Catalytic Oxidation of Phenol Analogues in Aqueous Medium Over Fe/SBA-15

Suranjana V. Mayani, Vishal J. Mayani, and Sang Wook Kim[*]

Department of Advanced Materials Chemistry, College of Science and Technology, Dongguk University, Gyeongju, Gyeongbuk 780-714, Korea. [*]E-mail: swkim@dongguk.ac.kr

This study evaluated the use of iron-impregnated SBA-15 (**Fe/SBA-15**) as a catalyst for the oxidative degradation of persistent phenol analogues, such as 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2-nitro-phenol (2-NP), 4-nitrophenol (4-NP) and 2,4,6-trichlorophenol (2,4,6-TCP) in water. The oxidation reactions were carried out with reaction time, concentration of the phenols, amount of the catalysts, reaction temperature, pH of the reaction mixture as the process variables with or without using hydrogen peroxide as the oxidizing agent. The conversion achieved with **Fe/SBA-15** at 353 K for 2-CP, 4-CP, 2-NP, 4-NP, 2,4,6-TCP was 80.2, 71.2, 53.1, 62.8, 77.3% in 5h with a reactant to H_2O_2 mole ratio of 1:1, and 85.7, 65.8, 61.9, 63.7, 78.1% in the absence of H_2O_2, respectively. The reactions followed pseudo first order kinetics. The leachability study indicated that the catalyst released very little iron into water and therefore, the possibility of secondary pollution is negligible.

Key Words : Fe/SBA-15, Hydrogen peroxide, Oxidative degradation, Phenol analogues

Introduction

Industrial processes produce a range of molecules that may pollute water due to the harmful impacts on ecosystems and humans. Soil, water and underground water pollution by aromatic organic pollutants in many areas has caused considerable concern around the world. Among the phenolic compounds, chlorinated phenols which normally occur in industrial waste water, are toxic to humans and aquatic life.[1] Phenol and its analogues are considered as pollutants, because they are toxic and hazardous to living organisms, even at very low concentrations.[2] Chlorophenols are used broadly in pesticide and chloro herbicide production. 2,4,6-Trichlorophenol (2,4,6-TCP) has been used as a wood pre-servative, pesticide, herbicide and defoliant since the early 1930s. They can be found at high concentrations in chlorine-disinfected drinking water, river water, sediments and land-fill leachate.[3] Chlorinated organic compounds, such as 2-chlorophenol (2-CP) is known as an uncontrollable pollutant, despite their useful applications as pesticides, lubricants and solvents.[4-6] Nitro phenol compounds are common poisonous, industrial and persistent pollutants.[5,7,8] Phenol and many substituted phenols are natural components of many sub-stances, such as tea, wine and smoked foods. 2,4,6-TCP is an environmental contaminant that is toxic, mutagenic and carcinogenic. This is recognized as another priority pollutant in the United States and China.[9] Considerable research has been focused on the removal of 2,4,6-TCP from the environ-ment owing to its high toxicity, carcinogenic properties and persistence in the environment.[10-12] Aromatic nitro compounds resist chemical or biological oxidation as well as hydrolysis because of the electron-withdrawing nitro group.[13] They break down readily in surface water but a long time is need-ed for the nitrophenols to break down in deep soil and groundwater. Common pesticides, such as lindane and hexa-chlorobenzene are metabolized to 4-chlorophenol (4-CP) by plants, animals and microorganisms. 4-CP is listed as hazardous for landfill disposal.[14-16] 4-Nitrophenol (4-NP) is more harmful than 2-nitrophenol (2-NP) when given in large amounts over a short time. Nitrophenols are, however, not classified as human carcinogens.[17] The US Environmental Protection Agency (EPA) has compiled a list of nine phenol compounds considered priority pollutants. Among them, chlorophenols, such as 2-CP, 2,4-dichlorophenol, 2,4,6-TCP, pentachloro-phenol are the most toxic and carcinogenic.[18,19]

The conventional pollutant destructive technologies include biological, thermal and physico-chemical treatments.[20] Bio-logical treatments normally require a long time for micro-organisms to degrade the pollutant because they are affected by CP and NP toxicity, thermal treatments produce consider-able emissions of other harmful compounds and physico-chemical techniques, such as flocculation, precipitation, adsorption on activated carbon and reverse osmosis, require a post treatment to remove the pollutant from a newly polluted environment.[21] Alternative methods to these well established techniques are advanced oxidation processes,[22] which have been reported to be useful for the near ambient degradation of soluble organic contaminants from water and soil providing almost total degradation.

Mesoporous MCM-41 is a well known catalyst for cata-lytic oxidation. Such materials have attracted considerable attention in separation, adsorption and catalysis owing to their high surface area, large pore volume, regular structure, uniform pore size distribution and relative high thermal stability.[23,24] On the other hand, pure silica porous materials are rarely used as catalysts because of their inadequate acidity and redox properties.[25] Many researchers have indicated that the incorporation of hetero atoms into the framework of

mesoporous materials can generate active sites and almost all kinds of transition metals have been incorporated into mesoporous materials.[26,27] SBA-15 has better mechanical and hydrothermal stability than MCM-41,[28] which suggests its wider and more important potential applications. However, it was very difficult to introduce other metal ions directly incorporated into the framework of SBA-15 because of the strong acidic conditions for SBA-15 synthesis.[28,29] Recently, several studies reported the incorporation of hetero atoms, such as Al, Fe, Cr and Ti, into the framework of SBA-15 by modification of the pH and/or hydrothermal methods.[30,31]

In the present work, **Fe/SBA-15** was used as a heterogeneous green catalyst for the oxidation of phenol analogues. This study examined the suitability and effectiveness of **Fe/SBA-15** catalyst with respect to the oxidation of 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2-nitrophenol (2-NP), 4-nitrophenol (4-NP) and 2,4,6-trichlorophenol (2,4,6-TCP) in water in the presence or absence of H_2O_2 as an oxidizing agent. The effects of pH, effect of reaction time and temperature, catalyst load, feed concentration, mole ratio of the reactant and the oxidant were examined by varying the reaction conditions. The release of the transition metal from the catalyst was carried out using a leachability study. Recyclability of the catalyst was also examined.

Experimental Section

Materials. Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (P123; Aldrich, USA), hydrochloric acid (Matsunoen Chemicals Ltd., Japan), tetraethyl orthosilicate (TEOS; Aldrich) and iron (III) nitrate, 9-hydrate (Yakuri pure Chemicals Co. Ltd, Japan) were used as received. The reactions were carried out with 2-CP, 4-CP, 2-NP, 4-NP and 2,4,6-TCP (Junsei Chemicals Co. Ltd, Japan) and stock solutions of each reactants at 10^{-3} M (mol L^{-1}) concentration were prepared in double distilled water.

Preparation of Fe/SBA-15. SBA-15 was synthesized using a hydrothermal crystallization method described previously.[28,29,32] The **Fe/SBA-15** sample was prepared by wet impregnation using $Fe(NO_3)_3 \cdot 9H_2O$ as an iron precursor. Equal amounts of $Fe(NO_3)_3 \cdot 9H_2O$ and SBA-15 were dissolved in a minimum volume of deionized water with constant stirring for 60 min. The mixture was dried at 353 K and calcined in air at 823 K for 3 h to obtain **Fe/SBA-15**. The dried material was ground well and sieved through 400 mesh (0.037 mm) size test sieves. FTIR (KBr) 457, 695, 790, 960, 1079, 1229, 1380, 1446, 1638, 2340, 3436 1635 cm^{-1}. ICP analysis of **Fe/SBA-15** catalyst revealed 11.8 wt % iron metal.

Measurements. Fe/SBA-15 synthesis was confirmed by powder X-ray diffraction (PXRD, Philips X'pert PRO MRD). The changes in the surface topography of the **Fe/SBA-15** catalysts were observed by scanning electron microscopy (SEM, S-4800, Hitachi, Japan) and transmission electron microscopy (TEM, Jeol, Jem 2011). The Fe(III) entering into SBA-15 was determined with inductively coupled plasma-

optical emission spectroscopy (ICP-OES, JY Ultima 2CHR). The catalyst was further characterized by Fourier transform infrared (FTIR, Bruker, Tensor-37) spectroscopy using the KBr self-supported pellet technique. The surface area, pore size and pore diameter were estimated by N_2 adsorption-desorption study (Micromeritics ASAP-2010, USA). The thermal stability of the catalyst was determined by thermogravimetric analysis (TGA, SDT600, TA instrument, USA). The characterization of the catalyst is given in the supporting information.

Catalytic Oxidation of 2-CP, 4-CP, 2-NP, 4-NP and 2,4,6-TCP. Catalytic oxidation was carried out in a high pressure stirred reactor under atmospheric pressure. After the reaction was complete, the mixture was centrifuged and reactants remaining unconverted were estimated in the supernatant layer spectrophotometrically (Varian, Cary-4000). Calibration curves obtained with a minimum of 5 standards were used to quantify the results. The total conversion of phenol was calculated from the decrease in phenol concentration. Product identification was performed by gas chromatography-mass spectrometry (GC-MS, Shimadzu GC 2010, USA). The percentage conversion was calculated using the relation:

$$\text{Conversion (\%)} = [(C_0 - C_t)/C_0] \times 100 \qquad (1)$$

where C_0 is the initial concentration (mol L^{-1}), C_t is the concentration at any time after the reaction starts, t the time (min).

To monitor the changes in the total organic carbon (TOC) content, limited monitoring of the TOC was performed before the commencement of a reaction and after completion the reaction (300 min of reaction time in all cases) was undertaken. The TOC measurement was carried out using a TOC analyzer (Elementar liqui TOC, Germany). The reaction conditions for the TOC measurements were similar to those already described, namely, a catalyst load of 2 g L^{-1}, phenol analogue concentration: 10^{-3} mole L^{-1} each, reactant: H_2O_2 mole ratio of 1:1, temperature of 353 K, and reaction time of 300 min. The equipment measures both the total carbon (TC) and total inorganic carbon (TIC). TOC was obtained by subtracting TIC from TC. The TOC reduction (%) was determined using the formula:

$$\text{(Initial TOC} - \text{final TOC)} \times 100/\text{Initial TOC} \qquad (2)$$

Results and Discussion

Catalytic Oxidation of 2-CP, 4-CP, 2-NP, 4-NP and 2,4,6-TCP: Blank Experiments. Before examining the efficiency of **Fe/SBA-15** for the catalytic oxidation of the phenol analogues, a set of blank experiments were carried out under the reaction conditions: (i) 2-CP, 4-CP, 2-NP, 4-NP, 2,4,6-TCP (10^{-3} mole L^{-1}) without a catalyst and H_2O_2, (ii) 2-CP, 4-CP, 2-NP, 4-NP, 2,4,6-TCP (10^{-3} mole L^{-1}) and H_2O_2 (1:1 molar ratio) without a catalyst, (iii) 2-CP, 4-CP, 2-NP, 4-NP, 2,4,6-TCP (10^{-3} mole L^{-1}) with SBA-15 as the catalyst (2 g L^{-1}), and (iv) 2-CP, 4-CP, 2-NP, 4-NP, 2,4,6-

TCP (10^{-3} mole L^{-1}) and H_2O_2 (1:1 molar ratio) with SBA-15 as the catalyst (2 g L^{-1}). The reactions were carried out at 353 K, atmospheric pressure, 200 rpm stirring and a time interval of 5 h. No considerable conversion was recorded in (i) and (iii), whereas very low conversion was observed in sets (ii) 2-CP 3.8%, 4-CP 3.2%, 2-NP 3.0%, 4-NP 2.8% and 2,4,6-TCP 4.2% and (iv) 2-CP 6.5%, 4-CP 5.2%, 2-NP 4.7%, 4-NP 5.8% and 2,4,6-TCP 7.2%. These blank experiments showed that 2-CP, 4-CP, 2-NP, 4-NP and 2,4,6-TCP are quite stable when left alone (i), and H_2O_2 on its own induced only a little decomposition of the reactants (ii) and (iv). The mesoporous material SBA-15 itself is a poor catalyst and could not cause any decomposition of the phenol derivatives (iii), which is again due to the very low adsorption of the reactants on SBA-15, whereas very low conversion was observed respectively in the sets (ii) and (iv). In sets (iii) and (iv) of the blank experiments, SBA-15 was used as a catalyst to determine if the support had any appreciable catalytic ability.

Effect of the Reaction Time and Kinetics. An increase in the reaction time from 15 to 300 min showed enhanced 2-CP, 4-CP, 2-NP, 4-NP and 2,4,6-TCP degradation, as shown in Figure 1. In a series of reactions, which were carried out in this time interval with phenolic compounds (10^{-3} mole L^{-1}) and H_2O_2 (10^{-3} mole L^{-1}) at 353 K using **Fe/SBA-15** as a catalyst with a load of 2 g L^{-1}, the conversion increased from 50.0 to 80.2% for 2-CP, 18.0 to 71.2% for 4-CP, 16.8 to 53.1% for 2-NP, 19.5 to 62.8% for 4-NP and 51.6 to 77.3% for 2,4,6-TCP. Although in the initial reaction time of 15 min, the conversion was ~50% for 2-CP/2,4,6-TCP and ~17-20% for 4-CP/2-NP/4-NP but later when the reaction time was increased up to 300 min, the conversion also increased 50-80% for all the compounds. The total organic carbon (TOC) results also support this conversion.

The trends were similar even in the absence of an oxidizing agent. The conversion of 2-CP was as high as 85.7%, 65.8% for 4-CP, 61.9% for 2-NP, 63.7% for 4-NP and 78.1% for 2,4,6-TCP. For a reaction time of 300 min, the catalyst converted more phenol analogues when no external oxidizing agent was fed into the reaction mixture. The catalyst, **Fe/SBA-15** was the most capable catalyst, indicating that wet impregnation might have left some Fe(III) on the accessible sites of SBA-15, which are responsible for converting more reactants.

Nanocomposite Fe_2O_3/SBA-15 was found to be an efficient catalyst for the catalytic wet peroxidation of phenolic aqueous solutions.[33] Total organic carbon (TOC) degradation over 75% was achieved at 373 K, hydrogen peroxide concentration of 3.8 g/L and a catalyst load of 0.6 g/L. In the present work, **Fe/SBA-15** could achieve phenol analogue conversion of 50-80% in presence and 60-85% in the absence of H_2O_2 at a lower temperature of 353 K, despite a higher dosage being employed (2 g L^{-1}). The important outcome of this study was that phenol analogues, such as 2-CP, 4-CP, 2-NP, 4-NP, 2,4,6-TCP which contain more electron withdrawing groups than phenol, and these analogues could be converted in larger amounts even without using an oxidizing agent.

The above set of experiments measuring the conversion of phenols with time was used to estimate the kinetics of the oxidation reaction.

$$C_t = C_0\, e^{-kt}$$
$$\text{or,} \quad \log C_t = \log C_0 - (k/2.303)\, t \qquad (3)$$

where C_0 is the initial concentration of the reactant, C_t is the concentration at any time after the reaction starts, and t is the time (min). The apparent kinetic constant obtained from the plots showed small differences with respect to the presence and the absence of H_2O_2. Table 1 lists the kinetic constants (k). The average values of the kinetic constants ranged from 3×10^{-3} to 5.9×10^{-3} $Lg^{-1}\,min^{-1}$ in the presence of H_2O_2 and 2.8×10^{-3} to 12×10^{-3} $Lg^{-1}\,min^{-1}$ in absence of
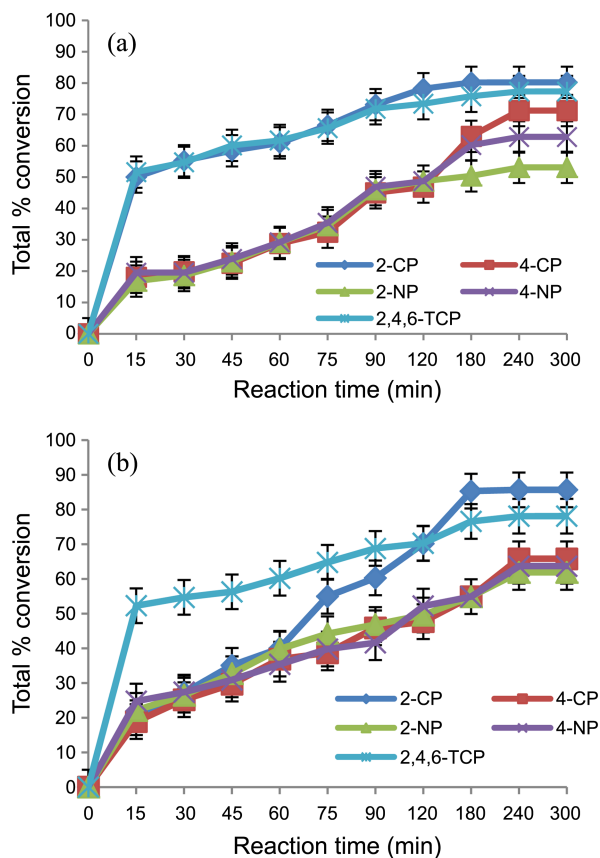

Figure 1. Effects of the reaction time on oxidation of 2-CP, 4-CP, 2-NP, 4-NP and 2,4,6-TCP with **Fe/SBA-15** as the catalyst (a) with H_2O_2 and (b) without H_2O_2 at 353 K.

Table 1. Kinetic constant (k) values for phenol analogues

Reactants	Apparent kinetic constant [L (g of catalyst)$^{-1}$ min^{-1})]	
	With H_2O_2	Without H_2O_2
2-CP	5.9×10^{-3}	1.2×10^{-2}
4-CP	5.1×10^{-3}	3.9×10^{-3}
2-NP	3.0×10^{-3}	2.8×10^{-3}
4-NP	4.4×10^{-3}	3.7×10^{-3}
2,4,6-TCP	4.8×10^{-3}	5.9×10^{-3}

H_2O_2. This indicates that Fe(III) affects the properties of SBA-15 for phenol analogue oxidation in the same way. Agreement with the first order rate equations showed that the catalytic oxidation follows a pseudo first order reaction mechanism with respect to the phenol analogues. Moreover, the reaction rate is independent of the concentration of reactants. In this study, compliance with second order kinetics was also tested by plotting the appropriate second order equation, but the plots showed very large deviations from linearity. Therefore, second order kinetics was rejected.

Effect of pH. The oxidation of phenols at 353 K was studied at pH 3.0 to 9.0, reactant concentration: 10^{-3} M, time: 300 min and catalyst load: 2 g L^{-1}. The results (Figure 2) show that in presence of an oxidizing agent, the conversion increased between pH 3.0 and 7.0. When H_2O_2 was present, 2-CP, 4-CP, 2-NP, 4-NP and 2,4,6-TCP conversion increased from 78.8 to 86.0%, 64.2 to 73.2%, 49.7 to 62.1%, 58.6 to 65.1% and 74.1 to 80.2%, respectively, in the pH range of 3.0 to 7.0. Between pH 7.0 and 9.0, the conversion for 2-CP, 4-CP and 4-NP decreased but remained constant for 2-NP and 2,4,6-TCP. When H_2O_2 was not present, the conversion increased from 84.8 to 92.0% (2-CP), 59.8 to 67.2% (4-CP), 56.2 to 64.1% (2-NP), 59.8 to 65.1% (4-NP), 76.6 to 84.8% (2,4,6-TCP) over the pH range of 3.0 to 7.0. When the pH was increased to 9.0, the conversion decreased
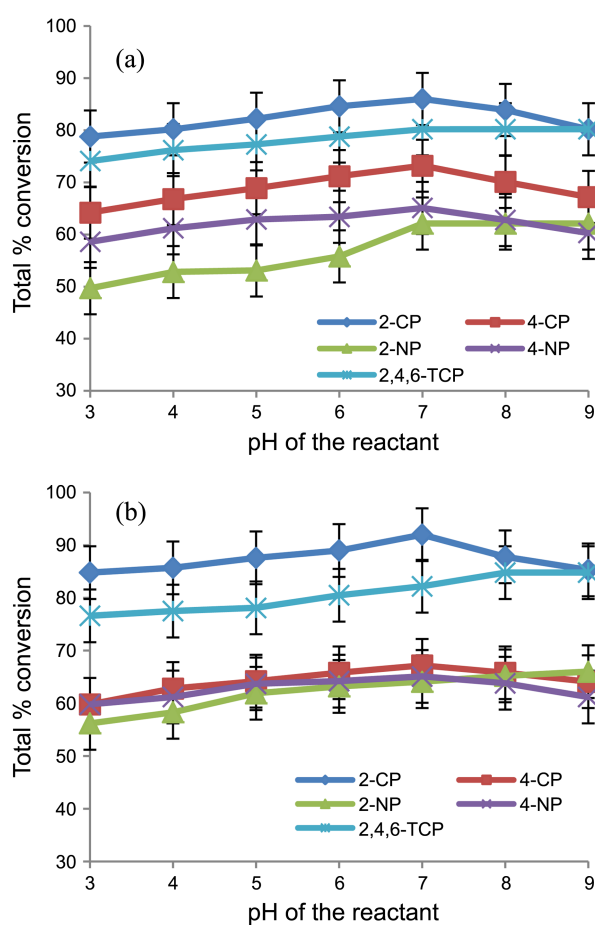
for 2-CP, 4-CP and 4-NP but increased for 2-NP and remained constant for 2,4,6-TCP.

As the catalyst contains the transition metal ion, Fe^{3+}, it is important to determine if this metal can cause secondary pollution after use. The possibility of Fe(III) leaching into the reaction mixture after a change in pH was investigated in a set of blank experiments in which the catalyst was agitated in an aqueous medium at pH 3.0-9.0 at 353 K for 5 h. Leaching was higher at basic pH. The Fe(III) released by **Fe/SBA-15** remained between 0.50 and 1.18%. At natural pH of the aqueous solution of 2-CP, 4-CP, 2-NP, 4-NP and 2,4,6-TCP (4.3, 6.8, 5.2, 5.5 and 5.6 respectively), Fe(III) leaching did not result in an undesirable Fe(III) concentration in water (the World Health Organization guideline value for Fe(III) in natural fresh water ranges from 0.5 to 50 mg L^{-1}). Therefore, this catalyst is unlikely to create new water pollution problems.[34]

Effect of the Reactant Concentration. The conversion decreased when the concentration of phenolic compounds was varied from 2×10^{-4} to 10×10^{-4} mole L^{-1} with a constant reaction time (5 h) and catalyst load (2 g L^{-1}), regardless of whether H_2O_2 (2×10^{-4} mole L^{-1}) was present in the reaction mixture (Figure 3). The decrease in conversion followed a similar pattern, *i.e.* 90.9 to 80.2% for 2-CP, 77.1 to 69.8% for 4-CP, 66.8 to 53.1% for 2-NP, 70.2 to 62.8% for
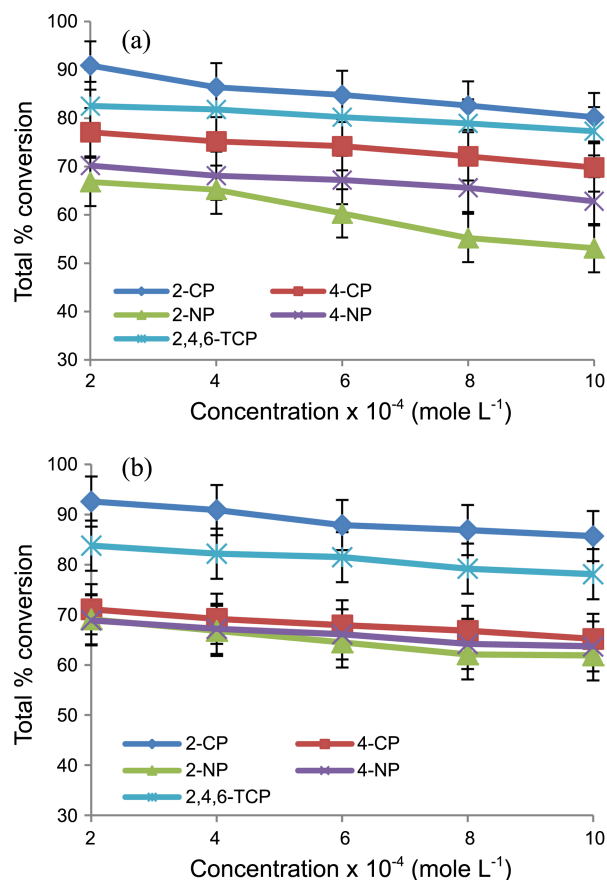

Figure 2. Effects of pH on oxidation of phenol analogues with H_2O_2 (a) and without H_2O_2 (b).

Figure 3. Effects of reactant concentration on oxidation of phenol analogues with **Fe/SBA-15** as the catalyst at 353 K (reaction time: 300 min, catalyst load: 2 g L^{-1}) in presence of H_2O_2 (a) and in absence of H_2O_2 (b).
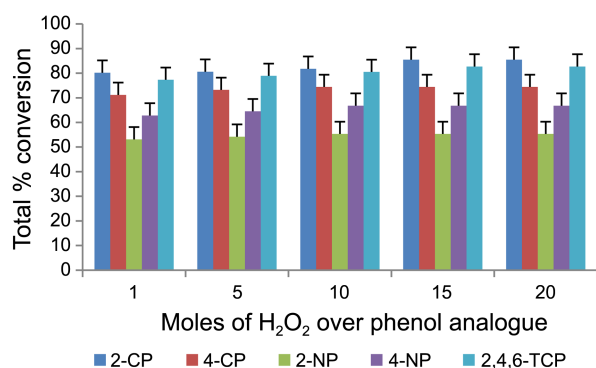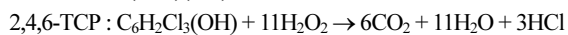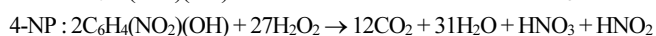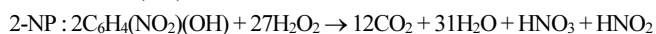
Figure 4. Effects of mole ratio on catalytic oxidation of phenol analogues.

Figure 5. Effects of the catalyst load on oxidation of phenol analogues at 353 K (reactant: H_2O_2 mole ratio of 1:1, reaction time: 300 min) with H_2O_2 (a) and without H_2O_2 (b).

4-NP and 82.5 to 77.3% for 2,4,6-TCP. On the other hand, without H_2O_2, the conversion for 2-CP, 4-CP, 2-NP, 4-NP and 2,4,6-TCP decreased from 92.6 to 85.7%, 71.1 to 65.2%, 69.1 to 61.9%, 68.9 to 63.7% and 83.8 to 78.1%, respectively. The decreased conversion of the phenol analogues with increasing concentration was attributed to competition for the active sites on the catalyst surface.

Effect of Mole Ratios of the Reactants. An increase in the mole ratio of hydrogen peroxide and the phenol analogues from 1:1 to 20:1 for a reaction time of 300 min (catalyst load 2 g L^{-1}) has little effect on the conversion (Figure 4), which changed from 80.2 to 85.5% for 2-CP, 71.2 to 74.4% for 4-CP, 53.1 to 55.3% for 2-NP, 62.8 to 66.8% for 4-NP and 77.3 to 82.7% for 2,4,6-TCP in the same range. A 1:1 the reactant to oxidant molar ratio was found to be sufficient for the maximum destruction of phenol analogues. The stoichiometric equation for complete oxidation of the phenol analogues with H_2O_2 are given below:

$$2\text{-CP}: C_6H_4Cl(OH) + 13H_2O_2 \rightarrow 6CO_2 + 15H_2O + HCl$$

$$4\text{-CP}: C_6H_4Cl(OH) + 13H_2O_2 \rightarrow 6CO_2 + 15H_2O + HCl$$

$$2\text{-NP}: 2C_6H_4(NO_2)(OH) + 27H_2O_2 \rightarrow 12CO_2 + 31H_2O + HNO_3 + HNO_2$$

$$4\text{-NP}: 2C_6H_4(NO_2)(OH) + 27H_2O_2 \rightarrow 12CO_2 + 31H_2O + HNO_3 + HNO_2$$

$$2,4,6\text{-TCP}: C_6H_2Cl_3(OH) + 11H_2O_2 \rightarrow 6CO_2 + 11H_2O + 3HCl$$
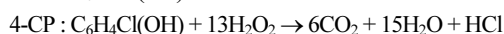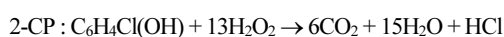
This suggests that mole ratios of 1:13 (2-CP, 4-CP), 1:27 (2-NP, 4-NP) and 1:11 (2,4,6-TCP) would be ideal for bringing about the complete oxidation of phenol analogues. The little influence of the mole ratio on phenol analogue oxidation suggests that the reactions do not undergo complete oxidation. On the other hand, the conversion increased up to a mole ratio of 1:10 (4-CP, 2-NP, 4-NP: H_2O_2) and 1:15 (2-CP, 2,4,6-TCP: H_2O_2), after which the conversion remained constant.

Effect of the Catalyst Load. Five different catalyst loadings of 2, 4, 6, 8 and 10 g L^{-1} were used in this study to determine the oxidation reactions at a constant reaction time of 300 min and a reactant: H_2O_2 mole ratio of 1:1 at 353 K (Figure 5). In the range of catalyst loadings from 2 to 10 g L^{-1}, 80.2 to 84.0% 2-CP could be converted in presence of H_2O_2 compared to 71.2 to 74.0% for 4-CP, 53.1 to 55.2% for 2-NP,
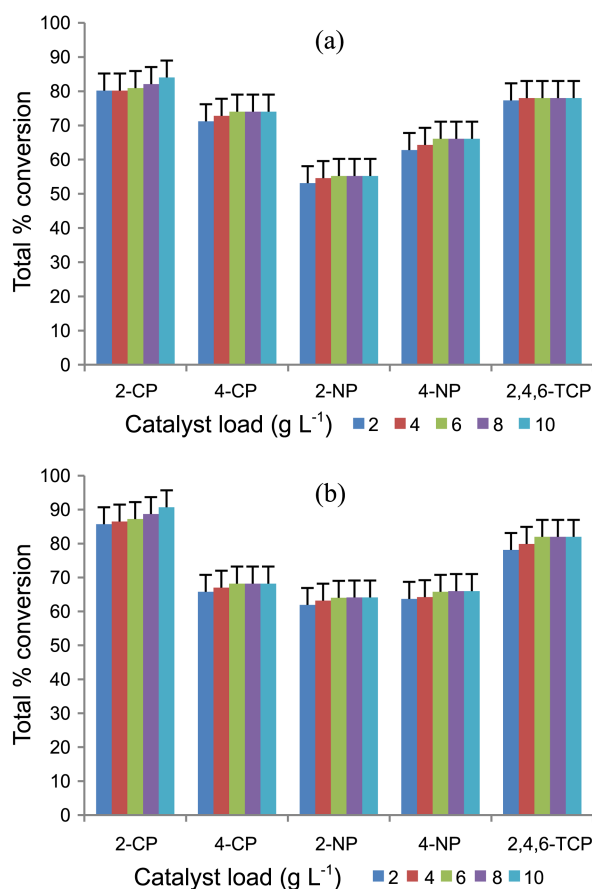
62.8 to 66.1% for 4-NP and 77.3 to 78.0% for 2,4,6-TCP. The conversion did not change significantly when the catalyst loading was increased to 10 g L^{-1}. When the reaction was carried out under the same set of conditions but without H_2O_2 in the reactant feed, at a catalyst load ranging from 2 to 10 g L^{-1}, the conversion was 85.7 to 90.7% for 2-CP, 65.8 to 68.2% for 4-CP, 61.9 to 64.1% for 2-NP, 63.7 to 66.0% for 4-NP and 78.1 to 82.0% for 2,4,6-TCP. The increase in conversion between the catalyst loadings of 2 and 10 g L^{-1} was not large. This might be because all loadings were much higher and the maximum surface area for optimum efficiency of the catalysts might have been reached at the minimum loading of 2 g L^{-1}.

Effect of the Reaction Temperatures. The reaction temperature had a positive effect on 2-CP, 2-NP and 2,4,6-TCP degradation. When the temperature was increased from 303 to 413 K in seven steps (Table 2), the conversion was increased from 75.2 to 82.9% for 2-CP, 49.8 to 58.5% for 2-NP and 74.3 to 81.5% for 2,4,6-TCP in presence of the oxidizing agent, H_2O_2. On the other hand, for the reactants, 4-CP and 4-NP, the conversion increased from 65.4 to 71.2% and 55.8 to 62.8% over temperature range 303 to 353 K, respectively, afterwards the conversion decreased with increasing temperature upto 413 K. Temperature affected the reaction similarly in absence of H_2O_2 in the feed. The

Table 2. Effects of reaction temperature on oxidation of 2-CP, 4-CP, 2-NP, 4-NP and 2,4,6-TCP in presence and in absence of H_2O_2 (catalyst load of 2 g L^{-1}, reactant and H_2O_2 concentration of 10^{-3} M)

Reactants		Total conversion (%) at reaction temperature (K)						
		303	323	333	353	373	393	413
2-CP	With H_2O_2	75.2	76.8	78.8	80.2	80.8	82.9	82.9
4-CP		65.4	67.5	69.8	71.2	69.7	67.2	65.5
2-NP		49.8	50.2	51.8	53.1	55.2	56.1	58.5
4-NP		55.8	59.9	60.9	62.8	60.1	58.8	56.4
2,4,6-TCP		74.3	75.8	77.3	77.3	78.1	81.5	81.5
2-CP	Without H_2O_2	80.2	82.9	84.0	85.7	86.0	88.0	88.0
4-CP		60.9	62.8	64.2	65.8	64.2	62.5	60.2
2-NP		52.8	56.3	58.2	61.9	64.3	72.9	72.9
4-NP		58.9	60.8	62.1	63.7	61.2	59.8	57.6
2,4,6-TCP		72.8	74.2	76.8	78.1	80.2	81.1	82.4

conversion increased from 80.2 to 88.0% (2-CP), 52.8 to 72.9% (2-NP), and 72.8 to 82.4% (2,4,6-TCP) with increasing temperature from 303 to 413 K. The level of conversion was even better at higher temperatures when no H_2O_2 was present. For 4-CP and 4-NP, however, the conversion increased from 60.9 to 65.8% and 58.9 to 63.7%, respectively, over the temperature range 303 to 353 K. The conversion decreased with further increases in reaction temperature to 413 K.

In the present work, the rate of H_2O_2 decomposition was not followed separately, but it was obvious that at higher temperature, the catalyst brought about rapid decomposition of H_2O_2 instead of oxidizing phenol analogues. This also explains why better conversion of the phenol analogues was obtained at higher temperatures when no H_2O_2 was present. 4-CP and 4-NP molecules need to adsorb on the catalyst surface first and then interact with OH radicals to undergo oxidation. Adsorption depends on temperature. With increasing temperature from 353 K, decreasing number of reactant molecules will be held on the catalyst surface by adsorptive forces and they desorb to the liquid phase, reducing the possibility of undergoing oxidation.

GC-MS Analysis. The proposed mechanism is based on ·OH radicals. These radicals have their origin either in metal oxides formed during calcination of the catalysts or in the breaking of hydrogen peroxide (or water) molecules under the influence of the transition metal cations. The formation of ·OH radicals on the surface of the catalysts will follow from interactions between the excited O-atoms of the catalyst and H-atoms cleaved from the substrate (from 2-CP, 4-CP, 2-NP, 4-NP, 2,4,6-TCP or even water because the reactions were carried out in an aqueous solution). The participation of dissolved oxygen in ·OH radical formation is unlikely because this will result in a drastic reduction in oxidation with increasing reaction temperature (consequent to a decrease in dissolved oxygen level).[35]

GC-MS analysis identified the following: pyrocatechol and 2-chloro-1,4-benzoquinone in the product mixture of 2-CP oxidation; chlorocatechol, hydroquinone, 2,5-dioxo-3-

hexenedioic acid, maleic acid, oxalic acid and acrylic acid in 4-CP oxidation; 2-nitrohydroquinone and 2-nitro-1,4-benzo-quinone in the product mixture from 2-NP oxidation; 4-nitrocatechol, 4-nitropyrogallol, 1,2,4-trihydroxybenzene, hydroquinone, acrylic acid, malonic acid and oxalic acid in the product mixture of 4-NP; and 2,6-dichloro-1,4-benzo-quinone, maleic acid, fumaric acid, oxalic acid, glyoxylic acid in the reaction products of 2,4,6-TCP.

Conversion Measurement of the Phenol Analogues by the Total Organic Carbon (TOC). All the reaction conditions (catalyst load 2 g L^{-1}, concentration of 2-CP, 4-CP, 2-NP, 4-NP, 2,4,6-TCP: 10^{-3} mole L^{-1}, phenol:H_2O_2 ratio 1:1, temperature 353 K, reaction time 300 min, pressure atmospheric) were kept identical for TOC monitoring. The TOC decreased significantly with oxidation. Table 3 lists the values measured before and after oxidation of the phenol analogues. For 2-CP, the maximum decrease (80.0%) in TOC was observed for the catalyst **Fe/SBA-15**, after 300 minutes. 4-CP conversion showed a 70.0% decrease in TOC. For 2-NP and 4-NP oxidation, the decrease in TOC with **Fe/SBA-15** was 52.1 and 60.0%, respectively. With respect to 2,4,6-TCP oxidation, the decrease in TOC was 75.0%.

In a similar study, Li *et al.* (2007)[36] reported almost complete mineralization of 2-CP (TOC removal 88%) over a Ru/ZrO$_2$ catalyst at a relatively mild temperature of 413 K with a catalyst load of 3.3 g L^{-1} (other conditions: pressure 5 MPa, rotation speed 1300 rpm and 2-CP concentration 2 g L^{-1}, time 24 hours). Qin *et al.* (2001)[37] obtained a 68.3% TOC reduction by carrying out 4-CP oxidation at 453 K at a pressure of 2.6 MPa using a 1% Pt/activated carbon catalyst for 300 min. Abecassis-Wolfovich *et al.* (2007)[38] observed almost complete mineralization (> 95% total organic carbon elimination) of 2,4,6-trichlorophenol by catalytic wet oxidation under mild operating conditions (393 K, pO$_2$ 10 bar, TCP 100 mg L^{-1}, LHSV = 20 h^{-1}) using a nano-casted Mn–Ce-oxide catalyst. Considering the relatively mild reaction conditions of a shorter reaction time (5 h), lower reaction temperature (353 K) and normal atmospheric pressure (~0.1 MPa), the present work achieved a similar TOC reduction and elimination of persistent phenols. Suarez-Ojeda *et al.* (2005)[39] observed very little wet air oxidation of 4-NP over an activated carbon catalyst from the TOC measurement as the TOC decreased by ≤ 5%. Compared to these results, the present work achieved a much better result, indicating the

Table 3. TOC reduction in oxidation of phenol analogues at 353 K

Phenol analogues	Catalyst	TOC of the reaction mixture (mg L^{-1})		TOC Reduction (%)
		Initial	Final (300 min)	
2-CP	Fe/SBA-15	139.2	27.8	80.0
4-CP		54.8	16.4	70.0
2-NP		65.8	31.5	52.1
4-NP		167.2	25.1	60.0
2,4,6-TCP		316.2	79.0	75.0

Table 4. Recycling study of catalytic oxidation of phenol analogues with **Fe/SBA-15**

Catalytic run	Total % conversion				
	2-CP	4-CP	2-NP	4-NP	2,4,6-TCP
1	80.2	71.2	53.1	62.8	77.3
2	79.8	70.5	52.4	62.0	77.0
3	79.0	69.9	52.0	61.8	76.9
4	79.0	69.9	52.0	61.5	76.9

catalyst, used in the work, to be much more capable for oxidation than activated carbon. The TOC results in the present work were similar to the result of spectrophotometric % conversion.

Recyclability of the Catalyst Fe/SBA-15. An attempt was made to recycle catalyst **Fe/SBA-15** after catalytic oxidation of the phenol analogues under the optimized reaction conditions. After the first catalytic reaction in the presence of H_2O_2, the catalyst was isolated by filtration and the solid mass was Soxhlet-extracted with ethanol and water. The recovered solid was then dried in a vacuum desiccator overnight and used directly as a catalyst in the next catalytic reaction. Four catalytic runs were carried out successfully with the same catalyst with no observable loss in performance (Table 4).

Conclusions

SBA-15 itself is catalytically inactive, but the introduction of a transition metal (Fe(III)) to SBA-15 can convert the material into an active and effective oxidative catalyst for treating water contaminated with phenol analogues. These results show a catalytic method can be developed for the detoxification of phenol-containing wastewater. **Fe/SBA-15** exhibited various levels of activity towards the oxidation of phenol analogues. The phenol analogues could be oxidized on the catalyst without the necessity of adding an external oxidant (H_2O_2). The degradation products identified were not persistent pollutants. The recyclability of the catalyst was another advantage of the catalytic oxidative degradation process. The leaching experiment showed that iron metal did not create any new water pollution problems.

Supporting Information. Supplementary data associated with this article can be found, in the online version.

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