 1250  $\text{cm}^{-1}$  in the MCM41 samples (1100 and 1210.3  $\text{cm}^{-1}$  in uncalcined MCM41, 1090.6 and 1206.1  $\text{cm}^{-1}$  in calcined MCM41, 1090.5 and 1199.6  $\text{cm}^{-1}$  in Fe(III)-MCM41, 1089.7 and 1219.2  $\text{cm}^{-1}$  in Co(II)-MCM41, 1083.3 and 1219.2  $\text{cm}^{-1}$  in Ni(II)-MCM41) may be assigned to the asymmetric stretching of Si–O–Si bridges.
- (iv) FTIR bands in the regions, 720–740 and 1400–1500  $\text{cm}^{-1}$  have been shown to correspond to aliphatic C–H bending vibrations and in the region, 2800–3100  $\text{cm}^{-1}$  to aliphatic C–H stretching vibrations [23]. In the present

work, no significant band has been observed in the region of aliphatic C–H bending, but a few bands could be seen for aliphatic C–H stretching (2923.8  $\text{cm}^{-1}$  uncalcined MCM41, 2930.6  $\text{cm}^{-1}$  Fe(III)-MCM41, 2920.8  $\text{cm}^{-1}$  Co(II)-MCM41 and 2925.0  $\text{cm}^{-1}$  Ni(II)-MCM41). The C–H stretching and bending vibrations obviously refer to the presence of the template or its fragments in the material synthesized which might indicate that calcination did not completely remove the template used in synthesis of MCM41.

- (v) Some other bands observed in the present work (799.4  $\text{cm}^{-1}$ : uncalcined MCM41; 794.4  $\text{cm}^{-1}$ : calcined MCM41; 797.4  $\text{cm}^{-1}$ : Co(II)-MCM41; 799.3  $\text{cm}^{-1}$ : Ni(II)-MCM41; 802.3  $\text{cm}^{-1}$ : Fe(III)-MCM41) could not be properly assigned.

AAS measurement of the metal-impregnated MCM41 materials shows that 0.36, 1.91, and 2.20% (by weight) of Fe(III), Co(II) and Ni(II), respectively, have entered into the mesoporous material. The impregnation has been done by treating 0.1 g of MCM41 with 0.1 g of a water soluble salt of the metal (containing 0.014 g Fe(III), 0.020 g Co(II) and 0.020 g Ni(II) in 0.1 g of salt). The actual amount of metal that entered into MCM41 was Fe(III): 3.55 mg/g, Co(II): 19.08 mg/g and Ni: 22.03 mg/g.

The CEC of calcined MCM41 has been found to be 20.5 mequiv./100 g. Metal impregnation of MCM41 has caused significant change in the CEC. The CEC of Fe(III), Co(II) and Ni(II) impregnated MCM41 has changed to 25.5 mequiv./100 g, 24.2 mequiv./100 g and 26.0 mequiv./100 g. The CECs of the three metal-impregnated MCM41 differ from one another by an appreciable amount, and the difference is quite significant when compared to the CEC of the calcined MCM41. The ion exchange capacity may be attributed to structural defects, broken bonds and structural hydroxyl transfers as in the case of clays [24], and the values indicate that introduction of Fe(III), Co(II) and Ni(II) enhances the same by 24.4, 18.0, 26.8%, respectively. The incorporation of Fe(III), Co(II) and Ni(II) into MCM41 has resulted in a substantial increase in the number of exchange sites which follows the order Ni(II) > Fe(III) > Co(II). However, since the AAS measurement has indicated the actual amount of the metal ions entering into MCM41 to be in the order of Ni(II) > Co(II) > Fe(III), it is likely that the trivalent Fe ions have a much greater influence on promoting cation exchange.

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

#### 3.2.1. Blank experiments

Before investigating the effectiveness of Fe(III)-MCM41, Co(II)-MCM41 and Ni(II)-MCM41 as catalysts for wet oxidation of 2,4,6-trichlorophenol in water, blank experiments were carried out for the systems (i) 2,4,6-TCP alone without any catalyst and  $\text{H}_2\text{O}_2$ , (ii) 2,4,6-TCP and  $\text{H}_2\text{O}_2$  (1:1 molar ratio) without any catalyst, (iii) 2,4,6-TCP with MCM41 as the catalyst, and (iv) 2,4,6-TCP and  $\text{H}_2\text{O}_2$  (1:1 molar ratio) with MCM41 as the catalyst under the same conditions of temperature and pressure as used with the metal-impregnated MCM41 catalysts. No measurable conversion could be recorded in (i) and (iii) while



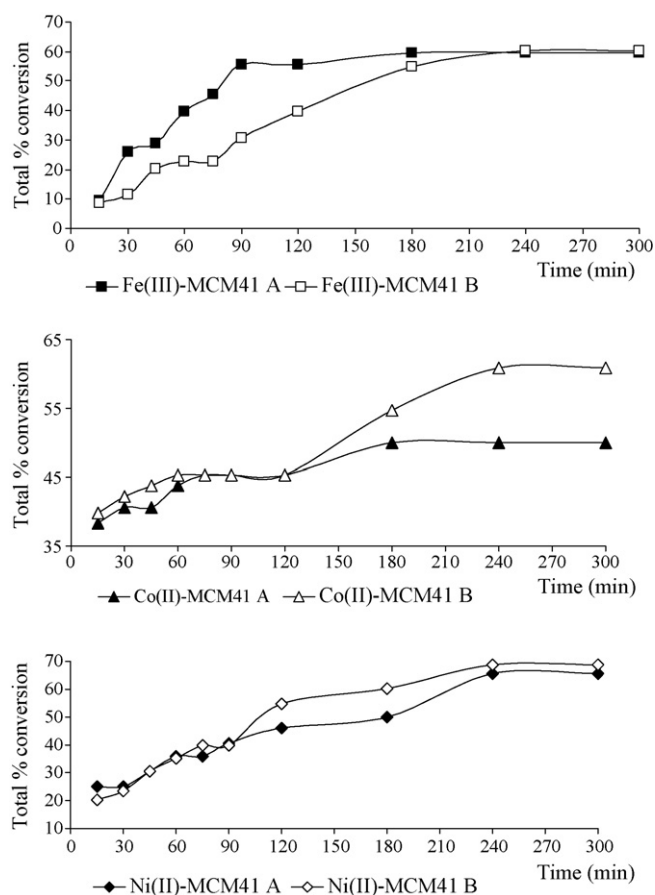


Fig. 4. Effect of reaction time on wet oxidation of 2,4,6-TCP (2 mM) (A, 2,4,6-TCP:H<sub>2</sub>O<sub>2</sub> mole ratio 1:1; B, without H<sub>2</sub>O<sub>2</sub>, temperature 353 K, catalyst load 2 g/L).

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 15 to 300 min (2,4,6-TCP:H<sub>2</sub>O<sub>2</sub> mole ratio 1:1) during which the conversion increased from 9.40–59.4% for Fe(III)-MCM41, 38.3–50.0% for Co(II)-MCM41 and 25.0–65.6% for Ni(II)-MCM41 (Fig. 4). Interestingly, even with a reaction time of 15 min, Co(II)-MCM41 can bring about 38.3% transformation of 2,4,6-TCP.

The catalysts are effective even without the presence of the oxidizing agent, H<sub>2</sub>O<sub>2</sub>. Stirring 2,4,6-TCP with the catalysts utilizes oxygen molecules from the atmosphere to bring about wet air oxidation. If the stirring time is 300 min, the conversion of 2,4,6-TCP may be as high as 60.2% for Fe(III)-MCM41, 60.9% for Co(II)-MCM41 and 68.8% for Ni(II)-MCM41 (Fig. 4). Comparing these results with those in presence of the oxidizing agent (H<sub>2</sub>O<sub>2</sub>), it is seen that when the reaction time is 300 min, all the three catalysts convert more 2,4,6-TCP when there is no oxidizing agent in the reaction mixture although initially the results may be different.

Oxidation of styrene with dilute hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30 wt.%) has been carried out by Luo et al. [14] with Ti-MCM41

as the catalyst and a maximum conversion of 42.8% could be obtained in 180 min of reaction time. They have established that the transition metal ions are the active sites for oxidation. Compared to these results, the present work has achieved a maximum conversion of 68.8% with Ni(II)-MCM41 as the catalyst even without an oxidizing agent in the reaction mixture with 2,4,6-TCP as the target contaminant.

The catalytic reactions followed first order kinetics. By plotting  $\log C_t$  (averages of three different sets of measurements under identical conditions) versus time according to the first order kinetic equation:

$$C_t = C_0 e^{-kt} \quad \text{or} \quad \log C_t = \log C_0 - \left( \frac{k}{2.303} \right) t$$

Good linear plots were obtained up to a reaction time of 180 min when H<sub>2</sub>O<sub>2</sub> was present ( $R=0.92$ – $0.98$ ), and up to 240 min when no H<sub>2</sub>O<sub>2</sub> was present ( $R=0.96$ – $0.99$ ). The first order rate constant obtained from these plots shows only minor differences with respect to the presence and the absence of H<sub>2</sub>O<sub>2</sub>. The rate constant has average values of  $4.8 \times 10^{-3}$ ,  $1.2 \times 10^{-3}$  and  $2.8 \times 10^{-3} \text{ min}^{-1}$  with H<sub>2</sub>O<sub>2</sub> and  $3.9 \times 10^{-3}$ ,  $1.8 \times 10^{-3}$  and  $4.4 \times 10^{-3}$  without H<sub>2</sub>O<sub>2</sub> for Fe(III)-, Co(II)- and Ni(II)-MCM41, respectively. Among the catalysts, it was observed that Fe(III)-MCM41 with H<sub>2</sub>O<sub>2</sub> and Ni(II)-MCM41 without H<sub>2</sub>O<sub>2</sub> oxidized 2,4,6-TCP at a slightly faster rate than the others.

Benitez et al. [25] studied the kinetics of the decomposition of 2,4,6-trichlorophenol by ozonation, by Fenton's reagent reaction, and by a polychromatic UV radiation. These authors have found that the oxidation by Fenton's reagent (Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>) follows a pseudo-first-order kinetics. Pera-Titus et al. [8] have also reported a first order reaction in chlorophenol oxidation with Fenton's reagent, for which mass balance study, in a batch reactor, yielded an exponential relationship between concentration and reaction time. These results are found to be in conformity with the present work when the ratio,  $C_t/C_0$  ( $C_0$  is the initial concentration of 2,4,6-TCP and  $C_t$  is the concentration at time  $t$  after the wet catalytic oxidation reaction commenced) is plotted (Fig. 5) against the reaction time for each of the catalysts, Fe(III), Co(II) and Ni(II) incorporated MCM41. Significant decrease in 2,4,6-TCP concentration is 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 240 min, the ratio,  $C_t/C_0$ , becomes nearly constant implying attainment of equilibrium.

Posada et al. [26] have shown catalytic wet air oxidation of aqueous solutions of phenol, 2-chlorophenol (2CP) and 4-nitrophenol (4NF) by using Cu/CeO<sub>2</sub> as the catalyst. These workers achieved complete degradation of phenol and 2-chlorophenol respectively in 100 and 130 min, and about 60% destruction with 4-nitrophenol in 200 min. They have proposed the composite Cu/CeO<sub>2</sub> catalyst as a better catalyst for oxidation of phenols than the two individual oxides of Cu or Ce. In the present work, the maximum conversion achievable at 353 K is 68.8% with Ni(II)-MCM41 in 240 min (without any oxidant), but the advantages are (i) inexpensive catalyst compared to Cu/CeO<sub>2</sub>, (ii) the catalysts can bring about very good conversion even without the need for an oxidizing agent, further

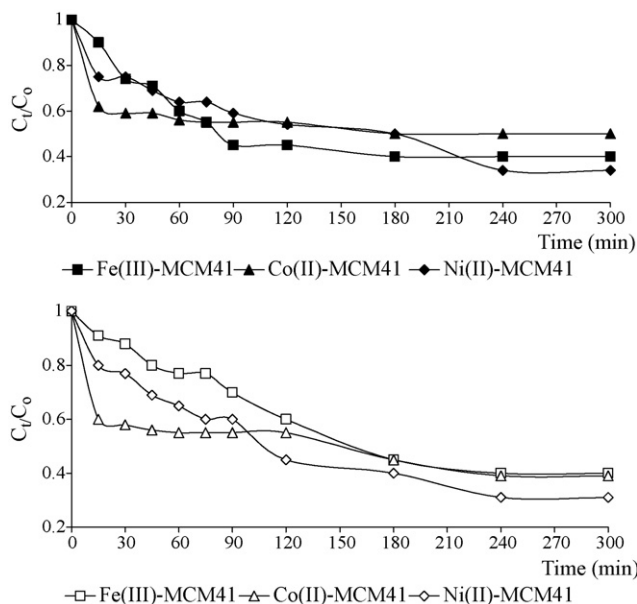


Fig. 5. Conversion of 2,4,6-TCP as a function of reaction time by wet oxidation at 353 K (catalyst load, 2 g/L; top, 2,4,6-DCP:H<sub>2</sub>O<sub>2</sub> mole ratio 1:1; bottom, without H<sub>2</sub>O<sub>2</sub>).

saving on cost, (iii) the catalysts are effective even at a comparatively lower temperature of 353 K whereas Cu/CeO<sub>2</sub> catalyst gave maximum conversion at 433 K.

### 3.2.3. 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 2 g/L) has very little effect on the conversion, which changes only from 59.0 to 59.4% for Fe(III)-MCM41, remains constant at 50.0% for Co(II)-MCM41 and from 64.9 to 65.0% for Ni(II)-MCM41. It is found that 1:1 molar ratio of the reactant to oxidant is found to be sufficient for maximum destruction of 2,4,6-TCP (Fig. 6).

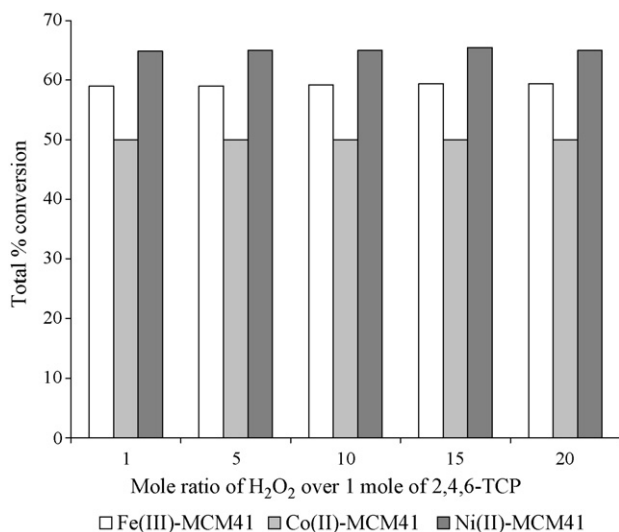


Fig. 6. Effects of mole ratio of feed on catalytic wet oxidation of 2,4,6-TCP (2 mM) with H<sub>2</sub>O<sub>2</sub> at 353K (reaction time, 300 min; catalyst load, 2 g/L).

In oxidation of anthracene to *tert*-butyl hydroperoxide (*t*-BHP), Srinivas et al. [16] 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 mole ratio with respect to *t*-BHP might have been necessary as the oxidant itself undergoes non-selective thermal decomposition. In the present work, the exact stoichiometric ratio (2,4,6-TCP:H<sub>2</sub>O<sub>2</sub>) is difficult to work out due to multiplicity of likely products and the uncertainty about the mechanism. Even then, it is found that 1:1 ratio has been the most effective and no better conversion is possible by enhancing H<sub>2</sub>O<sub>2</sub> quantity in the reaction mixture.

### 3.2.4. Effects of catalyst load

With the lowest catalyst load of 2 g/L used in the present work, Fe(III)-MCM41 could convert 59.0% of 2,4,6-TCP in presence of H<sub>2</sub>O<sub>2</sub> compared to 50.0% for Co(II)-MCM41 and 65.0% for Ni(II)-MCM41. When the catalyst load is increased to 10 g/L, the conversion does not change much. If the reaction is carried out with the same set of conditions as above but without taking H<sub>2</sub>O<sub>2</sub> in the reactant feed, again, no increase in conversion is observed with Co(II)- and Ni(II)-supported MCM41 when the catalyst load increases from 2 to 10 g/L, but the catalyst, Fe(III)-MCM41, shows some enhanced conversion (60.0–65.0%).

It is to be noted that the catalysts used in the present work have different metal loadings with respect to Fe(III), Co(II) and Ni(II), but for a particular catalyst, although the catalyst load is varied, the amount of the active phase per unit mass remains constant. This may be the reason why no significant change in conversion is observed even when the catalyst load has been increased substantially. Interestingly, a small amount of catalyst (2 g/L) has been effective in destroying a large amount of 2,4,6-TCP in water under moderate conditions.

### 3.2.5. 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 0.2 mM to 0.5, 0.8, 1.0 and 1.2 mM keeping a constant concentration of H<sub>2</sub>O<sub>2</sub> (0.5 mM) in the reaction mixture or not using H<sub>2</sub>O<sub>2</sub> at all. The conversion has declined from 60.0–35.5% for Fe(III)-MCM41, 65.7–55.7% for Co(II)-MCM41 and 70.0–50.6% for Ni(II)-MCM41 with H<sub>2</sub>O<sub>2</sub> and 60.5–40.0%, 75.0–55.0% and 65.0–45.8% for Fe(III), Co(II) and Ni(II) impregnated MCM41 without H<sub>2</sub>O<sub>2</sub> (Table 1) in the concentration range of 2,4,6-TCP used.

### 3.2.6. Effects of temperature

With the increase of the reaction temperature, 2,4,6-TCP degradation increases. In the present work, the temperature is increased from 333 to 413 K in five steps of 20 K each (Fig. 7). When the reaction is carried out with the oxidizing agent, H<sub>2</sub>O<sub>2</sub>, the percentage conversion has increased from 59.0–64.0% with Fe(III)-MCM41, 50.0–56.8% with Co(II)-MCM41, and

Table 1  
Effects of concentration of 2,4,6-TCP on its wet oxidation at 353 K (reaction time 300 min, catalyst load 2 g/L; A: H<sub>2</sub>O<sub>2</sub> 0.5 mM; B: without H<sub>2</sub>O<sub>2</sub>)

2,4,6-TCP (mM)	Total conversion (%) of 2,4,6-TCP					
	Fe(III)-MCM41		Co(II)-MCM41		Ni(II)-MCM41	
	A	B	A	B	A	B
0.2	60.0	60.5	65.7	75.0	70.0	65.0
0.5	55.5	55.5	60.6	65.5	65.3	60.3
0.8	53.1	50.0	60.1	60.0	60.8	55.8
1.0	40.5	45.5	55.7	55.0	53.3	50.0
1.2	35.5	40.0	55.7	55.0	50.6	45.8

65.2–68.1% with Ni(II)-MCM41. The temperature influences the reaction almost similarly even when there is no H<sub>2</sub>O<sub>2</sub> in the feed, the conversion being 60.0–65.0% (Fe(III)-MCM41), 60.0–64.0% (Co(II)-MCM41) and 68.1 to 72.9% (Ni(II)-MCM41). A better conversion is obtained at higher temperature when no H<sub>2</sub>O<sub>2</sub> is present. Such temperature-aided wet oxidation has also been observed by Parvulescu et al. [17] when they have used bimetallic Ru-(Cr, Ni, or Cu) into MCM-41 molecular sieves to catalyze the oxidation of styrene.

### 3.2.7. Effects of pH

The pH of the reaction medium influences the catalytic reactions of 2,4,6-TCP in a positive manner. In the presence of H<sub>2</sub>O<sub>2</sub>, as the pH was increased from 3 to 8, the conversion had an upward trend: 59.0–64.9% for Fe(III)-MCM41, 50.0–58.2% for Co(II)-MCM41 and 65.2–68.2% for Ni(II)-MCM41. In

the absence of the oxidizing agent, the conversion similarly increased from 60.0–67.0% (Fe(III)-MCM41), 60.2–66.0% (Co(II)-MCM41) and 68.6–70.5% (Ni(II)-MCM41), respectively. At the natural pH of 2,4,6-TCP aqueous solution (pH 5.5), the conversion is: (59.4% with H<sub>2</sub>O<sub>2</sub>, 60.2% without H<sub>2</sub>O<sub>2</sub>) for Fe(III)-MCM41 (50.0, 60.9%) for Co(II)-MCM41 and (65.6, 68.8%) for Ni(II)-MCM41. The results show that with all the three catalysts, the conversion does not increase appreciably up 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 slowly with Ni(II)-MCM41 catalyst up to pH 8.0, while catalysis with Fe(III)-MCM41 and Co(II)-MCM41 follows a different pattern with the conversion almost becoming constant after pH 7.0. 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 as discussed later.

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. [11] have indicated the optimum pH to be around 3.5. On the other hand, Benitez et al. [25] have carried out oxidation of 2,4,6-TCP by ozone at pH 2.0 in presence of radical scavengers. Doong et al. [13] 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. It is likely that the wet oxidation of 2,4,6-TCP does not require a very high concentration of H<sup>+</sup> ions. It is to be noted that the conversion is around 60% at the natural pH of the aqueous solution of 2,4,6-TCP and when the pH is increased to ~7.0, the conversion increases only by an additional 8–10%.

### 3.2.8. Mechanism of oxidative destruction

The probable multistep pathway in oxidative destruction of 2,4,6-TCP (I) initiated by Fe(III), Co(II) and Ni(II) incorporated MCM41 catalysts is likely to proceed via oxidative dechlorination reaction to produce 2,6-dichloro-1,4-benzoquinone(II). The quinone may be reduced to 2,6-dichloro-1,4-dihydroxybenzene(III), which in turn is likely to be reductively dechlorinated yielding 2-chloro-1,4-dihydroxybenzene(IV). This product (IV) may be degraded further by one of two parallel pathways: (i) it is likely to undergo further reductive dechlorination to yield 1,4-hydroquinone(V), which is then *ortho*-hydroxylated to produce 1,2,4-trihydroxybenzene (VI), and (ii) it is hydroxylated to yield 5-chloro-1,2,4-trihydroxybenzene (VII), which undergoes reductive dechlorination to produce the metabolite 1,2,4-trihydroxybenzene (VI). This product (VI) is likely to be converted through ring cleaving and subsequent degradation to simple carboxylic acids, which are eventually mineralized to CO<sub>2</sub>. In this pathway, the chlorine at C-4 is oxidatively dechlorinated, whereas the other chlorines are removed by a reductive process in which chlorine is replaced by hydrogen. A similar mechanism has been proposed by Reddy et al. [27] for degradation of 2,4,6-trichlorophenol by the lignin-degrading basidiomycete *Phanerochaete chrysosporium*.

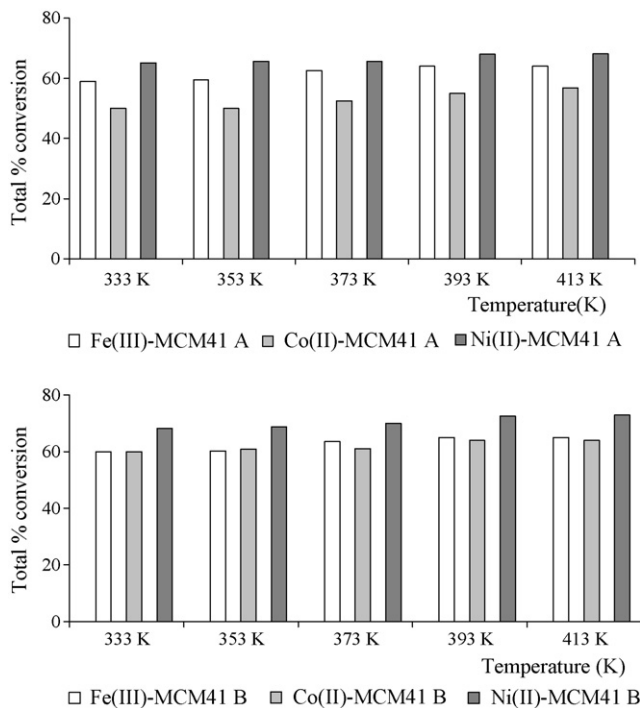
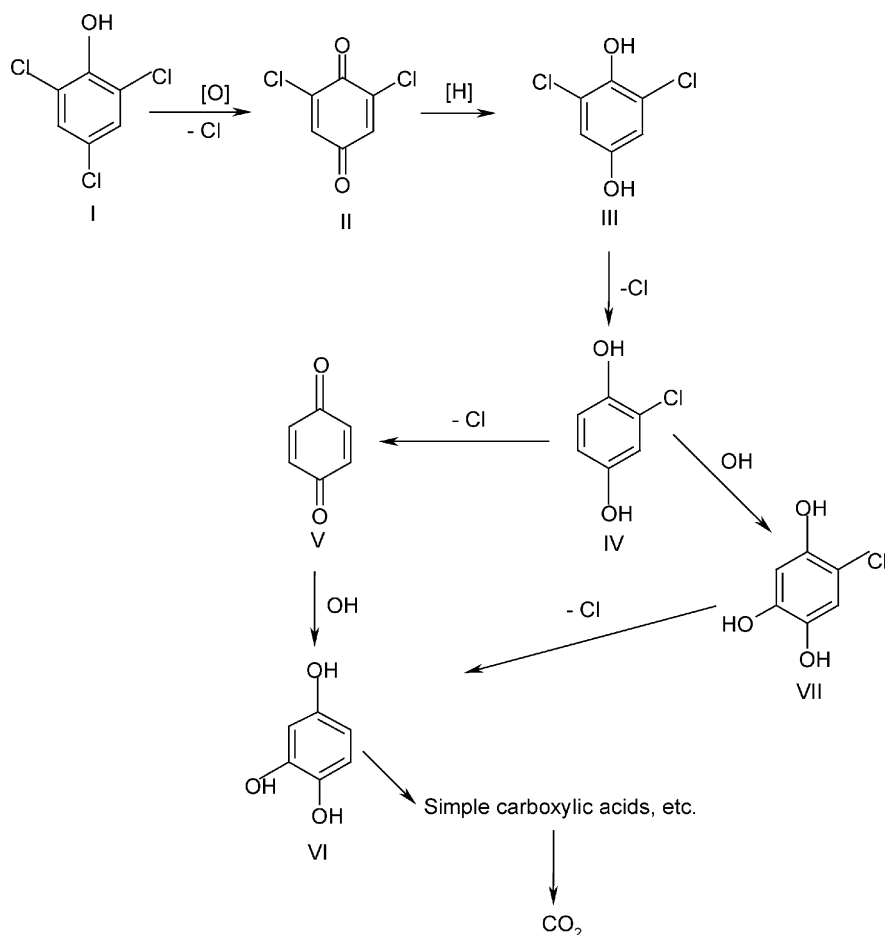


Fig. 7. Effects of temperature of 2,4,6-TCP on its wet oxidation at reaction time 300 min, 2,4,6-TCP 2 mM (A, 2,4,6-TCP:H<sub>2</sub>O<sub>2</sub> mole ratio 1:1 (top); B, without H<sub>2</sub>O<sub>2</sub> (bottom)).



Further work to separate and identify the products (II–VII) has been under progress. However, the above mechanism appears to be the most likely pathway for oxidative destruction of 2,4,6-TCP.

#### 4. Conclusion

The results show that introduction of the transition metals, Fe(III), Co(II) and Ni(II) into MCM-41 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:

- The conversion is not much dependent on the catalyst load and small amount of catalyst (2 g/L) has been found to be sufficient for maximum destruction of 2,4,6-TCP.
- Higher percentage of conversion is achieved when the pH is near 7.0 and the natural pH of 2,4,6-TCP aqueous solution (5.5) is sufficient to bring about considerable destruction of the target pollutant. At higher pH, the catalyst performance is in the order of Ni(II)-MCM41 > Fe(III)-MCM41 > Co(II)-MCM41 in presence or absence of  $\text{H}_2\text{O}_2$ .
- As the temperature increases, the conversion also improves with more and more destruction of 2,4,6-TCP. The catalysts follow the order Ni(II)-MCM41 > Fe(III)-MCM41 > Co(II)-MCM41 indicating that Ni(II)-MCM41 is the best catalyst of the three to oxidatively destroy 2,4,6-TCP.

Of the different reaction variables, it was observed that reaction time, temperature, 2,4,6-TCP concentration and pH had the maximum influence on the conversion while the effects of catalyst load and reactant mole ratio (2,4,6-TCP/ $\text{H}_2\text{O}_2$ ) were not very significant.

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