



Removal of phenol from water by catalytic wet air oxidation using carbon bead – supported iron nanoparticle – containing carbon nanofibers in an especially configured reactor



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ABSTRACT

Catalytic wet air oxidation (CWAO) is extensively used for the destruction of organic contaminants in wastewater. The present study describes the removal of phenol from water, used as a model organic contaminant, by CWAO with iron (Fe) metal nanoparticles (NPs)-doped carbon microbeads (~0.6 mm) as the catalyst. The Fe-carbon composite was prepared by the carbonization and activation of the phenolic precursor-based polymeric beads in which the Fe NPs were in-situ added during the polymerization stage. Carbon nanofibers (CNFs) were grown on the carbon microbead substrate by catalytic chemical vapor deposition with acetylene as the carbon source. Oxidation reactions were carried out under different operating conditions in a high pressure-stirred reactor, viz., temperature, catalyst loading, and speed of the stirrer. The reactor was fitted with an especially configured impeller cum catalyst basket which held the prepared CNF-decorated Fe-doped carbon beads. The data showed an efficient remediation of the phenol-laden water, indicating the potential scale-up of the proposed CWAO catalyst and impeller cum catalyst holder-assembly in this study.

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1. Introduction

Pharmaceutical, petrochemical and various chemical industries discharge a large quantity of aqueous effluents containing various organic compounds. With the existing stringent environmental regulations and increasing necessity of recycling spent water, an efficient technology is required for treating the industrial effluents containing the organic compounds. At present, various methods such as adsorption, incineration, wet air oxidation (WAO), catalytic wet air oxidation (CWAO), advanced oxidation, biological degradation, etc., and all possible combinations are used for treating the wastewater effluents containing different types of organic compounds [1,2]. The CWAO process is suitable for treating organic wastes. In this process, waste materials are either completely or partially destroyed, or converted to less harmful species, with significant reduction in total organic carbons (TOCs). This process uses air as the oxidant and a heterogeneous catalyst at elevated temperatures (80–200 °C) and pressures (1–50 bar). Although unsupported metal and metal oxide catalysts are generally more

effective than the supported catalysts, additional steps such as precipitation, adsorption, etc., are required to separate the unsupported spent catalysts from the reaction mixture [3].

Most of the CWAO studies have used phenol as the model compound for the organic contaminants present in the effluent streams, because it is an intermediate product in the oxidation pathway of high molecular weight-aromatic compounds [4]. Moreover, it is toxic and commonly found in various industrial wastewaters [5]. In the present context of treating the phenol-laden wastewater by CWAO, various supported catalysts, discussed in the literature can be grouped into two categories: noble metal-based catalysts and transition metal- and metal oxide-based catalysts. Noble metals such as platinum (Pt), ruthenium (Ru) and palladium (Pd) have been extensively studied as the CWAO catalysts for phenol. To mention a few salient studies performed on the removal of phenol from water by CWAO, Keav et al. [3] prepared the ceria (CeO₂)-supported Pt and Ru metal catalysts and found ~98% conversion in a 2000 ppm-phenol-containing water at 160 °C and the 20 bar-oxygen (O₂) partial pressure in the batch reactor, using 4 g/L-catalyst. Rocha et al. [6] studied the CWAO reaction using the titanium oxide (TiO₂)- and cerium oxide (CeO₂)-supported Pt and found 96% conversion for the 1000 ppm-phenol concentration in water at 160 °C and 10 bar-O₂ partial pressure, using the catalyst loading of 1 g/l. Pintar et al. [7] used

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TiO₂-supported Ru and showed complete phenol conversion for the 1000 ppm-concentration in water at temperatures above 210 °C and 10 bar-O₂ pressure. Vaidya and Mahajani [8] carried out the CWAO reaction using Ru/TiO₂ catalyst and also found the complete conversion of phenol. This study used a range of reaction temperatures (175–200 °C), O₂-partial pressures (0.34–13.8 bar) and catalyst loadings (0.5–1 g/l). Barbier et al. [9] performed a comparative study of the Ru, Pt, and Pd noble metal catalysts, each supported in CeO₂, and found Ru/CeO₂ to be the best performing catalyst with complete conversion in the 2000 ppm-phenol-contaminated water at 160 °C and 20 bar-O₂ pressure, using 4 g/l of the catalyst. The authors attributed the superior activity of Ru to less amount of carbonaceous products formed during the reaction, in comparison with those formed during the oxidation reactions using Pd/CeO₂ and Pt/CeO₂. Masende et al. [10] studied different supports for Pt, namely, graphite, TiO₂ and alumina, and found Pt to be more stable and effective in the graphitic support than in the other two supports used for the CWAO reactions, which was also attributed to the less amounts of carbonaceous products formed in the graphitic support, and therefore, less deactivation of the catalyst.

Despite exhibiting a lower catalytic activity than noble metals, a number of transition metal-based catalysts have been used for the CWAO of organic wastes in water, because these catalysts are relatively inexpensive. Also, noble metals are prone to poisoning by sulphur, phosphorus and halogen-containing compounds [5]. Among the several salient studies performed on the CWAO of phenol over the transition metal- and metal oxide-based catalysts, Lin et al. [11] carried out the oxidation of phenol-containing water over CeO₂ catalyst and found more than 90% conversion at 160 °C and ~10 bar-O₂ pressure. Singh et al. [12] studied the CWAO of phenol in a trickle bed reactor using copper oxide supported on alumina catalyst. The experiments were performed over the temperature range of 373–403 K, pressure range of 1–15 bar and initial phenol-concentration range of 500–2000 ppm. The maximum phenol conversion obtained in this study was ~56%. Santos et al. [13] studied the CWAO of phenolic water at basic pH (~8), using copper (Cu) as the catalyst in the fixed bed reactor. The basic pH was used to prevent the leaching of Cu from the substrate. Approximately 77% conversion was measured in the 1000 ppm-phenol-containing water at 160 °C and 16 bar-O₂ pressure. Chen et al. [14] used CeO₂/alumina as the CWAO catalyst in a 1000 ppm-phenolic water, with Cu as the promoter. The Cu metal, dispersed in the matrix of CeO₂ enhanced the catalytic activity, with complete conversion found within 1 h at 180 °C and 15 bar-O₂ pressure, using 3 g/l-catalyst. However, leaching of the Cu ions drastically reduced the activity of the catalyst. The deactivation of Cu-based catalysts due to the leaching of the metal from different substrates has also been reported by Alvarez et al. [15] and Miro et al. [16]. On the contrary, Quintanilla et al. [17,18] tested the iron (Fe) catalyst, supported on activated carbon, for the CWAO of phenol (1000 ppm), and found complete conversion without leaching of the metal during the oxidation at 127 °C and 8 bar of O₂-pressure, indicating the stability of the carbon-supported Fe metal catalysts.

The CWAO method has also been successfully used for the removal of substituted phenols from water. Ojeda et al. [19] investigated the CWAO of *o*-cresol and 2-chlorophenol over activated carbon in a fixed bed reactor and showed ~80% conversion at 160 °C and 2 bar. Tu et al. [20] studied the CWAO of 2-chlorophenol over sewage sludge-derived carbon-supported iron oxide catalyst and showed the complete conversion at 120 °C and the 9 bar-O₂ partial pressure, with the 2 g/l-catalyst loading. The reaction times in all the aforementioned studies using noble or transition metal/metal oxides-based catalysts varied between 1 and 5 h.

Carbonaceous materials such as granular activated carbons (GACs) and activated carbon fibers are commonly used as a support to metals for different adsorption and reaction applications, including CWAO processes, because of a large porosity and stability of the materials in acidic as well as basic media [5]. Carbonaceous materials without metals have also been directly used as the CWAO catalyst for phenol degradation. Wang et al. [21] used various acid functionalized carbon materials such as multi-walled carbon nanotubes (MWCNTs), carbon fibres and graphite, as the CWAO catalyst. The study showed 100% conversion for the 2000 ppm-phenol concentration in 2 h over MWCNTs at 160 °C and 25 bar, using the 0.8 g/l catalyst-loading. The activated carbon materials were used by Santos et al. [22] also for the CWAO of phenol, showing more than 90% conversion over the similar temperature- and pressure ranges.

In the recent studies, porous carbon beads were used as the support to Fe metal for environmental remediation applications [23,24]. In such catalyst-support, the Fe metal nanoparticles (NPs) were incorporated in-situ during the synthesis stage. The method yielded a highly porous carbon-metal composite with significant Fe loadings and a uniform dispersion of the metal in the carbon matrix. More recently, carbon nanofibers (CNFs) were grown on the carbon bead substrate by catalytic vapor deposition (CVD) with the incorporated metal NPs serving as the CVD catalyst [25,26]. The growth of the CNFs occurred by the tip growth mechanism, with the metal NPs located at the tips of the CNFs, which increased the exposure of the metal to the surrounding liquids.

The present study describes the preparation of the Fe NP-dispersed and CNF-decorated carbon microbeads for the CWAO of phenol-contaminated water. The CNFs were grown over porous carbon beads by CVD. The Fe NPs served a dual role: (1) the CVD catalyst for growing CNFs, (2) the CWAO catalyst for the destruction of phenol molecules in water. Oxidation reactions were carried out under different operating conditions in a high pressure-stirred reactor, viz., temperatures, catalyst loadings, and speeds of the stirrer. An especially configured impeller cum catalyst holder was designed and fabricated for holding the *fibrous* carbon bead-supported Fe NP catalysts. The novelty of the present study is in the development of the CWAO catalyst and reactor for the treatment of the organics-laden wastewater. Further, the catalysts were doped in situ with the Fe NPs during a synthesis stage, and an especially configured impeller was designed and fabricated for holding the *fibrous* carbon bead-supported Fe NP catalysts.

2. Materials and method

2.1. Materials

All chemicals used in this study were of analytical grade. Phenol, formaldehyde (37%), triethylamine (TEA), hexamethylenetetramine (HMTA), polyvinyl alcohol (PVA) (MW = 95000) were purchased from Merck, Germany. Iron(III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O) (purity > 95%), and potassium hydroxide (KOH) were purchased from Fisher Scientific, USA. Nitrogen (N₂), hydrogen (H₂), O₂ and acetylene (C₂H₂) gases were of high purity grade and purchased from Sigma Gases, India. All solutions were prepared in Milli-Q water.

2.2. Catalyst preparation

The detailed procedure of the catalyst preparation is available in the previous study [26]. Briefly, the phenolic beads were prepared by the suspension polymerization method. A reaction mixture of phenol (50 g), formaldehyde (63 ml) and TEA (1.5 ml) was prepared. These reagents were used as the monomer, solvent for phenol and the catalyst for polymerization, respectively. The

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