

Article

Oxidation of 4-chloro-3-methylphenol using zeolite Y-encapsulated iron(III)-, nickel(II)-, and copper(II)-*N*,*N*'-disalicylidene-1,2-phenylenediamine complexes

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ABSTRACT

The degradation of 4-chloro-3-methylphenol (PCMC) using zeolite-encapsulated iron(III), nickel(II), and copper(II) complexes of *N*,*N*'-disalicylidene-1,2-phenylenediamine as catalysts, in a heterogeneous Fenton-like advanced oxidation process, was studied. The physicochemical properties of the catalysts were determined using powder X-ray diffraction, thermogravimetric analysis, Brunauer–Emmett–Teller surface area analysis, Fourier-transform infrared spectroscopy, elemental analysis, and scanning electron microscopy. The effects of four factors, namely initial H₂O₂ concentration, catalyst dosage, temperature, and pH, on the degradation of a model organic pollutant were determined. The results show that at low acidic pH, almost complete removal of PCMC was achieved with the iron(III), nickel(II), and copper(II) catalysts after 120 min under the optimum reaction conditions: catalyst dosage 0.1 g, H₂O₂ concentration 75 mmol/L, initial PCMC concentration 0.35 mmol/L, and 50 °C. The reusability of the prepared catalysts in PCMC degradation was also studied and a possible catalyst deactivation mechanism is proposed. The possible intermediate products, degradation pathway, and kinetics of PCMC oxidation were also studied.

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1. Introduction

The increasing awareness of the need to protect the environment has made environmental legislation more stringent. Industrial wastewater often contains highly toxic compounds such as phenol and its derivatives. The treatment and disposal of industrial wastewater containing toxic phenolic pollutants have become a serious concern worldwide [1]. These derivatives of phenolic compounds adversely affect ecosystems and human health because of their carcinogenic and mutagenic properties [2]. There is increasing concern about refractory organic compounds, which are difficult to remove using conventional wastewater abatement techniques [3,4]. One such pollutant, which is widely used as a preservative in leather processing, metal working, construction materials, medicines, and glues, is 4-chloro-3-methylphenol (*p*-chlorocresol, PCMC) [5]. It poses risks to mammalian and aquatic organisms because of its potential carcinogenic and mutagenic effects.

The toxicity and persistence of phenolic pollutants in the environment cause much concern and they have been listed as hazardous pollutants by the U.S. Environmental Protection Agency and the European Union [6,7]. Many procedures are

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available for treating this type of hazardous pollutant, but attention is now being focused on environmentally friendly and cost-effective removal of these phenolic pollutants from the environment. Advanced oxidation processes (AOPs) are efficient techniques for removing resistant, toxic, and poorly biodegradable pollutants from wastewater [8–10]. AOPs that enable degradation and/or almost total mineralization of recalcitrant organic pollutants via fast, effective, and inexpensive methods are receiving increasing attention [1]. Among these methods, heterogeneous Fenton-like systems, using zeolites as inorganic supporting materials, are useful for wastewater treatment over a wide pH range. Such systems have the advantages of being environmentally friendly and reusable, and the nanopores in the supporting materials give size and shape selectivity for given pollutants [11–14].

The boundary or space constraints imposed by zeolite walls change the structural and electronic behaviors of encapsulated complexes compared with those of their homogeneous counterparts [15,16]. These changes in the properties of transition-metal complexes on encapsulation in zeolites are the driving force for generation of hydroxyl radicals (•OH) from H₂O₂ in Fenton-like reactions. The catalytic performance of a zeolite-based heterogeneous catalyst depends on the amount of transition metal or its complex that resides in the zeolite cages. The method used to encapsulate metal complexes in zeolite nanopore cages therefore significantly affects the amount of active sites present in the cage and the overall catalytic performance. The ship-in-a-bottle method of synthesizing metal complexes encapsulated in zeolite cages is advantageous, because the metal complexes are synthesized in situ by reacting with the metal ion and ligand species in the nanocage voids. The formed metal complex therefore cannot be removed from the nanoporous cages unless the lattice is destroyed [14,17].

Few researchers have reported the design and synthesis of zeolite-encapsulated metal complexes of N,N'-disalicylidene-1,2-phenylenediamine (salophen) for catalytic applications; however, such catalysts have been synthesized using flexible ligand methods [18,19]. The degradation of PCMC by various techniques such as heterogeneous electro-Fenton processes using iron-loaded activated carbon [20], heterogeneous Fenton-like systems using nanoparticulate zero-valent iron [5], oxidation using liquid- and vapor-phase pressurized hot water [7], oxidation in pressurized hot water/supercritical water with potassium persulfate as the oxidant [6], and oxidation with temperature-activated Fenton reagents [21] has been investigated. However, to the best of our knowledge, there have been no reports of the synthesis of zeolite-encapsulated Fe(III)-, Ni(II)-, and Cu(II)-salophen complexes using ship-in-a-bottle (in situ) methods, and their use in the catalytic oxidation of PCMC. The aim of the present work was to synthesize Fe(III)-, Ni(II)-, and Cu(II)-salophen complexes using a ship-in-a-bottle method and to investigate their use in the Fenton-type heterogeneous catalytic degradation of a model pollutant, i.e., PCMC, in a water matrix. In this study, the heterogeneous and corresponding homogeneous Fenton-type processes were compared and their efficiencies were estimated based on PCMC degradation. The catalyst reusability and deactivation

mechanisms, kinetics of PCMC oxidation, and intermediate products were also investigated.

2. Experimental

2.1. Materials

NaY zeolite, standard PCMC, and *o*-phenylenediamine were purchased from Sigma Aldrich, India. Salicylaldehyde was purchased from the Southern India Scientific Corporation. Other chemicals used were AR grade.

2.2. Catalyst preparation

The salophen ligand was synthesized as follows. An ethanolic solution of salicylaldehyde (0.112 g) was added dropwise to an ethanolic solution of *o*-phenylenediamine (0.054 g). The reaction mixture was refluxed in a water bath at 50 °C for 2 h with constant stirring. The solution was cooled under ambient conditions and the obtained yellow solid was washed several times with cold ethanol, and then recrystallized from ethanol. The salophen-metal, i.e., Fe(III), Ni(II), and Cu(II), complexes were prepared by reacting equimolar amounts of salophen in methanol with the appropriate salts, i.e., FeCl₃, NiCl₂, and CuSO₄. The homogeneous solution was stirred for 6 h and kept for crystallization.

The metal-exchanged zeolite was prepared using a modified version of a previously reported method [16,22,23]. The appropriate salt, i.e., FeCl₃, NiCl₂, or CuSO₄ (3 g), was dissolved in warm distilled water (250 mL). In the case of the Fe(III)-exchanged zeolite, the solution pH was adjusted to 3.5–4.0 to avoid precipitation of ferric ions as Fe(OH)₃. Zeolite Y (5 g) was added to the solution with stirring. The reaction mixture was heated under reflux for 24 h and cooled. The solid was filtered and washed thoroughly several times with hot distilled water, until all the unfixed metal ions were removed from the zeolite surface. The washed solids were dried for 15 h at 150 °C in an air oven. The metal exchange process was repeated twice more.

Ligand encapsulation in the zeolite supercages was achieved using a ship-in-a-bottle method. The metal-exchanged zeolite, i.e., FeY, NiY, or CuY (1 g), was mixed with a methanolic solution of salicylaldehyde (2.44 g) and the mixture was refluxed under constant stirring for 12 h in an oil bath; the temperature was maintained at 150-200 °C. The solution was filtered and a methanolic solution of o-phenylenediamine (1.08 g) was added to the solid filtrate; this mixture was refluxed for 12 h. The solution was filtered and the obtained solid was kept in an air oven at 95 ± 3 °C for 8 h. The final products were subjected to Soxhlet extraction with ethanol, dichloromethane, and acetonitrile until the washings were colorless. This extraction was performed to ensure the removal of surface-adsorbed ligands and metal complexes. Finally, the products were back exchanged with 0.01 mol/L NaCl solution for 3 h under stirring to remove any uncomplexed metal ions remaining on the surface or inside the zeolite nanopores. The obtained solid products were washed with hot water to remove chloride ions and dried

at 100 °C for 8-10 h.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns of the neat zeolite and solid catalysts were obtained using a Miniflux 11 Rigaku diffractometer with Cu K_{α} radiation ($\lambda = 0.1548$ nm). Scanning electron microscopy (SEM) images were obtained using a Quanta FEG 200 high-resolution scanning electron microscope. The surface areas and pore volumes of the neat zeolite and catalysts were determined using the Brunauer-Emmett-Teller (BET) and Horvath-Kawazoe (HK) methods, based on nitrogen adsorption (ASAP-2020, Micromeritics). Fourier-transform infrared (FT-IR) spectra of the neat zeolite, metal complexes, and solid catalysts were recorded in the range 400-4000 cm⁻¹ using KBr mulls (Perkin-Elmer FT-IR spectrometer). Thermogravimetric analyses (TGA) of the neat zeolite, metal complexes, and zeolite-encapsulated metal complexes were performed from room temperature to 800 °C at a heating rate of 10 °C/min in a nitrogen atmosphere (Q50 thermal analyzer, TA Instruments). After complete destruction of the zeolite framework using hot concentrated H₂SO₄ and HF, the contents of Na, Al, Fe, and Ni metal ions were determined using inductively coupled plasma atomic emission spectroscopy (Prodigy Xp high-dispersion instrument). The Si content was determined gravimetrically. CHN analysis was performed using a Vario Macro cube elemental CHN analyzer.

2.4. Catalyst testing

The optimum H₂O₂ concentration for PCMC degradation was identified experimentally by keeping the amount of catalyst fixed and varying the H₂O₂ concentration. The effect of the catalyst dosage was also investigated by varying the amount of catalyst at fixed concentrations of H₂O₂. The effect of pH was investigated by performing experiments at pH 3.0, 5.0, 7.0, and 9.0 at room temperature (29 \pm 2 °C). The effect of temperature was investigated by performing experiments at 25, 30, 40, and 50 °C at constant pH (5.3). All the experiments were conducted in 250-mL conical flasks, using 0.35 mmol/L PCMC solution (50 mL) under dynamic conditions on a universal shaker (80 r/min). The percentage degradation was monitored at time intervals ranging from 15 to 120 min using high-performance liquid chromatography (HPLC). Reuse of the Fe(III)-, Ni(II)-, and Cu(II)-salophen catalysts in 10 consecutive cycles of PCMC degradation was studied. After each cycle, the solid catalyst was removed from the reaction mixture by filtration, washed thoroughly with organic solvents, and dried in an oven at 150 °C for 1 h.

All experiments were conducted at room temperature (29 ± 2 °C) in a conical flask (250 mL) placed on a universal shaker (80 r/min). The experiments were initiated by adding 0.35 mmol/L PCMC, a given amount of H₂O₂, and catalyst to the solution. Samples were taken at given time intervals during the reaction and filtered through a 0.22-µm filter paper to remove catalyst particles before the sample was injected into the HPLC column to determine the PCMC concentration. The HPLC sys-

tem (515 Series; Waters) was equipped with a C18, 5- μ m (4.6 mm × 250 mm) reverse-phase column (WAT 054275, Waters) and a photodiode array detector. Aliquots (10 mL) were used for PCMC quantification. The detector wavelength was 200–380 nm and the mobile phase was acetonitrile/water (50/50, *v*/*v*) at a flow rate of 1.0 mL/min.

3. Results and discussion

3.1. Catalyst synthesis and characterization

Formation of the Schiff-based ligand was confirmed using ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopies, FT-IR spectroscopy, and CHN analysis. ¹H NMR (500 MHz, DMSO-*d*₆): δ 6.91–6.93 (m, 2H, aromatic), 7.02–7.05 (d, 2H, aromatic), 7.20–7.28 (m, 2H, aromatic), 7.30–7.35 (m, 2H, aromatic), 7.35–7.40 (d, 4H, aromatic) 8.62 (s, 2H, 2 –N=CH–), 13.03 (s, 2H, 2 –OH). ¹³C NMR (500 MHz, DMSO-*d*₆): δ 163.74, 161.36, 142.57, 133.38, 132.36, 127.71, 119.75, 119.25, 118.99, 117.56. IR: 1629 cm⁻¹ (–CH=N–). CHN analysis (C₂₀H₁₆N₂O₂): Anal. C 76.21, H 5.23, N 8.93; Calcd. C 75.93, H 5.10, N 8.86. These data confirm synthesis of the salophen ligand.

A ship-in-a-bottle method was used to encapsulate Fe(III)-, Ni(II)-, and Cu(II)-salophen complexes into NaY zeolites. The ligand reacts with the pre-exchanged metal ions in the zeolite cavities to give encapsulated metal-salophen complexes. Free ligands and surface-adsorbed metal complexes were removed using Soxhlet extraction with diethyl ether, acetonitrile, and ethanol, to ensure that all the metal complex species resided in zeolite Y cavities. Uncomplexed metal ions present in the zeolite lattice were removed by back exchange of encapsulated complexes with 0.01 mol/L NaCl solution.

The XRD patterns of neat zeolite Y and zeolite-encapsulated metal-salophen complexes were recorded at room temperature at $2\theta = 5^{\circ}-50^{\circ}$; the results are shown in Fig. 1. The XRD patterns of the zeolite-encapsulated metal complexes are similar to that of neat zeolite Y, apart from slight changes in the peak intensities; this indicates that the zeolite framework did not undergo any significant structural changes during encapsulation. The order of the peak intensities for neat zeolite is $I_{331} > I_{220} > I_{311}$, but as Fig. 1 clearly shows, the order of the intensities



Fig. 1. Powder XRD patterns of neat zeolite and catalysts.

changes (i.e., $I_{331} > I_{311} > I_{220}$) on impregnation of NaY with metal-salophen complexes. These changes in the peak intensities show that the metal complexes are distributed over the entire zeolite cage following complex formation. It has been reported that there is an empirically derived relationship among the peak intensities at $2\theta < 20^\circ$, i.e., I_{220} at $2\theta = 10^\circ$, I_{311} at $2\theta = 12^\circ$, and I_{331} at $2\theta = 16^\circ$, and the cation location in Faujasite zeolites [24]. No new peaks were detected from the zeolite-encapsulated complexes because of the low concentration of metal complexes in the zeolite nanopores; similar observations have been previously reported [16,25,26].

The encapsulation of metal complexes of salophen ligands in zeolite cages was achieved using a ship-in-a-bottle synthetic scheme. The ligand species, which are flexible enough to diffuse through the zeolite nanopores, reacted with pre-exchanged metal ions in cages to form encapsulated complexes. The final catalyst was washed by extensive Soxhlet extraction with organic solvents to ensure complete removal of ligand species, surface complexes, and metal ions. The efficiency of the Soxhlet extraction was checked by obtaining SEM images of the metal catalysts before and after Soxhlet extraction; the results are shown in Fig. 2. The SEM images of the samples taken before Soxhlet extraction clearly show aggregates of species on the surface. However, the surface is clean, with well-defined zeolite crystals after Soxhlet extraction. This confirms that Soxhlet extraction effectively removed surface-adsorbed metal complexes and/or metal ions.

The TGA-differential thermal gravimetry (DTG) curves of neat zeolite Y and metal-salophen complexes encapsulated in zeolite cages are shown in Fig. 3. Unlike neat zeolite Y, the metal catalysts show two-stage weight losses; this indicates the



Fig. 2. SEM images before and after Soxhlet extraction. (a) Fe-salophen Y before; (b) Fe-salophen Y after; (c) Ni-salophen Y before; (d) Ni-salophen Y after; (e) Cu-salophen Y before; (f) Cu-salophen Y after.



Fig. 3. TGA-DTG curves of neat zeolite Y and zeolite-encapsulated metal-salophen complexes. (1) Neat zeolite Y; (2) Fe-salophen Y; (3) Ni-salophen Y; (4) Cu-salophen Y.

presence of organic species in the zeolite cages. The first stage weight loss occurs at 35-250 °C; the weight losses for the Fe(III), Ni(II), and Cu(II) catalysts are about 13%, 11%, and 15%, respectively. These weight losses correspond to desorption of physically adsorbed and occluded water molecules from the zeolite. As the temperature increases, the three metal catalysts show different TGA-(DTG) patterns because the concentrations of metal-salophen complexes inside the zeolite nanopores differ. The exothermic loss starts immediately after the first stage in the range 250–650 °C, suggesting slow decomposition of the chelated salophen ligands. The TGA-DTG curves show peaks at 305 and 448 °C, corresponding to weight losses of about 11.4%, for Fe(III), at 356 and 438 °C, corresponding to a weight loss of about 9.5%, for Ni(II), and at 332 and 401 °C, corresponding to a weight loss of about 12.4%, for Cu(II). These weight losses are associated with decomposition of the zeolite-encapsulated salophen-metal complexes. The weight losses associated with the second stage are in good agreement with the C, H, and N contents of the zeolite-encapsulated metal complexes (Table 2).

The N₂ adsorption-desorption isotherms for zeolite Y, and the encapsulated complexes of salophen and Fe(III), Ni(II), and Cu(II), are shown in Fig. 4. The adsorption-desorption isotherms for zeolite Y and the synthesized catalysts show typical type I hysteresis loops, based on the International Union of Pure and Applied Chemistry and BET classifications [30]. This is characteristic of microporous materials and shows that the crystalline structure of the zeolite is not affected by encapsulation. The surface areas and micropore volumes were calculated using the BET and HK methods, respectively; the values are listed in Table 1. They show that the surface areas and pore volumes of all three zeolite-encapsulated metal complexes are lower than those of neat zeolite. The nitrogen sorption isotherms (Fig. 4) show that the zeolite framework structure is not affected by encapsulation, therefore the decreases in the surface areas and pore volumes of the catalysts indicate that the metal complexes formed using the ship-in-a-bottle approach reside in the zeolite supercages rather than on the ex-



Fig. 4. N_2 sorption isotherms for neat zeolite Y and zeolite encapsulated metal Salophen complexes.

 Table 1

 BET surface areas and pore volumes of neat zeolite Y and catalysts.

Sample	BET surface area (m ² /g)	Pore volume (cm ³ /g)
Neat zeolite Y	567	0.3237
Fe-salophen Y	437	0.2788
Ni-salophen Y	447	0.2928
Cu-salophen Y	420	0.2754

ternal surfaces. Similar results were reported for inclusion of metal-dimethylglyoxime and metal-salen complexes in zeolite Y [14]. The decreases in the surface area and pore volume of the catalyst depend on the amount of incorporated metal complex and its molecular size and geometry inside the zeolite host [31]. Encapsulation of salophen complexes of Fe(III), Ni(II), and Cu(II) reduced the pore volume by 23%, 21%, and 26%, respectively, compared with that of neat zeolite Y. These results are consistent with the quantitative data obtained from TGA and CHN analysis.

A preliminary confirmation of the successful formation of metal-salophen complexes in the zeolite nanopores was made by comparing the FT-IR spectra of the zeolite-encapsulated metal-salophen complexes, the ligand, and neat zeolite Y; the spectra are shown in Fig. 5. All the zeolite-encapsulated metal-salophen complexes and neat zeolite Y show intense bands at 1022, 791, and 463 cm⁻¹, attributable to the asymmetric stretching, symmetric stretching, and bending frequencies, respectively, of the Al–O–Si framework [27–29]. This indicates



Fig. 5. FT-IR spectra of neat zeolite and zeolite-encapsulated metal-salophen complexes.

that encapsulation of the metal complex did not significantly change the zeolite framework structure. The strong band at 1629 cm⁻¹ in the ligand is ascribed to v(C=N), and the band at 1293 cm⁻¹ is assigned to ν (phenolic C–O). The FT-IR spectra of the zeolite-encapsulated metal complexes differ from that of salophen. The azomethine, i.e., v(C=N), bands are shifted to lower wavenumbers by 13–16 cm⁻¹, and appear at 1613, 1615, and 1613 cm⁻¹. The v(phenolic C–O) bands also shift to lower wavenumbers and appear at 1276, 1276, and 1275 cm⁻¹ for the Fe(III), Ni(II), and Cu(II) catalysts, respectively. This indicates coordination of the imino nitrogen (-CH=N-) and phenolic oxygen (-OH) to the metal ions. The less intense bands in the region around 500 cm⁻¹ for the encapsulated complexes originate from ν (M–N=C) vibrations. The FT-IR results therefore provide evidence for the encapsulation of metal complexes in the zeolite matrix.

The elemental analysis data (Table 2) show that the silica to Al molar ratios of the zeolite-encapsulated Fe(III)-, Ni(II)-, and Cu(II)-salophen complexes are almost the same as that of the parent zeolite Y (i.e., 2.4). This consistency suggests that encapsulation does not change the zeolite framework and Al leaching does not occur. The data in Table 2 also show the purities and stoichiometries of the encapsulated complexes. Chemical analyses of the encapsulated samples show the presence of organic matter, with a C/N ratio similar to the theoretical value. The metal:carbon ratio is approximately 0.05 for all the catalysts, indicating successful formations of the metal complexes inside zeolite nanopores. The elemental analysis data also show

Table 2

Chemical compositions of neat zeolite Y, neat metal complexes, and metal catalysts.

1	,	F F	,	J				
Sample	Metal (%)	Si (%)	Al (%)	Na (%)	Si/Al	C (%)	N (%)	C/N
Fe-salophen complex	0.27 (0.27)*		_	_	_	5.42 (5.40)*	0.54 (0.54)*	9.97 (10.0)*
Ni-salophen complex	0.27 (0.26)*	_	_	_	_	5.45 (5.36)*	0.54 (0.53)*	9.95 (10.0)*
Cu-salophen complex	0.26 (0.26)*	_	—	—	_	5.33 (5.29)*	0.53 (0.52)*	9.98 (10.0)*
Neat zeolite Y	_	0.79	0.32	0.31	2.46	—	—	—
Fe-salophen Y	0.04	0.74	0.30	0.21	2.44	0.70	0.07	9.95
Ni-salophen Y	0.03	0.75	0.31	0.22	2.43	0.69	0.07	9.85
Cu-salophen Y	0.04	0.75	0.31	0.23	2.42	0.76	0.08	9.50

* Theoretical value

that the amounts of metal ions, carbon, and nitrogen in the catalysts are higher than those reported previously [14]. This indicates that the amounts of the metal complexes incorporated into the pores of the zeolite were higher than those achieved in previous studies.

3.2. PCMC degradation using synthesized catalysts

Zeolites are porous materials and can therefore adsorb organic pollutants from aqueous solutions. In this study, we investigated the contribution of the adsorption properties of zeolites in Fenton-like heterogeneous AOPs for the removal of pollutants from aqueous solutions. First, the adsorption properties of the zeolite-encapsulated metal-salophen complexes were investigated under appropriate experimental conditions without adding H₂O₂. No significant reduction in the pollutant concentration was observed. This suggests that the contribution of the adsorption properties of the zeolite-based catalyst to the removal of pollutants is insignificant.

The efficiencies of zeolite-based heterogeneous Fenton-like AOPs and the corresponding homogeneous Fenton processes were investigated using the same amounts of active metal complexes under similar experimental conditions; the results are shown in Fig. 6. All three heterogeneous metal catalysts have better overall catalytic efficiencies than their homogenous counterparts. This could be because the steric and electrostatic constraints imposed by the walls of the zeolite framework can influence the geometries of the metal complexes, and therefore change the redox properties of the encapsulated metal complexes, making them catalytically more active than the neat metal complexes [15,32,33]. However, the rate of pollutant removal in the heterogeneous phase is lower than that in the homogeneous phase. This can be attributed to the reduced accessibility of H_2O_2 to the catalyst active sites because the complex is residing in zeolite supercages.

3.2.1. Effects of operating parameters on PCMC degradation

Experiments to determine the effect of H_2O_2 concentration on PCMC degradation were performed using various H_2O_2 concentrations (25, 50, 75, and 100 mmol/L), a catalyst dosage of 0.10 g, pH 5.3, and 29 ± 2 °C. The initial PCMC concentration was maintained at 0.35 mmol/L and the experiments lasted 120 min. The results are shown in Fig. 7. The oxidative degradation of PCMC increased from 79.26% to 95.89%, 64.18% to 93.12%, and 75.36% to 96.86% with increasing H_2O_2 concentration from 25 mmol/L to 100 mmol/L for the Fe(III)-, Ni(II)-,



Fig. 6. Catalytic efficiencies of synthesized metal-salophen complexes in oxidation of PCMC in homogeneous (a) and heterogeneous (b) Fenton-like oxidation processes.



Fig. 7. Effects of H₂O₂ concentration on PCMC degradation. (a) Fe(III) catalyst; (b) Ni(II) catalyst; (c) Cu(II) catalyst. Reaction conditions: PCMC 0.35 mmol/L, catalyst dosage 0.1 g, 29 ± 2 °C, pH = 5.3.

and Cu(II)-based catalysts, respectively. This is because the amount of hydroxyl radicals generated in the reaction medium increased with increasing H_2O_2 concentration, leading to fast oxidative degradation of PCMC. However, when the H_2O_2 concentration was increased from 75 to 100 mmol/L, the PCMC degradation remained the same. This was the case for all three catalysts, and could be caused by H_2O_2 scavenging and generation of less-reactive radicals (HO_2), as shown in Eqs. (1) and (2). Similar results have been reported, in which higher H_2O_2 concentrations suppressed the degradation rate and catalyst efficiency [34–36].

$$H_2O_2 + \bullet OH \rightarrow HO_2 \bullet + H_2O \tag{1}$$

$$HO_2 \bullet + \bullet OH \to H_2O + O_2 \tag{2}$$

The effect of the catalyst amount on the oxidative degradation of PCMC was studied; the results are shown in Fig. 8. The PCMC degradation increased from 71.04% to 92.08%, 55.28% to 87.49%, and 72.00% to 90.83% as the amount of catalyst used increased from 0.05 to 0.10 g for the Fe(III)-, Ni(II)-, and Cu(II)-based catalysts, respectively, after 120 min. The increase in the percentage degradation with increasing catalyst dosage is mainly the result of the increasing amount of accessible active sites; this leads to decomposition of more H₂O₂, resulting in increased •OH radical production. However, when the amount of catalyst was increased to 0.125 g, the PCMC degradation increased only marginally. This is because catalyst agglomeration occurs, which reduces the number of surface active sites available for the reaction [5]. The amount of catalyst used in subsequent experiments was therefore 0.1 g.

The effect of solution pH on the degradation of a model pollutant was also investigated by varying the solution pH to 3.0, 5.0, 7.0, and 9.0. The pH was adjusted using either 0.1 mol/L NaOH or 0.05 mol/L H₂SO₄. The results are shown in Table 3. The data show that the pH significantly influences the degradation rate and catalyst efficiency. The PCMC degradation rate increased with decreasing solution pH from 9.0 to 3.0. The decrease in the percentage degradation of PCMC at higher pH could be caused by rapid decomposition of H₂O₂ to molecular oxygen and H₂O, resulting in reduced generation of hydroxyl radicals. H₂O₂ and transition-metal ions are more stable at low pH. Moreover, the oxidation potential of hydroxyl radicals de-

 Table 3

 Effects of pH and temperature on PCMC degradation.

Itom		Percentage of reduction (%)			
Item		Fe(III) catalyst	Ni(II) catalyst	Cu(II) catalyst	
рН	3	96.65	95.99	98.17	
	5	90.56	90.08	93.46	
	7	87.07	75.35	79.54	
	9	74.36	62.34	59.61	
Temperature	25	79.25	66.70	79.24	
(°C)	30	92.10	89.75	92.63	
	40	97.11	93.09	94.40	
	50	98.16	98.82	98.95	

creases with increasing pH: 2.65–2.80 V at pH 3.0 and 1.90 V at pH 7.0 [7]. It can therefore be inferred that the degradation efficiencies of the catalysts are best at pH 3.0.

The effect of temperature on the oxidative degradation of PCMC was investigated by performing experiments at 25, 30, 40, and 50 °C. The results are shown in Table 3. It shows that increasing the temperature increased oxidation of PCMC by the developed catalysts. The degradation efficiency for a reaction time of 120 min increased as the temperature increased from 25 to 50 °C. At higher temperatures, the rate of hydroxyl radical generation increases, resulting in increased degradation efficiency. In addition, a higher temperature provides more energy for the reactant molecules to overcome reaction activation energy barriers [37].

3.2.2. Catalyst recycling and stability

The possibility of reusing the catalysts in subsequent degradation experiments was investigated. The solid catalysts were removed by filtration, thoroughly washed with acetonitrile and ethanol, and kept in an air oven at 150 °C for 1 h. The dried samples were used for the next batch of degradation experiments. Reuse experiments were performed for 10 consecutive cycles; the results are listed in Table 4. The data show that after three consecutive runs, the percentage degradation of PCMC was only slightly lower. The decreases were 4.8%, 5.3%, and 3.7% for the Fe(III)-, Ni(II)-, and Cu(II)-based catalysts, respectively. However, when the catalysts were reused more



Fig. 8. Effects of catalyst concentration on PCMC degradation. (a) Fe(III) catalyst; (b) Ni(II) catalyst; (c) Cu(II) catalyst. Reaction conditions: PCMC 0.35 mmol/l, H₂O₂ 75 mmol/L, 29 ± 2 °C, pH = 5.3.

Table 4 Catalyst reusability.

Number of	Percentage of reduction (%)				
recycle	Fe-salophen Y	Ni-salophen Y	Cu-salophen Y		
Fresh	92.08	87.49	90.83		
1st	91.86	86.46	90.21		
2nd	89.38	85.19	88.65		
3rd	87.65	82.88	87.44		
4th	84.97	81.39	86.19		
5th	82.59	79.71	85.26		
6th	81.75	77.50	84.42		
7th	80.59	76.24	82.71		
8th	78.74	74.11	81.54		
9th	75.40	70.56	80.40		
10th	74.51	67.86	79.03		

than three times, the catalytic efficiency decreased. The decreases in the percentage degradation after 10 cycles were 14%, 25%, and 21% for the Fe(III)-, Ni(II)-, and Cu(II)-based catalysts, respectively. Although reductions in the catalytic activities were observed, the heterogeneous catalytic behaviors of the catalysts were not lost, because the zeolite framework prevents leaching of the metal-salophen complexes. These results indicate that these catalysts can be reused at least three to five times without significant loss of activity. The Fe(III) and Cu(II) catalysts retained 80% of their catalytic activities even after 10 cycles, therefore they have good potential recyclability. Moreover, there is no leaching of the metal complexes with repeated reuse, therefore the Fe(III) and Cu(II) complexes have potential commercial applications.

3.2.3. Mechanism of catalyst deactivation

Catalysts lose some of their catalytic activity with repeated use. This loss of catalytic activity, or deactivation, has chemical and physical causes, and occurs simultaneously with the main reaction. Catalyst deactivation is difficult to understand because of the diversity and complexity of the causes of deactivation. Also, their effects need to be studied under conditions close to those of the reaction process. However, it has been reported that decreases in catalytic activity with recycling have various causes, e.g., leaching of metal-ligand complexes, site blockage, and poisoning by impurities [38,39].

We investigated catalyst deactivation during recycling. Various parameters such as metal content in the filtrate remaining after treatment and the BET surface area of the recovered catalyst were examined. The metal contents in the collected filtrates were around 0.02 and 0.08 mg/L for the Fe(III) and Ni(II) catalysts, respectively. In the case of the Cu(II) catalyst, the metal concentration was well below the limit of detection. The BET surface areas after 10 consecutive cycles decreased from 437 to 425 m²/g, 447 to 434 m²/g, and 420 to 408 m²/g for theFe(III), Ni(II), and Cu(II) catalysts, respectively, compared with those of the fresh catalysts. Metal ion leaching from the catalysts during repeated use was negligible. It was therefore inferred that metal leaching from the catalyst did not cause catalyst deactivation.

The BET surface areas of the catalysts changed with re-

peated reuse. The most probable reason for the observed catalyst deactivation is therefore a reduction in its surface area as a result of masking or pore blockage caused by physical deposition of substances on active sites on the catalyst surface in the zeolite cage. Similar results have been reported for the degradation of orange II over Fe-saponite catalysts [40–42].

3.2.4. Identification of intermediate oxidation products and total organic carbon (TOC) removal

The main intermediate products in the catalytic oxidation of PCMC for each catalyst were identified by HPLC-mass spectrometry analysis of samples at different oxidation reaction times. After oxidation for 30 min, a species with m/z = 124 was detected for all the catalysts; this was ascribed to formation of methylhydroquinone. After 60 min, a species with m/z = 122was observed, from the formation of methyl-p-benzoquinone. The formation of these species can be rationalized by assuming that the PCMC molecule is initially attacked by hydroxyl radicals, giving methylhydroquinone, with loss of a chloride ion, and as the reaction time increases, methyl-p-benzoquinone is formed. Finally, methyl-p-benzoquinone undergoes benzene ring opening, followed by oxidative degradation, leading to the formation of smaller organic acids. The presence of smaller organic acids in solution after oxidation for 120 min was confirmed based on the solution pH and TOC analysis. The pH of the filtrate was less than 4.0 for all the catalysts and the residual TOC values were 19%, 28%, and 21% for the filtrates obtained using the Fe(III), Ni(II), and Cu(II) catalysts, respectively. These values confirm that some smaller organic acids remained in solution after a reaction time of 120 min.

3.2.5. Kinetic studies of PCMC degradation

Kinetic studies of catalytic reactions are important, and they help in identifying the reaction pathways and rate dependences of reaction systems. In this study, a pseudo-first-order model was used to describe the catalytic degradation of PCMC by the developed catalysts. It is assumed that the rate-determining step is generation of hydroxyl radicals and this is directly related to the degradation of organic pollutants. The first-order reaction model can be expressed as

$$\frac{-\mathrm{d}[\mathrm{PCMC}]_0}{\mathrm{d}t} = k_{\mathrm{obs}}[\mathrm{PCMC}]$$
(3)

$$\ln\left(\frac{[PCMC]}{[PCMC]_0}\right) = -k_{obs}t$$
(4)

where [PCMC] is the pollutant concentration at time t (min), [PCMC]₀ is the initial concentration of the pollutant, i.e., at time t = 0, and k_{obs} is the first-order reaction rate constant. For a first-order reaction model, the plot of $-\ln([PCMC]/[PCMC]_0)$ against t is a linear relationship, and can be used to determine k_{obs} . The pseudo-first-order rate constants k_{obs} and the linear regression coefficients (R^2) for different initial PCMC concentrations are shown in Fig. 9. The graph shows that the reaction proceeds according to pseudo-first-order kinetics and the rate constant (k_{obs}) decreases with increasing initial concentrations of pollutant. This is because as the initial concentration of the pollutant increases, pollutant molecules aggregate on the catalyst surface.



Fig. 9. Pseudo-first-order kinetic plots for degradation of PCMC using Fe(III) (a), Ni(II) (b), and Cu(II) (c) catalysts.

Figure 9 shows that PCMC degradation using the Fe(III), Ni(II), and Cu(II) catalysts can be represented by pseudo-first-order kinetics. This is validated by the linear regression coefficient (R^2) values, which are 0.9752, 0.9817, and 0.9590 for the Fe(III), Ni(II), and Cu(II) catalysts, respectively. The rate constant (k_{obs}) for PCMC oxidation with the Cu(II) catalyst, i.e., 0.0191 min⁻¹, is higher than those for the Fe(III) (0.0183 min⁻¹) and Ni(II) (0.0143 min⁻¹) catalysts. The Cu(II) catalyst therefore degrades PCMC more rapidly. These results show that the heterogeneous Fenton-like process for PCMC degradation follows pseudo-first-order kinetics.

4. Conclusions

Three heterogeneous catalysts, based on Fe(III)-, Ni(II)-, and Cu(II)-salophen complexes, were prepared. A ship-in-a-bottle method was effectively used to encapsulate the metal-salophen complexes in zeolite Y nanopores, to provide higher amounts of active catalytic sites. Powder XRD, SEM, TGA, BET surface area analysis, FT-IR spectroscopy, and elemental analysis confirmed that zeolite-encapsulated Fe(III)-, Ni(II)-, and Cu(II)-salophen complexes were synthesized without affecting the crystallinity of the zeolite cage and stability of the metal complexes. These

synthesized catalysts efficiently oxidized PCMC, with the generation of methylhydroquinone and methyl-*p*-benzoquinone as intermediate oxidation products. The zeolite-encapsulated metal-salophen complexes can be used more than 10 times without any significant loss of catalytic efficiency. PCMC degradation via a heterogeneous Fenton-like AOP follows pseudo-first-order kinetics.

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Iron(III), nickel(II) and copper(II)-*N*,*N*'-disalicylidene-1,2-phenylenediamine complex is successfully encapsulated through ship-in-a-bottle method into zeolite Y supercage. Zeolite encapsulated metal complexes show good catalytic efficiency towards degerdation of 4-chloro-3-methyl phenol.

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