



## Research article

## Wet peroxidation of resorcinol catalyzed by copper impregnated granular activated carbon



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## ABSTRACT

The present article reports the treatment of resorcinol using a catalytic wet peroxidation (CWPO) process in the presence of copper impregnated granular activated carbon (Cu/GAC) with a bench-scale batch reactor. The typical physico-chemical properties of synthesized catalyst were characterized with different equipment and methods. 90% resorcinol removal and 81% of TOC removal was achieved at optimum conditions (pH = 6, the stoichiometric ratio of H<sub>2</sub>O<sub>2</sub>/resorcinol = 1.2, catalyst dose = 0.5 g/L, initial concentration of resorcinol = 100 mg/L, temperature = 70 °C and time t = 4 h). Fourier-transform infrared spectroscopy (FTIR) measurements revealed that GAC possesses various conjugated hydrocarbon groups including aromatic hydrocarbons, carboxylic groups, carboxyl and carbonate. Cu/GAC catalyst has a surface smoother than that of pristine GAC. At neutral or natural pH (~6.4) of resorcinol, CWPO of resorcinol is favorable by Cu/GAC catalyst. Catalyst stability study revealed that Cu/GAC sustains its catalytic reactivity to over 76% in the five cycles without any regeneration. The thermogravimetric analysis confirmed that 350 °C temperature found to be optimum for calcination of Cu/GAC without any major losses. The mineralization mechanism was proposed based on intermediates identified during CWPO reaction.

## 1. Introduction

Recently, the advanced oxidation processes (AOPs) are receiving more attention and used for the degradation of organic compounds in water/wastewater. Compared to the other conventional techniques, AOPs can generate highly reactive hydroxyl radicals (·OH) with a redox potential of 2.80 eV at a moderate temperature and pressure that aid in mineralizing the organic molecules non-selectively into carbon dioxide and water. Among various AOPs, catalytic wet peroxidation (CWPO) is a potent alternative for treatment of non-biodegradable organic compounds in wastewater under the atmospheric pressure and mild operating temperature (< 80 °C) in the presence of catalyst and oxidant (Subbaramaiah et al., 2013a; Gosu et al., 2014; Tehrani-Bagha et al., 2016). CWPO, also called as a Fenton-like process, converts organic compounds into harmless organic/inorganic compounds using homogeneous or heterogeneous non-ferrous active species as a catalyst in the presence of hydrogen peroxide at a moderate temperature and atmospheric pressure. While the Fenton process has a restricted pH range (pH 3–4), the CWPO process can also perform well at neutral pH based

on the type of support and active metal used. In addition, sludge generation by CWPO is minimum. Recently, CWPO process was widely applied in various effluent treatment processes such as pharmaceuticals (Gosu et al., 2014; Munoz et al., 2017), dyes and dye intermediates (Zhan et al., 2010; Pinho et al., 2015; Han et al., 2016), nitrogenous aromatic compounds (Subbaramaiah et al., 2013a; b; c; Gosu et al., 2018), refractory organic compounds (Zazo et al., 2006), etc.

Currently, one of the major challenges of CWPO technique is the development of new catalyst with higher efficacy and separation of the catalyst after a reaction. Usually, transition group metals are used as active metal species (i.e. homogeneous catalyst) and are conventionally added in the form of fine particles in order to enhance reaction by providing maximum specific surface area. However, dispersion of active metal species into the reaction mixture leads to an unstable state because the surface tension favors a smaller interfacial area for a given mass. The aforementioned challenges can be overcome through heterogeneous catalyst where the active metal species are dispersed on the porous support, which has the advantages of producing a stable state of active metal and enhancing the catalytic reaction rate by favoring the

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adsorption of organic species on the support (Hu et al., 1999). In addition, using porous media as a catalyst support can be shortened to the reaction time, and therefore, reduce both investment and operating cost. Many researchers have explored various heterogeneous catalysts where active metals such as Cu, Ce, Fe, Mo,  $n\text{Fe}^0$  are supported on various materials (e.g., GAC, ZMS-5, SBA-15, MCM-41, Clay).

Among various supports, activated carbon (AC) material received immense attention in material science because of its high surface area, strong adsorption capacity, abundant porous structure, possess multi-functional groups and easily available. AC is widely used in many industrial applications including separation, adsorption and as a catalyst support (Ge et al., 2016). In this context, granular activated carbon (GAC) has been used as an active sorbent to absorb organic/inorganic pollutants for their later degradation via other mechanisms. However, the GAC performance often experiences a decreased adsorption capacity after the first cycle because of blocking of pores due to the incomplete regeneration of GAC (e.g., the residuals and formation of phenolic oligomers during the absorption/oxidation process reported) (Benhamed et al., 2016). Nevertheless, several works have suggested the modification of AC with metal oxides incorporation, including iron oxide, zinc oxide, zero-valent iron, manganese oxide, aluminum oxide and copper oxide to enhance the catalytic activity.

Among all metal oxides tested, copper oxide impregnated AC (Cu/AC) catalyst has been regarded as a promising catalyst for the oxidation of nitrogenous aromatic compounds; the catalyst can be easily separated from treated water with the filtration (Subbaramaiah et al., 2013b). In addition, Cu as active species in catalyst has gained more attention in recent days due to its non-toxic/low toxicity, easy availability and good catalytic properties. However, to the best of authors knowledge, there have been a limited number of studies regarding CWPO with Cu/AC as the catalyst (Priyanka et al., 2014). Priyanka et al. (2014) used Cu/AC for the degradation of nitrobenzene. However, it is unclear about mineralization mechanism. The current knowledge gaps are that copper impregnated GAC (i.e., Cu/GAC) was not tested for resorcinol bearing wastewater and degradation mechanism was not reported. Resorcinol (=1,3-dihydroxybenzene) was selected as a targeting pollutant because it is one of the major non-biodegradable pollutants in wastewater owing to its high toxicity, high oxygen demand and low biodegradability (Aghav et al., 2011; Agarwal and Rani, 2017). It has been listed as one of the potent endocrine disrupting chemicals (Lam et al., 2005). The major source of resorcinol is from various industrial effluent streams such as textile, steel, petrochemical, petroleum refinery, rubber, dyes, plastics, pharmaceutical, cosmetics, paper and pulp etc. (Kumar et al., 2003). Further, it is highly poisonous as compared to phenol, and found to show a negative impact on cardiovascular and central nervous system. Resorcinol is very detrimental to the living beings even at very trace amount because of its toxicity and carcinogenic nature (Aghav et al., 2011). Therefore, it drives to develop the efficient and effective method for the removal of resorcinol from water and wastewater.

In the present study, Cu/GAC was synthesized and then its performance was evaluated in terms of resorcinol mineralization by CWPO process using hydrogen peroxide as an oxidant. The main objectives of this study were to i) evaluate the key operating parameters for achieving an efficient process for resorcinol degradation, and ii) explore the mineralization mechanism of resorcinol.

## 2. Materials and methods

### 2.1. Chemical

All the chemicals used in the experimental studies were of analytical reagent (AR) grade. Resorcinol and hydrochloric acid were procured from CDH Pvt Ltd. India. Sodium hydroxide was purchased from Fisher Scientific, Mumbai, India. GAC, purchased from Lobha Chemie, Mumbai, India, had an iodine adsorption capacity of 800 mg/g and loss on drying

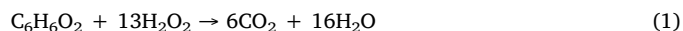
at 120 °C is 10%. Copper nitrate tri-hydrate was obtained from Merck Specialities Private Ltd, Mumbai, India, and 30 wt%  $\text{H}_2\text{O}_2$  was purchased from Rankem, Mumbai, India. The deionized (DI) water (resistivity-18 M $\Omega$ -cm) used in this study was procured from SM laboratories, Jaipur, India.

### 2.2. Synthesis of catalyst

Wet impregnation technique was used to synthesize the Cu/GAC. Firstly, GAC was washed with boiled (temperature = ~100 °C) DI water for the activation of pores and to eliminate impurities in the pore, and thereafter dried in an oven at 110 °C for 6 h. The impregnation of copper on GAC framework (Cu/GAC) used the procedure as follows: a required quantity of activated GAC (19.8 g) was added into a copper precursor solution (0.2 g) with a copper nitrate tri-hydrate, and the GAC-added solution was continuously stirred with a stirrer (RQ-121, REMI stirrer) at 500 revolution/min (rpm) for 30 min. Then, the GAC solution was filtered via a vacuum filter unit using Whatman filter paper grade 42 (2.5- $\mu\text{m}$  particle retention) and the GAC-impregnated with Cu retained by the filter paper was kept in an oven at 110 °C for 6 h for drying. The dried samples were calcined using muffle furnace at 350 °C temperature for 3 h and is denoted as Cu/GAC. This calcination step is required to increase the stability of catalyst and minimize the Cu leaching during the oxidation process.

### 2.3. Testing procedure and experiment design

Oxidation reaction was performed in three-necked round bottom flask, with the middle neck being enclosed with a reflux condenser to condense the vapor samples and to minimize the experimental errors. The two side necks were used for temperature measurement by the thermometer and to handle samples. The three-neck flask was placed in an oil bath, and the whole setup was kept on a hot plate to maintain the desired temperature (~40–70 °C) with the help of a proportional-integral-derivative (PID) controller (2 MLH, REMI). The reaction mixture was uniformly mixed with the magnetic stirrer at 300 rpm. Once the reaction solution achieved the desired temperature (~40–70 °C), the required quantity of catalyst (Cu/GAC) and the oxidizing agent ( $\text{H}_2\text{O}_2$ ) is added into the reaction solution.  $\text{H}_2\text{O}_2$  quantity was pre-decided based on stoichiometric quantity by assuming the complete degradation of reaction solution (resorcinol) with hydrogen peroxide into  $\text{CO}_2$  and  $\text{H}_2\text{O}$  via Eq. (1):



The initial pH of resorcinol was adjusted by using HCl or NaOH solution. After completion of 4 h reaction, the sample in the three-neck flask was filtered using 0.45  $\mu\text{m}$  syringe membrane filter (PTFE2545, MOXCARE), and the filtrate samples were analyzed with a UV spectrophotometer (see below).

### 2.4. Catalyst characterization and analytical methods

Catalyst characterization was done to understand the physical and chemical properties of the synthesized catalyst. Fourier transform infrared spectrophotometer (FTIR) (Spectrum Two, Perkin Elmer) was carried out in order to determine the various functional groups present in the synthesized catalyst. For the analysis, KBr pellet (pressed-disk) technique was employed with a spectral range of 4000 to 400  $\text{cm}^{-1}$ . To explore the surface morphology of catalyst scanning electron microscope (SEM) (Nova Nano FE-SEM 450, Thermo Fisher Scientific) was used. The thermal stability of the catalyst sample was analyzed in the range of 30–900 °C through the thermogravimetric analyzer (TGA) (STA 6000, Perkin Elmer). Thermogravimetric analysis was performed in an air atmosphere at a heating rate of 10 °C/min. Synthesized catalyst samples were analyzed using High-resolution transmission electron

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