



Catalytic decoloration of commercial azo dyes by copper-carbon composites derived from metal organic frameworks



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ABSTRACT

Porous copper-carbon composites were synthesized via one-step heat treatment of copper-based metal organic frameworks (MOFs), MOF-199. The prepared composites, Cu-CC-550 and Cu-CC-650, were applied as catalysts for catalytic decoloration of two commercial azo dyes, methylene blue (MB) and rhodamine B (RB) in the presence of NaBH₄. The composites were characterized by a series of spectroscopic instruments and a surface analyzer. The characterization confirmed the presence of Cu₂O and Cu in the amorphous carbon network with high porosity. The composites were very active in decolorizing MB, RB, and their mixture. In particular, Cu-CC-550 exhibited a great reusability to complete five consecutive MB reduction cycles with a minimal loss of catalytic capability and structural integrity. The prepared Cu-CC composite can be considered as a promising material for catalytic decoloration of dyes as well as a potential alternative to replace noble metal-based catalysts.

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1. Introduction

During the last few decades, the consumption of synthetic dyes in different industries including paper, plastics, textile, leather, and food processing has significantly increased, and wastewater effluents from those industries have created a great public concern about dye pollution in the receiving water bodies [1]. In last decade, over 7×10^5 tons of around 100,000 different types of commercial dyes were produced and roughly 100 tons of dyes were discharged into water streams [2,3]. Many of these colored contaminants are toxic, carcinogenic and non-biodegradable [4]. Overexposure to dyes can cause skin irritation, respiratory problems, kidney dysfunction, damage of reproductive system, liver or brain, and impairment of central nervous system in humans [5]. In addition, dyes consume dissolved oxygen, and interfere with photosynthetic activity of aquatic plants [4].

The conventional microbial mediated wastewater treatments often suffer from low efficiencies in dyes removal because of poor biodegradability of dyes and the deterrent effects of high salt concentration in dye-wastewaters [6]. As a consequence, a number of methods have been reported for dyes removal including

coagulation/flocculation [7], adsorption [6], photo-catalysis [8], and oxidation processes [9]. Most of the existing methods are more or less effective in removal of dyes, however, some of them have encountered operational disadvantages. For example, a large amount of sludge is generated in coagulation/flocculation because of the use of various chemical reagents including polyelectrolytes and coagulants [10]. Fenton's reagent (H₂O₂/Fe²⁺) or ozone-assisted advanced oxidation process can effectively remove dyes without sludge production, however, it suffers from high operating cost and short lifetime of oxidants [11]. The photocatalytic degradation of dyes under UV radiation needs long operating time and the use of UV radiation limits its large-scale application [12]. On the other hand, removal of dyes via adsorption has practical advantages due to its simple operation and good efficiencies, but it has problems associated with adsorbent disposal and post-contamination by used adsorbents [6]. For these reasons, research interests over-development of new types of adsorbents, catalysts and other effective methods for dyes treatment still continue to grow.

Recently, NaBH₄-assisted catalytic reduction of dyes is gaining much attention because of its fast and simple operation procedure [6,13–19]. As catalysts, noble metal nanoparticles (e.g., Pd, Pt, Au, Ag, and Ru) on silica or carbon supports have been widely used for their high efficiencies [13–15]. However, the scarcity and high cost of noble metals impede wide and practical application of noble

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metal catalysts [6,16]. As a consequence, substitution of noble metal based catalysts by non-noble metal based catalysts has become an important research topic in recent years.

As an effort to develop non-noble metal catalysts, several researchers have investigated the use of metal-organic frameworks (MOFs) as a base material [20–23]. MOFs materials have several advantageous properties such as high porosity, controllable pore size, and ability to impart specific functionalities or active species without altering the framework topology [24–26]. In preparation of catalysts, MOFs are used as a sacrificing template or platform while providing carbon sources such as farfural alcohol, phenolic resin, glycerol, and carbon tetrachloride [27]. Recently, direct calcination of MOFs (without any additional carbon source) has also been reported to prepare MOF-derived metal or metal oxide/carbon composites [21–23]. These metal/carbon composites showed promising performances as catalysts or adsorbents [22,23,28].

In this study, Cu-carbon composites (Cu-CC) were prepared via simple calcination of a Cu-based MOF, MOF-199 (Cu linked by 1,3,5-benzinetricarboxylic acid [29]), under N_2 atmosphere, and the composites were used as catalysts for decoloration of two common industrial dyes, methylene blue (MB) and rhodamine B (RB) (Scheme 1). The prepared composites were characterized using various spectroscopic methods and a surface analyzer, and a series of batch reduction experiments were carried out to demonstrate the catalytic capability of the composites.

2. Experimental methods

2.1. Materials

All the chemicals and reagents were purchased from commercial vendors and used as received. 1,3,5-benzinetricarboxylic acid ($C_9H_6O_6$, H_3BTC , 98%), RB ($C_{28}H_{31}ClN_2O_3 > 95\%$), and MB ($C_{16}H_{18}N_3S$) were obtained from Alfa Aesar, USA. Copper (II) nitrate hemihydrate ($(Cu(NO_3)_2 \cdot 2.5H_2O, > 97\%)$, sodium borohydride ($NaBH_4$, extra pure), methanol ($CH_3OH, > 99.5\%$), ethanol ($C_2H_5OH, 99.9\%$), *N,N*-dimethylformamide ($C_3H_7NO, > 99.5\%$), hydrochloric acid ($HCl, 35.5\%$) and nitric acid ($HNO_3, 60\%$) were purchased from Daejung Chemical, South Korea.

2.2. Synthesis of MOF-199

MOF-199 was prepared according to the method of Hu et al. [30] with a minor modification. In brief, 1.0 g H_3BTC and 1.95 g

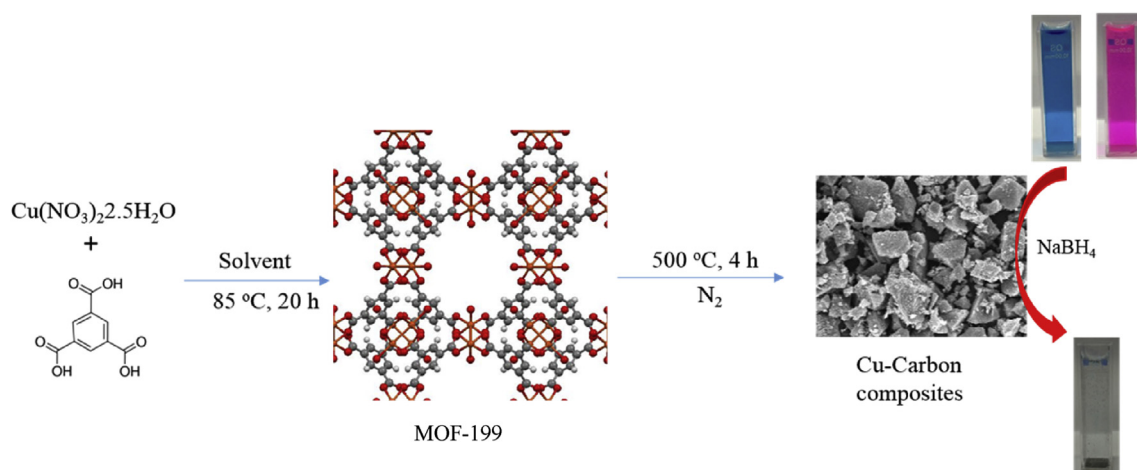
$Cu(NO_3)_2 \cdot 2.5H_2O$ were dissolved in 51 mL solvent mixture (water: ethanol: *N,N*-dimethylformamide, 1:1:1 (v/v/v)), and the mixture was mixed for 10 min with magnetic stirring. The solution was taken into a Teflon lined autoclave vessel, sealed and placed in an oven (wiseven, Korea), and heated for 20 h at 85 °C. After the reaction, the solution was cooled down while allowing precipitation of blue solid products. The precipitates were collected by filtration, washed with ethanol several times to remove residual H_3BTC , and dried for 12 h at 100 °C.

2.3. Synthesis of Cu-carbon composites

MOF-199 was taken in an alumina crucible, and placed in a tubular reactor for thermal treatment. A 610 mm long quartz tube with 25.4 mm outer diameter (Chemglass CGQ-0900T-13) was used as a tubular reactor. The reactor was heated at 550 °C or 650 °C for 4 h using a split-hinged furnace (AsOne, Japan). The heating rate was 5 °C min^{-1} and an S-type thermocouple was used to monitor the temperature. The N_2 gas flow rate was fixed at 500 mL min^{-1} using a Brooks mass flow controller (5850 series E), and a computer-aided control system by LabVIEW (National Instrument, USA) was employed to control the flow. After cooling to room temperature, the powder products were retrieved, washed several times with water and ethanol, dried at 100 °C overnight, and kept in a sealed vial before use. The products were designated as Cu-CC-550 or Cu-CC-650 depending on the heating temperature.

2.4. Characterization

X-ray powder diffraction (XRD) analysis was conducted with the Rigaku DMax-2500 diffractometer using $CuK\alpha$ radiation. The surface area and pore size of the prepared samples were obtained from nitrogen adsorption method using a BELSORP-mini II (MicrotracBEL, Japan). The samples were evacuated at 150 °C for 12 h before nitrogen adsorption at -196 °C. Raman spectra were taken using an inVia reflex Raman microscope (Renishaw, UK). The morphologies and composition of the samples were examined with a field emission scanning electron microscope (FE-SEM, JEOL-JSM7401F). Surface analysis of the samples was conducted using a theta probe angle-resolved X-ray photoelectron spectrometer (ARXPS) system equipped with the monochromatic Al $K\alpha$ line (1486.7 eV). A Gaussian (30%)-Lorentzian (70%) model (defined in CasaXPS as GL (70)) was employed to generate the curve-fitting spectra of the Cu 2p_{3/2}, Cu 1p_{1/2}, O 1s, and C1s in depth XPS



Scheme 1. Preparation of Cu-CC composite and its application in dye decoloration.

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