Performance of heterogeneous catalytic wet oxidation for the removal of phenolic compounds: Catalyst characterization and effect of pH, temperature, metal leaching and non-oxidative hydrothermal reaction

Rajendra G. Mohite, Anurag Garg*

Centre for Environmental Science and Engineering, Indian Institute of Technology Bombay, Mumbai 400076, India

ARTICLE INFO

Article history:

Received 22 September 2016

Received in revised form 7 November 2016

Accepted 17 December 2016

Available online 19 December 2016

Keywords:

Copper based supported heterogeneous catalyst

Metal leaching

Phenolic compounds

Wet oxidation

Wastewater treatment

ABSTRACT

The present study investigated the efficiency of catalytic wet oxidation (CWO) for the destruction of three phenolic compounds (phenol, *o*-cresol and 2,5-dimethylphenol) individually as well as in mixture (phenolics concentration = 10 g/L, NaOH concentration = 10 g/L, chemical oxygen demand (COD) = 24000 mg/L, total organic carbon (TOC) = ~7800 mg/L and pH ~13). The oxidative hydrothermal reaction was carried out in a laboratory scale high pressure batch reactor (capacity = 0.7 L) at moderate temperature (120–160 °C) and pressure (oxygen partial pressure = 0.8 MPa) conditions in the presence of a heterogeneous catalyst (i.e., 5% Cu/activated carbon). After 4 h CWO reaction on the mixture of phenolics at a reaction temperature of 160 °C and initial reaction pH of 9.0, TOC and COD were reduced by ~90% and 82%, respectively. The phenolics removal was mainly due to the oxidation reaction and the contribution of other reactions such as adsorption and/or hydrolysis was lower. The copper leaching in the solution was found to be 15–26 ppm. The characterization of recovered catalyst showed increase in carbon content thus confirming the deposition of carbonaceous deposit.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Water pollution from the increasing industrial activities is a major concern worldwide. To alleviate this problem, the local regulatory bodies are imposing stricter limits on effluent discharge from various process industries. Due to high toxicity of the phenols, the Environmental Protection Agency has complied standard of less than 1 part per billion (ppb) of phenol in surface waters [1]. Petroleum refineries, pesticide manufacturing units, paper and pulp industries and chemical manufacturing industries discharge phenol and its derivatives in concentrations sufficiently high enough to have adverse impact on the water resources. Due to their hazardous nature, such pollutants are also harmful to the microorganisms which assist in conventional biological treatment processes [2].

Various advanced oxidation techniques such as ozonation, Fenton and Fenton like processes, microwave assisted Fenton's oxidation, electro-Fenton, can be used to treat wastewaters containing recalcitrant compounds [3–6]. These processes can degrade persistent compounds even at ambient conditions by

means of strong hydroxyl radicals (oxidation potential = 2.8 eV). In ozonation and Fenton's oxidation processes, such radicals are generated using oxidants such as ozone and H₂O₂, respectively. Homogeneous iron catalyst is also used during classical Fenton's oxidation process. In electro-Fenton process, the hydroxyl radicals are produced either in-situ by electricity. However, the majority of these processes are suitable for mild strength wastewater streams. Catalytic wet oxidation (CWO) is a potential alternative for the destruction of toxic and persistent organic compounds present in high strength aqueous solutions. CWO can be performed at low to medium temperature and pressure conditions in the presence of suitable catalyst for converting the wastewater amenable to biological process.

Garg and coworkers have investigated the CWO process for synthetic waste streams containing recalcitrant organic compounds such as phenol and ferulic acid [7–11]. In these studies, several homogeneous (CuSO₄ and FeSO₄) and heterogeneous (such as activated carbon (AC), ceria and alumina supported non-noble metals) catalysts were tested for low concentrations of phenol as well as ferulic acid. Homogeneous catalysts have exhibited the superior activity compared to heterogeneous catalysts. In one of the studies on the catalytic oxidative treatment of synthetic phenolic wastewater (initial phenol concentration = 0.5–10 g/L) with homogeneous copper salts (sulfate and nitrate) at low

* Corresponding author.

E-mail address: a.garg@iitb.ac.in (A. Garg).

temperature and pressure conditions (i.e., 120 °C temperature and 0.5 MPa oxygen pressure), the maximum phenol, chemical oxygen demand (COD) and total organic carbon (TOC) removals of ~90% were achieved within 2 h of reaction [9]. Similar phenol degradation was reported by Garg and Mishra [7] in the presence of copper sulfate after 4 h of reaction at same temperature and 0.5 MPa total air pressure.

Apart from the above studies, several other research groups have also reported catalytic degradation of phenol with activated carbon as catalyst support in the recent past [12–15]. It was observed that the majority of studies report only the degradation of phenol (C_6H_5OH) present in comparatively low concentrations (<1.5 g/L). From the previous studies, it can be considered that copper and activated carbon combination as active metal species and catalyst support, respectively, should be an efficient catalyst for CWO process. However, the stability of catalyst in corrosive and hot environment has been a major challenge. Moreover, improved understanding needs to be developed on various reactions (apart from oxidation) and their contribution in the removal of pollutants. Up to the best of our knowledge, none of the studies have explored heterogeneous CWO for highly alkaline wastewater containing a mixture of phenolic compounds at elevated concentrations such as 10 g/L.

For the present research work, the partial degradation of phenolic compounds (present either singly or in mixture in aqueous solution) by WO/CWO was investigated. The concentration of phenolics was chosen based on those typically found in the spent caustic generated from petroleum refinery. The major constituents of wastewater may contain 0–4 wt% phenolic compounds such as phenol, *o*-cresol, *p*-cresol, 2,5-dimethylphenol (2,5 DMP) and 3,4 DMP [16,17]. The addition of NaOH solution during scrubbing process makes the waste stream highly alkaline ($pH > 12$). Due to high concentration of phenolic compounds, the alkaline wastewater is rendered unsuitable for conventional biological treatment.

Hence, the present research work investigated the degradation pattern of phenolic waste stream by CWO process using AC supported copper oxide catalyst at moderate temperature (120–160 °C) and pressure conditions (oxygen pressure = 0.8 MPa) with 3 g/L of catalyst concentration (for catalytic runs). The above conditions were selected based on our previous findings from CWO

of phenol [7–9]. The purpose of choosing the moderate conditions was to reduce the severity of oxidation conditions which may reduce capital and operating cost of the overall treatment. Three phenolics, namely, phenol, *o*-cresol and 2,5 DMP-, representing different categories of phenolic compounds in actual petroleum refinery spent caustic, were selected for the preparation of synthetic wastewater. The catalyst was synthesized and characterized to determine its properties. The catalyst stability was assessed by measuring dissolved copper concentration in wastewater during and after CWO treatment. The contribution of adsorption process for the removal of contaminants from wastewater was also determined.

2. Material and methods

2.1. Chemicals

The individual as well as combined synthetic wastewater samples were prepared by dissolving pre-determined concentrations analytical grade (AR) phenol (supplied by Merck Specialties Private Limited, Mumbai), *o*-cresol (procured from Spectrachem Pvt. Ltd., Mumbai) and 2,5 DMP (Sigma Aldrich Ltd, Mumbai) in water.

Four types of synthetic wastewater (phenolics concentration = 10 g/L) were prepared with: (i) phenol; WW1, (ii) *o*-cresol; WW2, (iii) 2,5 DMP; WW3, and (iv) a mixture of phenol, *o*-cresol and 2,5 DMP in equal proportion (by weight); WW4. pH of the wastewater samples was raised to ~12.8 by adding 10 g/L of NaOH (Merck Specialties Private Limited, Mumbai) solution which represent the pH of spent caustic. In experimental run, the initial pH of 12.8 was used unless stated. Oxygen (99.9% pure) was used as oxidant for the wet oxidation (WO)/CWO process and supplied in cylinder by Alchemie Gases & Chemicals Pvt. Ltd., Mumbai, India.

The AC supported copper oxide catalyst was synthesized using the powdered AC (peat derived) and hydrated copper nitrate salt (supplied by Merck Specialties Private Limited, Mumbai).

2.2. Catalyst preparation and characterization techniques

AC supported copper catalyst (5% Cu/AC) was prepared by impregnation method as described by Abdullah, Yuan and Yaziz

Fig. 1. SEM images (a) untreated AC (b) fresh Cu/AC (c) used catalyst.

[18]. The predetermined amount of AC was washed with deionized water before keeping it in 1 M HCl for 24 h at room temperature. The solution was then refluxed with 8 M HNO₃ solution for 4 h at 65 °C temperature and washed with deionized water. The resulting material is termed as 'treated activated carbon' in the present study. The stoichiometric amount of copper nitrate (corresponding to 5% copper) was dissolved with washed AC in 100 mL deionized water to prepare Cu/AC mixture. The solution was gently stirred by means of magnetic stirrer while heating at 60 °C temperature on a hot plate equipped until a thick paste was produced. This paste was oven-dried at 100 °C temperature for 24 h to strike off the surface moisture from the dried material which was subsequently calcined in the covered porcelain crucible at 500 °C temperature for 4 h.

Sauter mean diameter is defined as diameter of a sphere with same volume to surface ratio as that of the catalyst particles [19]. It represents an average of particle size. Sauter mean diameter (d_s) of the synthesized catalyst was determined by sieve analysis. For this purpose, British standard sieves (BSS 500–BSS 52) with a corresponding sieve opening from 25 to 300 μm were used. To obtain the particle size distribution, 5 g of the catalyst was added on the top sieve assembly which was then shaken for sufficient duration. The fraction retained at each sieve was measured to calculate d_s by the following relation [19]:

$$d_s = \frac{1}{\sum \left(\frac{x_i}{d_i} \right)} \quad (1)$$

where, x_i and d_i are the fractional mass of the catalyst retained on screen and screen size (μm), respectively.

The catalyst was also characterized by scanning electron microscope (SEM) using a Jeol JSM-7600F, Japan. Brunauer–Emmett–Teller (BET) surface area of the catalyst was determined at –195.6 °C temperature using N₂ adsorption on a Micromeritics machine (model: ASAP-2000, USA). The nitrogen adsorption isotherm was produced at relative pressure of 0.06–0.2. The equivalent BET particle diameter (d_{BET} , in nm) was calculated according to the following equation assuming a mono-disperse particle distribution and spherical particle shape [20]:

$$d_{\text{BET}} = \frac{6000}{\rho \times S_{\text{BET}}} \quad (2)$$

where ρ (g/cm³) and S_{BET} (m²/g) are density and specific surface area, respectively, of the catalyst.

Fig. 2. XRD pattern of Cu/AC catalyst, activated carbon and used catalyst.

Fig. 3. FTIR spectra of untreated AC, catalyst and used catalyst (5% Cu/AC).

The heterogeneous catalyst was also subjected to X-Ray diffraction (XRD) analysis for phase identification. X-ray source was Cu-K α and the sample was scanned through an angle ranging from 20 to 90°. The various peaks in the XRD spectra were identified using Joint Committee on Powder Diffraction Standard (JCPDS) data files. The average crystallite size was calculated using modified Scherrer equation [21]:

$$\ln \beta = \frac{K\lambda}{d_{\text{XRD}}} + \ln \frac{1}{\cos \theta} \quad (3)$$

where λ , θ and β are the X-ray wavelength, Bragg diffraction angle and the full width at half-maximum (FWHM) of the diffraction peak, respectively. K is dimensionless shape factor and was taken as 0.90.

Fourier transform infrared (FTIR) spectroscopy (3000 Hyperion Microscope with Vertex 80 FTIR System, Bruker, Germany) was performed on AC, and fresh as well as used catalyst. The fresh and recovered catalysts were subjected to X-ray photoelectron spectroscopy (XPS) which was performed on ULVAC-PHI 5000 Versaprobe-II, USA. Binding energies were calibrated relative to the C 1s peak of carbon samples at 284.6 eV. Peaks were fitted using the Gaussian function. The elemental composition (i.e., CHNSO) of the untreated AC and catalyst was determined using CHNSO analyzer (Thermo Finnigan FLASH EA 1112, USA). Total copper concentration in the treated wastewater was analyzed using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Spectro Arcos, Germany).

2.3. Wet oxidation/catalytic wet oxidation experimentation

The oxidation of phenolic compounds was carried out in a 0.7 L stainless-steel high pressure reactor (purchased from Amar Equipments Pvt. Ltd., Mumbai). The oxidation runs were performed in the temperature range of 120–160 °C, and at initial oxygen pressure of 0.8 MPa. During the catalytic runs, the catalyst loading of 3 g/L was used. The reactor assembly consists of double six pitched-bladed impeller, electrical heating device with proportional integral controller (PID), gas introduction port, liquid sampling port and pressure relief valve. The reactor was charged with 0.3 L of the synthetic phenolic wastewater and catalyst (for catalytic runs). Subsequently, temperature of the reactor was increased to the set level. At this moment, a sample was withdrawn

Fig. 4. XPS results of Cu 2p_{3/2} spectral region for fresh (a) and recovered catalyst (b) and C 1s, spectral region of fresh catalyst (c) and recovered catalyst (d) (the numbers 1, 2, 3, 8 on various curves represent the peak of a particular ion or function group as presented in Table 1).

just before injecting oxygen into the reactor. The reactor content was agitated at a constant stirrer speed of 1000 rpm. Periodically, the samples were withdrawn during the reaction for determining the change in TOC, COD and pH. The residual phenol concentration was also measured after treatment of WW1. The wastewater samples were subjected to copper leaching tests for determining catalyst stability in hot aqueous medium. For copper determination, the treated wastewater samples were filtered through 0.2 μm filter to remove catalyst particles and other suspended impurities. All the experiments were carried in duplicate.

2.4. Analytical methods

COD was measured by standard closed reflux method using Hach COD digester purchased from USA [22]. Biochemical oxygen demand (BOD₅) was measured using standard membrane electrode method while phenol concentration was measured using photometric method [22]. TOC of the wastewater samples was measured using a Shimadzu TOC analyzer (TOC-VCSH, Japan).

Table 1
XPS deconvolution of C 1s and Cu 2p_{3/2} spectral regions of fresh and recovered catalyst ($T = 160^\circ\text{C}$, $P_{\text{O}_2} = 1.2\text{ MPa}$, $\text{pH} = 9.0$).

No	Peak position (eV)	Assessment	Percentage contribution	
			Fresh catalyst	Recovered catalyst
1	933.8	Cu ²⁺	88	–
2	932.8	Cu ¹⁺	12	–
3	284.4	C aromatic	70	39
4	285.1	C aliphatic	9	23
5	286	C–OH, C–O–C	9	24
6	287.1	C=O	5	6
7	288.5	COOH, COOC	4	7
8	290	PI–PI*	3	1

Copper concentration in the treated wastewater samples was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (SPECTRO Analytical Instruments, Germany).

The reaction by-products present in wastewater after CWO reaction were identified qualitatively by using high performance liquid chromatograph (HPLC) (Pump: Model PU-2089i, Intelligent HPLC Pump, Jasco, Intelligent UV/VIS Multi wavelength Detector, JASCO, set at 220 nm). Samples were filtered through 0.2 μm and diluted to as at various dilution to detect peaks. Acids were analyzed using SynergiTM Hydro-RP column, while phenols were determined using KinetexTM provided by Phenomenex Inc., India.

3. Results and discussion

3.1. Catalyst characterization

SEM images for untreated AC and 5 wt% Cu/AC are presented in Fig. 1. No definite particle size and shape could be observed in images obtained for both the materials. Copper deposition on the carbon surface seems non-uniform as visualized from the tiny spots at few locations at Cu/AC catalyst surface.

Specific surface area is one of the important properties of activated carbon. N₂ adsorption/desorption isotherms for Cu/AC and untreated AC catalysts are shown in Supporting information (Fig. S1). According to International Union of Pure and Applied Chemistry (IUPAC) classification code, the isotherm and observed hysteresis loop can be classified as type I and H4 respectively [23]. This type of hysteresis is generally associated with narrow slit-like pores. Higher N₂ adsorption was observed on Cu/AC catalyst possibly due to the improved pore size distribution resulted from calcination of the catalyst. BET test results show the average pore

Table 2
Properties of AC and Cu/AC catalyst.

Parameter	AC	5% Cu/AC
Sieve analysis		
Sauter mean diameter (μm)	57	65
BET analysis		
A_{BET} (m^2/g)	874.81	924.66
Pore volume (cm^3/g)	0.183	0.220
Pore diameter (nm)	4.57	3.98
d_{BET} (nm)	–	3.2
XRD analysis		
CuO peak position (2θ)	–	35.6°, 38.7°, 48.8° and 61.6°
C peak position (2θ)	26.6° and 81.4°	26.6° and 81.4°
d_{XRD} (nm)	–	18
FTIR		
Alcohol, carboxylic acids, esters absorption (cm^{-1})	1556, 1385, 1117	1701, 1555, 1157
Elemental analysis (% dry weight basis)		
C	72.1	66.8
H	0.9	1.3
N	0	1.0
O	14.1	18.6

diameter in both untreated and AC supported catalysts in mesopore range (i.e., 2–50 nm). The plot of the cumulative pore volume against pore diameter confirms the presence of the majority of mesopores in both the materials (Fig. S1). BET equivalent particle diameter (d_{BET}) for Cu/AC catalyst was 3.2 nm. High surface area of a mesoporous material can provide large number of adsorption active sites for the reactant molecules.

In XRD spectra of AC and Cu/AC catalysts (Fig. 2), two peaks of AC appeared at 2θ position of 26.6° and 81.4° (JCPDS # 00-026-1076-6). The broad peak at lower 2θ position indicates the amorphous structure of AC. In the diffraction pattern of Cu/AC catalyst, the peaks for CuO could be detected at 35.6°, 38.7°, 48.8° and 61.6° (JCPDS # 00-041-0254). The locations of CuO peaks were also confirmed by comparing their XRD spectra reported in previous studies [18,24–27]. The average crystallite size of Cu/AC catalyst particle was 18 nm while the sauter mean diameter of AC and Cu/AC catalyst particles were 57 and 65 μm , respectively.

In FTIR spectra of the two materials (i.e., untreated AC and Cu/AC), the presence of similar functional groups could be observed (Fig. 3). A stronger broad band observed at 1150 cm^{-1} was attributed to either Si–O–C or Si–O–Si group on AC [28]. The broad band at approximately 1500 cm^{-1} was expected due to the overlapping of C–O–C stretching, C–O stretching and O–H bending modes of alcoholic, phenolic and carboxylic groups [29]. The adsorption behavior of a catalyst is significantly influenced by surface functional groups and porosity. For example, the hydration of oxygen containing functional groups may produce water complexes blocking pore entrance which ultimately lead to the reduction in adsorption of the reactant molecules [30] while the oxygenated groups help in generation of active hydroxyl radicals for oxidation reaction.

XPS spectrum of fresh Cu/AC catalyst was recorded for $\text{Cu}2p_{3/2}$ and $\text{C}1s$ binding energies (Fig. 4 and Table 1). From Fig. 4a, the peaks of Cu_2O and CuO could be observed at the binding energies of

932.8 and 933.8 eV, respectively, which is in agreement with the published literature [31–33]. Copper was mainly present in +2 oxidation state ($\sim 88\%$). The peaks centered at lower binding energies (ranging from 284.4 to 287 eV) indicated the presence of aliphatic as well as aromatic organic compounds (Table 1) whereas the peak centered at 290.0 eV corresponds to $\Pi \rightarrow \Pi^*$ transitions [34,35].

From elemental (CHN) analysis, it was found that the carbon content in Cu/AC catalyst was lower than that found in untreated AC (Table 2) whereas the use of HNO_3 and copper nitrate during the catalyst preparation could be a reason for the presence of nitrogen in the catalyst. The physical as well as elemental characteristics of the catalyst are summarized in Table 2.

3.2. Wastewater characteristics

The characteristics of four types of synthetic wastewater samples (phenolics concentration = 10 g/L) are presented in Table 3. COD and TOC of the wastewater samples were varied from 24000–26000 mg/L and 7600–7900 mg/L, respectively. The biodegradability ratio (in terms of BOD_5/COD) of the wastewater samples was above 0.4 but still the aerobic biological method would not be feasible due to very high organics concentration. By the addition of NaOH, pH of the wastewater samples was increased to ~ 13 .

3.3. Performance of non-catalytic and catalytic wet oxidation of different synthetic wastewater samples

3.3.1. Treatment of phenol, o-cresol and 2,5-dimethylphenol containing individual samples

In the initial runs, the effectiveness of 5% Cu/AC catalyst (catalyst concentration = 3 g/L) was compared for the oxidative degradation of WW1 (the wastewater containing phenol only) with non-catalytic WO process (Fig. 5). The experiments were

Table 3
Synthetic wastewater compositions and characteristics.

Wastewater type	Constituent(s)	Concentration (g/L)	pH	COD (mg/L)	BOD_5 (mg/L)	TOC (mg/L)
WW1	Phenol	10	12.8 ± 0.14	24000 ± 1040	14800 ± 234	7600 ± 145
WW2	o-Cresol	10	12.8 ± 0.21	25000 ± 995	11400 ± 345	7800 ± 231
WW3	2,5-DMP	10	12.8 ± 0.15	26000 ± 896	12200 ± 123	7900 ± 153
WW4	Phenol + o-Cresol + 2,5-DMP	10 (1:1:1 by wt.)	12.8 ± 0.12	25000 ± 1103	13500 ± 543	7800 ± 196

Fig. 5. Non-catalytic and catalytic WO of WW1 at different temperatures: (a), (c) and (e) non-catalytic WO and (b), (d) and (f) catalytic WO, (g) pH variation during WO and CWO; (oxygen partial pressure = 0.8 MPa, Reaction pH = ~ 13).

performed at 120–150 °C temperatures and total reaction pressure of 1.0–1.3 MPa (oxygen pressure = 0.8 MPa) for a duration of 4 h.

During the heating period, phenol decomposition was observed to be in the range of 5–15% for non-catalytic WO and CWO reactions.

Fig. 6. Non-catalytic and catalytic WO of WW2 and WW3 at 130 °C temperature (oxygen partial pressure = 0.8 MPa, catalyst concentration = 3 g/L, pH = ~13) (a) TOC, and (b) COD reduction.

The presence of catalyst caused minor increase in phenol decomposition at the elevated temperatures. During WO and CWO, the maximum phenol reduction was 88% and 94%, respectively at 150 °C temperature (Fig. 5a&b). In contrast, TOC and COD removals during non-catalytic WO were only 50% and 56%, respectively at 150 °C temperature (Fig. 5 c&e) whereas catalytic oxidation resulted in corresponding removals of 60% and 72%, respectively, even at lower temperature (120 °C) (Fig. 5d&f).

COD or TOC removal from the wastewater can be attributed to the conversion of phenol into low molecular weight compounds (possibly with some degree of mineralization) and adsorption on the catalyst. Phenol oxidation may result several intermediates and by-products including hydroquinone, *p*-benzoquinone, catechol, maleic acid, fumaric acid, formic acid and acetic acid, depending upon the reaction conditions [36,37]. The reduction in wastewater pH during the reaction indicates formation of acidic compounds as final pH of the treated wastewater was reduced to 8.3–9.5 from an initial value of ~13 (Fig. 5g). The pH drop was occurred within first 60 min and it was higher for the reactions performed at higher temperature.

The initial reaction pH (~13) was higher than the pK_a value for phenol (~10) which will result in the dissociation of phenol into phenolate and hydrogen ion. The formation of phenolate ions may

lead to better phenol oxidation since phenolate ion reacts at 10^7 times faster rate with oxygen than phenol [38]. Though, the presence of excessive OH^- ions will have detrimental impact on the phenol removal due to its scavenging tendency for hydroxyl radicals ($OH^\bullet$) [39]. However, the production of carboxylic acids ($pK_a = 1-4$) at later stage may release more hydronium ions into the solution which would be neutralized by excess OH^- (imparted from NaOH) in the solution.

The efficiency of WO process for the removal of *o*-cresol and 2,5-DMP from the individual wastewater samples was investigated at 130 °C temperature and a total pressure of 1.05 MPa (oxygen pressure = 0.8 MPa). For *o*-cresol, it was found that the addition of catalyst caused a TOC reduction of 50% compared to ~37% obtained in the absence of the catalyst (Fig. 6). During the catalytic oxidation of wastewater containing 2,5-DMP, the TOC reduction was increased progressively till 60 min beyond which no significant degradation could be found. During non-catalytic WO, the reductions in TOC and COD were 30% and 58%, respectively whereas the addition of catalyst enhanced the removals to 52% and 66%, respectively (Fig. 6). It has been reported that two methyl groups in 2,5-DMP molecule would make the compound relatively unstable due to which it could have been broken easily into other smaller molecules. The colorless synthetic wastewater turned into dark brown color during the reaction possibly due to the formation of intermediate compounds such as benzoquinone.

From the above experiments with individual WW1, WW2 and WW3 samples, it can be suggested that COD removal was ranged from 3.83 to 6.83 g per g of AC supported catalyst. The above COD reduction per unit weight of catalyst concentration was much higher than 0.086 g of COD per g of catalyst obtained after CWO of ethylene spent caustic which was carried out at high temperature (280 °C temperature for 1 h duration) in the presence of 70/30 mol % Mn/Ce catalyst [40].

3.3.2. Non-catalytic and catalytic wet oxidation of phenolic mixture

The oxidative treatment of phenolic mixture (i.e., WW4) was performed at temperatures ranging from 130 to 160 °C and 0.8 MPa oxygen pressure. In addition to 5% Cu/AC catalyst, AC (untreated and treated) and homogeneous copper were used as the catalysts. To observe the effect of pH, the runs were carried out at original wastewater pH (~13) and at an adjusted pH of 9.0. The catalytic oxidation (with 5% Cu/AC) at an initial pH of 9.0 showed ~70% reduction in both TOC and COD at 130 °C which was further increased to ~85% at 160 °C temperature (Fig. 7). To examine the effect of AC alone on CWO reaction, the efficacy of treated AC was also tested as catalyst at 160 °C temperature. The reaction was carried out at original pH of the wastewater (i.e., ~13). After 3 h treatment in the presence of treated AC catalyst, the reduction in COD of WW4 was 51% compared to 55% obtained in the presence of 5% Cu/AC catalyst (Fig. 7).

Moreover, two runs were also performed at reaction temperatures of 130 °C and 160 °C with homogeneous copper (in the form of copper nitrate) to determine its effect on CWO reaction without adjusting initial pH. The concentration of copper in these runs was taken 15 ppm and 26 ppm which was detected in the solution during hetero-catalytic oxidation at 130 °C and 160 °C temperatures, respectively. Upon comparison with Cu/AC mediated CWO, no significant difference in COD and TOC removals was observed (Fig. 7).

The effect of temperature on the WO and CWO of WW4 is presented in Fig. 8. The maximum TOC and COD removal of 60% was obtained at a temperature of 160 °C (initial reaction pH = 13 and catalyst concentration = 3 g/L). In comparison, ~48% reduction in TOC and COD was found after non-catalytic WO.

The variation in pH with time at different conditions is presented in Fig. S2.

Fig. 7. TOC and COD reduction patterns during non-catalytic and CWO of WW4 at 130 °C (a&b) and 160 °C (c&d) ($P_{O_2} = 0.8$ MPa).

An effort was also made to identify the reaction by-products present in treated wastewater for the CWO run performed on WW4 (i.e., mixture of phenolic compounds) at 160 °C temperature and oxygen pressures of 0.8 MPa. Initial reaction pH and catalyst concentration were 9.0 and 3.0 g/L, respectively. At the end of reaction (i.e., after 240 min), mainly carboxylic acids such as oxalic, malonic, maleic, acetic and fumaric acid could be identified qualitatively. No peak for phenols could be observed after the run.

3.3.3. Change in average oxidation state of carbon during non-catalytic and catalytic wet oxidation

Average oxidation state of carbon (AOSC) in a wastewater provides an idea about the nature of compounds. AOSC value can vary from -4 (for CH_4) to $+4$ (CO_2) and it is determined using the following expression [41]:

$$\langle H1 \rangle AOSC = 4 \left[1 - 0.375 \left(\frac{COD}{TOC} \right) \right] \quad (5)$$

The theoretical AOSC of phenol, *o*-cresol and 2,5-DMP are -0.67 , -0.857 and -1 , respectively. For non-catalytic WO of WW1, AOSC

ranged from -1.6 to -0.7 ($T = 120$ °C – 150 °C, $P_{O_2} = 0.8$ MPa and $pH \approx 13$) and found to increase with transformation of phenol into other probable intermediate compounds such as catechol, hydroquinone and low molecular weight acids. For other CWO processes, the AOSC was found to increase in general (ranging from -2.0 to 0.4). Higher AOSC values indicate the better degradation of the phenolic compounds. The results only suggest that some mineralization of the compounds has essentially happened which caused significant removals in TOC and COD. The results are presented in Table S1 (Supplementary information).

3.3.4. Reaction kinetics of catalytic and non-catalytic wet oxidation

In the present study, the reaction rate of WO/CWO was predicted using pseudo first order kinetic model (Equation (6)):

$$-\ln \frac{[TOC]}{[TOC_0]} = kt \quad (6)$$

where, k , TOC_0 and TOC are reaction rate constant, initial TOC and TOC after time t , respectively. The rate constants for various runs were obtained by plotting $\ln(TOC_0/TOC)$ against time (Table 4). The

Fig. 8. Catalytic and non-catalytic WO of WW4: (a) TOC, and (b) COD reduction ($P_{O_2} = 0.8$ MPa, catalyst concentration = 3 g/L, pH = ~13).

corresponding coefficients of regression (R^2) are also given in the table. The rate constant for various runs were calculated for the duration of 240 min except for the reaction at 160 °C temperature with 5% Cu/AC catalyst (at initial pH=9.0) in which all TOC degradation occurred within 60 min (Fig. 7c). The regression coefficients obtained were high enough to fit the experimental data properly with rate equation. The reaction rate of catalytic WO for WW3 was higher than WW1 and WW2. The catalytic WO reaction rate constants were higher those obtained for non-catalytic runs. Elevated temperature caused a significant increase

in the reaction rate. The non-catalytic oxidation reaction rate for WW1 was increased from 0.0013 min^{-1} and 0.0030 min^{-1} with rise in temperature from 120 °C to 150 °C while for CWO the reaction rate was found in the range of 0.0022 – 0.0045 min^{-1} . The significant increase in the rate showed the favorable performance of catalyst towards phenolic compounds. At pH of to 9.0, rate constant was increased to almost twice as compared with reaction at higher pH (~13). For AC ($k = 0.0028 \text{ min}^{-1}$) and homogeneous copper ($k = 0.0018 \text{ min}^{-1}$ at 130 °C, and $k = 0.0052 \text{ min}^{-1}$ at 160 °C), the rate was lower compared to the catalyst at respective temperature.

3.3.5. Copper leaching during catalytic wet oxidation

The results for copper leaching from the catalyst during CWO of all the synthetic wastewater samples are illustrated in Fig. 9. The metal leaching was increased at higher reaction temperatures. Since pH of the solution was decreased with time, acidic environment in the reactor might have promoted the copper leaching with time. Moreover, the loosely bound copper would have been removed from the catalyst surface in hot environment. ICP-AES analysis results showed actual copper concentration in the fresh catalyst was 4.6% (by weight) which was slightly lower than the targeted metal concentration of 5%. The maximum copper in the wastewater was ~26 ppm after the reaction which is approximately 19% of the total copper in catalyst.

3.3.6. Characterization of the recovered catalyst after catalytic wet oxidation

After CWO of WW4 at 140 °C temperature, 0.8 MPa oxygen pressure and initial reaction pH of ~13.0, the spent catalyst was recovered and oven-dried at 100 °C for 24 h before subjecting to various analytical techniques. The catalyst particle size was smaller compared to the fresh catalyst and white spots could also be seen at its surface (Fig. 1c). Disintegration of the catalyst particles may be due to attrition in the reactor vessel. In XRD spectrum of the spent catalyst, short peaks of cupric oxide (Cu_2O) could be observed at 2θ angle of 36.5° and 42.4° (Fig. 2). A prominent peak corresponding to Cu_3O_4 could also be detected at 32° angle.

FTIR spectrum of the recovered catalyst (Fig. 3) showed comparatively two narrow prominent peaks at 1200 cm^{-1} and 1600 cm^{-1} . Smaller peaks could be observed on the shoulder of peak at 1600 cm^{-1} . These peak positions indicate the attachment of carboxylic and aromatic groups to the carbon surface. CHNO analysis of the recovered catalyst confirmed the deposition of organic compounds on its surface with C and H in the spent catalyst increased to ~73% and 2.1% from ~67% and 1.3% (in fresh catalyst), respectively.

Table 4
Kinetic rate constants of WO and CWO runs for different wastewater samples.

Wastewater	Temperature (°C)	WO		CWO	
		k (min^{-1})	(R^2)	k (min^{-1})	(R^2)
WW1	120	0.0013	0.97	0.0022	0.98
	130	0.0020	0.98	0.0030	0.90
	140	0.0026	0.93	0.0034	0.90
	150	0.0030	0.97	0.0045	0.80
WW2	130	0.0022	0.95	0.0032	0.94
WW3	130	0.0018	0.84	0.0046	0.71
WW4	130	0.0021	0.92	0.0024	0.90
	160	0.0027	0.95	0.0059	0.83
	130	0.0027	0.93	0.0055	0.94
WW4 (initial pH=9)	160	0.0048	0.97	0.0224	0.98
WW4 with homogeneous copper	130 (15 ppm Cu)	–	–	0.0041	0.94
	160 (26 ppm Cu)	–	–	0.0052	0.81
WW4 with treated AC	160	–	–	0.0033	0.88

Fig. 9. Copper leaching from the catalyst (Reaction pH = ~13, Initial copper concentration in catalyst = 138 mg/L).

The Cu 2p_{3/2} XPS spectra (Fig. 4c) of the spent catalyst showed no distinct peak of copper at the respective binding energy. Copper leaching may be the major reason and at the same time, carbonaceous deposition could have hindered the detection of copper peaks. Moreover, aliphatic carbon was increased possibly due to carbonaceous deposition on the surface of catalyst during reaction (Fig. 4d and Table 1). The BET surface area of the used catalyst was reduced significantly to 98 m²/g which was around 90% lower than that of fresh catalyst (924 m²/g) possibly due to pore blocking by deposited organics.

3.3.7. Catalytic hydrothermal degradation of synthetic wastewater in the absence of oxygen

The four wastewater samples were subjected to catalytic hydrothermal treatment (using 5% Cu/AC as catalyst) in the oxygen starving environment. The results were compared with the adsorption studies performed at ambient temperature (~25 °C). The catalyst concentration was kept as 3 g/l for all runs. The maximum TOC removal of ~37% was obtained from WW3

(containing 2,5-DMP) after the reaction at 130 °C temperature whereas only ~19% TOC removal was achieved from WW4 at the same temperature (Fig. 10). At ambient temperature, the TOC removal from WW3 and WW4 was 8.8% and 6.3%, respectively. Apart from adsorption, hydrolysis and other chemical reactions (such as polymerization, decarboxylation and oxidation) could have contributed to the enhanced TOC removal at elevated temperature. Increase in reaction temperature to 160 °C exhibited slight decrease in TOC removal from WW4. It could possibly be due to lower adsorption of compounds at the higher temperature.

Few experimental runs were also planned for the non-oxidative treatment of WW4 at 160 °C temperature with untreated and treated activated carbon (concentration = 3 g/L) only. The purpose of the runs was to determine the impact of copper on the organics removal during hydrothermal process. It can be seen (Fig. 10) that TOC removal with 5% Cu/AC catalyst was two times higher than with AC (only 8.5% TOC reduction compared to ~16% with the latter). TOC removal with the treated AC was improved to ~21% when the initial reaction pH was adjusted to 9.0. The results clearly demarcate the utility of copper metal as catalyst in the thermal degradation of phenolic mixture.

4. Conclusions

Heterogeneous 5% Cu/AC catalyst showed promising performance under mild to moderate temperatures for the degradation of phenolic compounds present in high concentrations in synthetic wastewater. After catalytic oxidation, around 90% phenol and TOC reductions from the wastewater containing a mixture of phenolic compounds (WW4) were obtained at 150 °C temperature and low oxygen pressure of 0.8 MPa. A copper leaching of 15–26 ppm was observed from the catalyst during CWO process which is around 19% of the initial copper loading. Non-oxidative hydrothermal runs with catalyst and AC exhibited lower TOC reduction thus confirming the occurrence of oxidation for the removal of phenolic compounds. From the study, it can be suggested that slightly alkaline pH of 9 is favorable for organics reduction compared to the runs performed at a pH of ~13 which is normally found in petroleum refinery wastewater. The drop in pH and improvement in AOSC values after the treatment indicates the formation of acidic organic compounds during the reaction. The rate constants for CWO were found almost twice to those obtained for non-catalytic

Fig. 10. TOC removal after reaction in absence of oxygen (Catalyst concentration = 3 g/L).

WO. A carbonaceous deposition was detected by CHNO analysis, XPS and FTIR analyses. SEM of the recovered also showed some accumulation of carbon compounds on the catalyst surface.

In future studies, the quantification of major intermediates and by-products formed during CWO of wastewaters having high concentration of phenolics should be done.

Acknowledgments

The authors are thankful to Council for Scientific and Industrial Research (CSIR), New Delhi for providing the financial support to carry out the presented study. We are also thankful to Sophisticated Analytical Instrumentation Facility (SAIF) and Chemical Engineering Department, IIT Bombay for their timely help in the characterizing the catalyst.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jece.2016.12.024>.

References

- [1] G. Busca, S. Berardinelli, C. Resini, L. Arrighi, Technologies for the removal of phenol from fluid streams: a short review of recent developments, *J. Hazard. Mater.* 160 (2008) 265–288.
- [2] H.F. Stich, The beneficial and hazardous effects of simple phenolic compounds, *Mutat. Res. Genet. Toxicol.* 259 (1991) 307–324.
- [3] N. Wang, T. Zheng, G. Zhang, P. Wang, A review on Fenton-like processes for organic wastewater treatment, *J. Environ. Chem. Eng.* 4 (2016) 762–787.
- [4] R. Carta, F. Desogus, The enhancing effect of low power microwaves on phenol oxidation by the Fenton process, *J. Environ. Chem. Eng.* 1 (2013) 1292–1300.
- [5] A. Babuponnusami, K. Muthukumar, A review on Fenton and improvements to the Fenton process for wastewater treatment, *J. Environ. Chem. Eng.* 2 (2014) 557–572.
- [6] Y. Wang, W. Yang, X. Yin, Y. Liu, The role of Mn-doping for catalytic ozonation of phenol using Mn/ γ - Al_2O_3 nanocatalyst: performance and mechanism, *J. Environ. Chem. Eng.* 4 (2016) 3415–3425.
- [7] A. Garg, A. Mishra, Degradation of organic pollutants by wet air oxidation using nonnoble metal-based catalysts, *J. Hazard. Toxic Radioactive Waste* 17 (2013) 89–96.
- [8] A. Garg, I.M. Mishra, S. Chand, Oxidative phenol degradation using non-noble metal based catalysts, *Clean Soil Air Water* 38 (2010) 27–34.
- [9] K. Lal, A. Garg, Catalytic wet oxidation of phenol under mild operating conditions: development of reaction pathway and sludge characterization, *Clean Technol. Environ. Policy* 17 (2015) 199–210.
- [10] B.R. Yadav, A. Garg, Efficacy of fresh and used supported copper-based catalysts for ferulic acid degradation by wet air oxidation process, *Ind. Eng. Chem. Res.* 51 (2012) 15778–15785.
- [11] B.R. Yadav, A. Garg, Catalytic wet oxidation of ferulic acid (a lignin model compound) in the presence of non-noble metal based catalysts at mild conditions, *Chem. Eng. J.* 252 (2014) 185–193.
- [12] F. Martínez, M.I. Pariente, J.A. Botas, J.A. Melero, A. Rubalcaba, Influence of preoxidizing treatments on the preparation of iron-containing activated carbons for catalytic wet peroxide oxidation of phenol, *J. Chem. Technol. Biotechnol.* 87 (2012) 880–886.
- [13] W.T. Mohamed, S.A. Ghani, S.M. Rasheed, Fe/activated carbon as a catalyst in wet oxidation of phenolic compounds in a trickle bed reactor, *Energy Sources A* 35 (2013) 299–311.
- [14] J.C. Moreno-Pirajan, L. Giraldo, Comparison of the oxidation of phenol with iron and copper supported on activated carbon from coconut shells, *Arabian J. Sci. Eng.* 38 (2013) 49–57.
- [15] E. Saputra, S. Muhammad, H.Q. Sun, S.B. Wang, Activated carbons as green and effective catalysts for generation of reactive radicals in degradation of aqueous phenol, *RSC Adv.* 3 (2013) 21905–21910.
- [16] F.J. Suarez, Pluses and minuses of caustic treating, *Hydrocarbon Process.* 75 (1996).
- [17] A. Olmos, P. Olguin, C. Fajardo, E. Razo, O. Monroy, Physicochemical characterization of spent caustic from the OXIMER process and sour waters from Mexican oil refineries, *Energy Fuels* 18 (2004) 302–304.
- [18] A.H. Abdullah, W.W. Yuan, M.I. Yaziz, Decolourisation of reactive Orange 16 by activated carbon and copper oxide catalysts supported by activated carbon, *J. Phys. Sci.* 21 (2010) 29–40.
- [19] J.F. Richardson, J.H. Harker, J.R. Backhurst, fifth ed., Coulson and Richardson's Chemical Engineering, vol. 2, Butterworth-Heinemann, Woburn, 2002.
- [20] R.M. German, S.J. Park, Handbook of Mathematical Relations in Particulate Materials Processing, John Wiley & Sons, Danvers, 2008.
- [21] A. Monshi, M.R. Foroughi, M.R. Monshi, Modified Scherrer equation to estimate more accurately nano-crystallite size using XRD, *World J. Nano Sci. Eng.* 2 (2012) 154.
- [22] APHA, Standard Methods for the Examination of Water and Wastewater, 21st ed., American Public Health Association, Washington, D.C, 2005.
- [23] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol, T. Siemieniowska, Reporting physisorption data for gas solid systems with special reference to the determination of surface-area and porosity (recommendations 1984), *Pure Appl. Chem.* 57 (1985) 603–619.
- [24] U.R. Pillai, S. Deevi, Room temperature oxidation of carbon monoxide over copper oxide catalyst, *Appl. Catal. B* 64 (2006) 146–151.
- [25] H.-H. Tseng, M.-Y. Wey, Study of SO_2 adsorption and thermal regeneration over activated carbon-supported copper oxide catalysts, *Carbon* 42 (2004) 2269–2278.
- [26] F.L.Y. Lam, X. Hu, A new system design for the preparation of copper/activated carbon catalyst by metal-organic chemical vapor deposition method, *Chem. Eng. Sci.* 58 (2003) 687–695.
- [27] X. Hu, L. Lei, H.P. Chu, P.L. Yue, Copper/activated carbon as catalyst for organic wastewater treatment, *Carbon* 37 (1999) 631–637.
- [28] O. Duggan, S.J. Allen, Study of the physical and chemical characteristics of a range of chemically treated, lignite based carbons, *Water Sci. Technol.* 35 (1997) 21–27.
- [29] M. Jung, K. Ahn, Y. Lee, K. Kim, J. Rhee, J. Tae Park, K. Paeng, Adsorption characteristics of phenol and chlorophenols on granular activated carbons (GAC), *Microchem. J.* 70 (2001) 123–131.
- [30] R.W. Coughlin, F.S. Ezra, Role of surface acidity in the adsorption of organic pollutants on the surface of carbon, *Environ. Sci. Technol.* 2 (1968) 291–297.
- [31] M.C. Biesinger, L.W. Lau, A.R. Gerson, R.S.C. Smart, Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: sc, Ti, V, Cu and Zn, *Appl. Surf. Sci.* 257 (2010) 887–898.
- [32] Y. Iijima, N. Niimura, K. Hiraoka, Prevention of the reduction of CuO during x-ray photoelectron spectroscopy analysis, *Surf. Interface Anal.* 24 (1996) 193–197.
- [33] I.H. Tseng, J.C. Wu, H.-Y. Chou, Effects of sol–gel procedures on the photocatalysis of Cu/TiO₂ in CO₂ photoreduction, *J. Catal.* 221 (2004) 432–440.
- [34] H. Estrade-Szwarcopf, XPS photoemission in carbonaceous materials: a defect peak beside the graphitic asymmetric peak, *Carbon* 42 (2004) 1713–1721.
- [35] J. Zazo, A. Fraile, A. Rey, A. Bahamonde, J. Casas, J. Rodriguez, Optimizing calcination temperature of Fe/activated carbon catalysts for CWPO, *Catal. Today* 143 (2009) 341–346.
- [36] A. Santos, P. Yustos, A. Quintanilla, F. Garcia-Ochoa, Kinetic model of wet oxidation of phenol at basic pH using a copper catalyst, *Chem. Eng. Sci.* 60 (2005) 4866–4878.
- [37] A. Santos, P. Yustos, S. Rodriguez, F. Garcia-Ochoa, Wet oxidation of phenol, cresols and nitrophenols catalyzed by activated carbon in acid and basic media, *Appl. Catal. B* 65 (2006) 269–281.
- [38] F.J. Rivas, S.T. Kolaczowski, F.J. Beltran, D.B. McLurh, Development of a model for the wet air oxidation of phenol based on a free radical mechanism, *Chem. Eng. Sci.* 53 (1998) 2575–2586.
- [39] S.K. Bhargava, J. Tardio, J. Prasad, K. Föger, D.B. Akolekar, S.C. Grocott, Wet oxidation and catalytic wet oxidation, *Ind. Eng. Chem. Res.* 45 (2006) 1221–1258.
- [40] C. Maugans, B. Kumfer, The use of catalyst to enhance the wet oxidation process, *Water Sci. Technol.* 55 (2007) 189–193.
- [41] F. Vogel, J. Harf, A. Hug, P.R. Von Rohr, The mean oxidation number of carbon (MOC)—a useful concept for describing oxidation processes, *Water Res.* 34 (2000) 2689–2702.