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Carbon bead-supported copper-dispersed carbon nanofibers: An efficient catalyst for wet air oxidation of industrial wastewater in a recycle flow reactor

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ABSTRACT

Copper nanoparticle-doped and graphitic carbon nanofibers-covered porous carbon beads were used as an efficient catalyst for treating synthetic phenolic water by catalytic wet air oxidation (CWAO) in a packed bed reactor over 10–30 bar and 180–230 °C, with air and water flowing co-currently. A mathematical model based on reaction kinetics assuming degradation in both heterogeneous and homogeneous phases was developed to predict reduction in chemical oxygen demand (COD) under a continuous operation with recycle. The catalyst and process also showed complete COD reduction (>99%) without leaching of Cu against a high COD (~120,000 mg/L) containing industrial wastewater.

Introduction

Catalytic wet air oxidation (CWAO) is an efficient method for treating the refractory organic compounds containing water. The method requires oxygen (O_2) or air as an oxidant at the elevated temperature (130–250 °C) and pressure (10–50 bar) conditions [1,2]. Although the biological method is widely used for treating wastewater, long hydraulic residence times associated with the micro-organisms used for the degradation of organic pollutants and the requirement of large volumes are often not desirable. It is also mentioned that the biological treatment is not suitable for high organic concentrations (>50 ppm) [1,3]. Thus, CWAO offers an alternative technology for treating bio-toxic and bio-refractory organic pollutants in water. Noble metals such as Pt [4–9], Pd [4], Ru [6,8,10–12] and Ir [6,13] have been used as the CWAO catalysts because of the high catalytic activities of the metals. Noble metals are, however, expensive and vulnerable to poisoning by the sulfur, halogen and phosphorus containing compounds. Transition metal and their oxides have been recommended as the CWAO catalysts, potentially substituting noble metals [14–19]. Among these, Cu-based catalysts show relatively higher activities [1,15,17–20]. Different metal oxides have also been used for various other applications such as photocatalysts [21] and in thin films [22].

It is significant to note that only few studies have demonstrated the viability of CWAO in treating wastewater under a continuous operation (i.e., flow condition) [2,3,23–29]. However, the liquid flow through the packed beds of powdery (micron-sized) catalysts is invariably prone to maldistribution and channeling. On the other hand, activities of extrudate or pelletized catalysts are relatively lower because of pore diffusion limitations. Therefore, further light needs to be shed on the CWAO of aqueous organics in a packed or trickle bed reactor using pelletized or extruded catalysts.

Reaction pathway of the CWAO of phenol is well established and has been discussed in several studies [30–36]. Alvarez et al. [30] and Pintar et al. [34] have, however, cautioned that the produced intermediate refractory acids may potentially hinder complete oxidation under high liquid to solid ratio and/or leaching of Cu from the catalyst, leading to the formation of polymers of Cu-acetate at the surface of the catalyst. Most recently, Zapico et al. [31] have presented a detailed reaction pathway for the free-radical mechanism of CWAO on Cu, including the possible formation of polymer and incomplete conversion of organics into CO_2 and water. Therefore, stability of the Cu-based catalysts is a concern in the CWAO processes for wastewater treatment.

From the reaction mechanism point of view, simple power law kinetics [28–33] to comprehensive Langmuir–Hinshelwood (L–H) [30,32–35] type kinetic rate expressions have been proposed in literature for CWAO. Reaction pathways for the CWAO reactions are

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based on the homogeneous autocatalytic free-radical and/or classical heterogeneous surface L–H reaction mechanisms [37]. The free radical autocatalytic path relates to the active metal phase leaching from the metal oxide catalysts, leading to a parallel homogeneous reaction path and the formation of the low carbon chain refractory acidic intermediates [37–39]. On the other hand, the heterogeneous L–H reaction mechanism assumes a fast adsorption rate for the reactant species and slow surface oxidation of the adsorbed species, the latter being the rate determining step, along with the deactivation of the solid phase by the carbonaceous deposits [37,40]. Santos et al. [32] and Guo et al. [33] were probably the first ones to propose the dependence of the kinetic rate on the catalyst concentrations. Therefore, the contributions from both heterogeneous and homogeneous reactions to the observed kinetic rate were considered. This formed the basis for the development of a CWAO kinetic model based on the L–H kinetic approach including the catalyst concentrations in this study.

This study for the first time describes the operation of a continuous flow packed bed reactor for treating the organic pollutants containing wastewater by CWAO using carbon beads (~0.5 mm) that were *in situ* dispersed with Cu metal nanoparticles (NPs) as the catalyst. At present, various carbon materials such as activated carbon, carbon xerogel, carbon nanofibers (CNFs) and carbon nanotubes have been effectively used as the substrate for metal catalysts because of their high chemical, thermal and mechanical stabilities [41,42]. The CNFs and other carbonaceous materials have also been used in various other applications, viz. reinforced nanocomposites [43,44], photocatalysis [45,46], strain sensing [47,48], organic vapor sensing [49], energy storage/conversion [50] and structural composites [51]. Recently, carbon beads were used as the substrate for growing CNFs [52,53]. The CWAO tests are performed first in a batch mode under different operating conditions to develop a L–H kinetic rate expression and then in a packed bed reactor with water and air flowing co-currently. Effects of recycling on COD removal are determined for the first time. A mathematical model is developed for predicting the performance of the CWAO reactor under flow conditions with/without recycle, and validated with the experimental flow data. Finally, the developed catalyst and the process in this study are tested against a very high chemical oxygen demand (COD) (~120,000 mg/L) containing industrial wastewater sample under flow conditions.

Materials and methods

Materials

Phenol, formaldehyde, hexamethylenetetramine (HMTA), triethylamine (TEA), copper nitrate tri-hydrate ($Cu(NO_3)_2{\cdot}3H_2O$) (purity >99%), polyvinyl alcohol (PVA), potassium permanganate ($KMnO_4$), potassium dichromate, silver sulphate (purity >98%), mercuric sulphate (purity >99%), ferrous ammonium sulphate, ferroin indicator, sulphuric acid, nitric acid (HNO_3) and sodium hydroxide (NaOH) were supplied from Merck, Germany. All gases including nitrogen (N_2), air, hydrogen (H_2), and acetylene (C_2H_2) were supplied by Sigma Gases, India. The industrial wastewater effluent sample was supplied by a chemical plant in The Netherlands. The sample contained a matrix of more than twenty aliphatic and aromatic organic compounds including phenol, aldehydes, ketones and alcohols as well as organic salts, with a very high COD content of ~120,000 mg/L. Main constituents of the wastewater sample were phenol (24%), methyl phenyl carbinol (19%), phenethyl alcohol (11%), propylene glycol (8%), benzyl alcohol (7%), methyl phenyl ketone (6%), benzene (4%) and benzaldehyde (7%). Therefore, approximately 70% contribution to the COD contents was attributed to alcohols, and this was the reason for selecting phenol as the model pollutant in this study.

Synthesis of catalyst

Fig. 1 shows the steps for the synthesis of the Cu-doped phenolic beads decorated with CNFs using chemical vapor deposition (CVD). The synthesis procedure is the same as that described in the previous study with modifications [52]. A homogeneous solution of formaldehyde (63 mL), phenol (50 g), and TEA (2–3 mL) was prepared in a round bottomed-flask fitted with a reflux-condenser. Polymerization reaction was performed at room temperature (~30 °C) using phenol as the monomer,

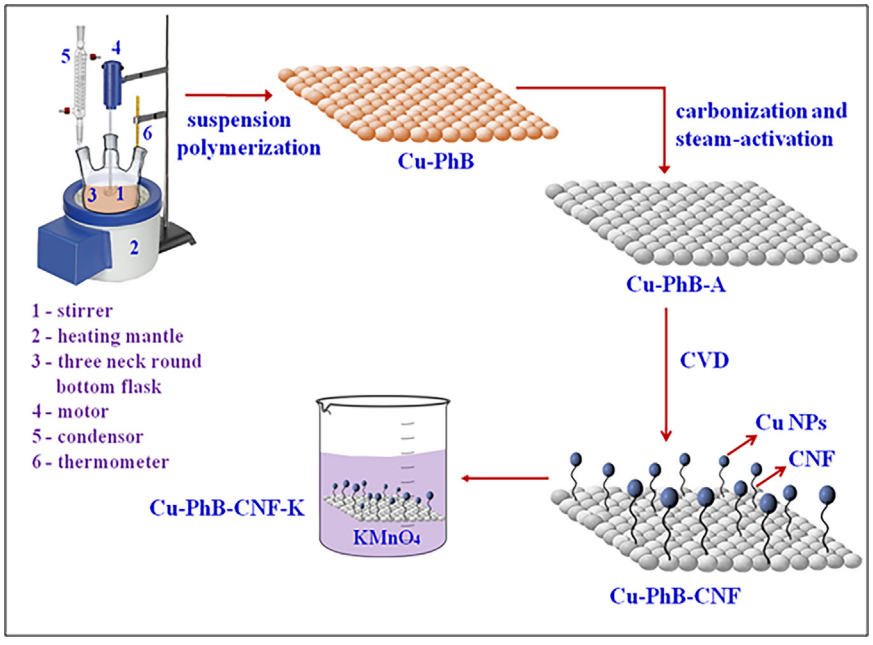

Figure 1. Schematic diagram for the preparation of Cu-PhB-CNF-K.

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