Chemical Engineering Journal 330 (2017) 783–791

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Degradation of humic acid using hydrogen peroxide activated by CuO-Co_3O_4@AC under microwave irradiation

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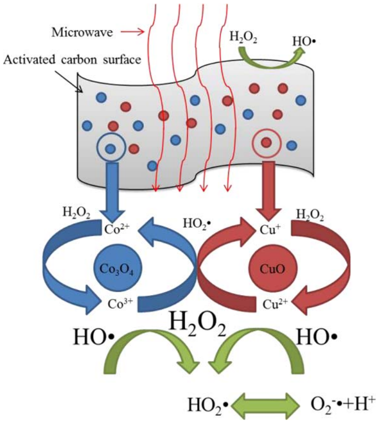
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
CuO-Co_3O_4@AC
Microwave
Hydroxyl radical
Superoxide radical
Humic acid

ABSTRACT

To investigate the degradation of humic acid (HA) in a CuO-Co_3O_4@AC/H_2O_2 system under microwave irradiation, a catalyst (CuO-Co_3O_4@AC) was prepared and characterized. The effects of several reaction parameters, such as the microwave temperature, initial pH, H_2O_2 concentration, catalyst dosage and inorganic anions (HCO_3^- and Cl^-) were investigated, and the synergetic effect of hydrogen peroxide among MW, AC and metal oxides was explored. The results indicated that cobalt and copper were supported on activated carbon and existed as Co_3O_4 and CuO. The removal efficiency of HA and TOC reached 88% and 71%, respectively, with 100 mg/L HA, 80 °C, 9.8 mM H_2O_2 and 0.5 g/L catalyst under 60 min of microwave irradiation. The existence of HCO_3^- and Cl^- had an inhibitory effect on the degradation of HA, and the effect of HCO_3^- was more evident. Quenching experiments and EPR tests confirmed that $^{\cdot}OH$ and $O_2^{-\cdot}$ were the main free radical species, and XPS analysis showed that the species present on AC were Co (II), Co (III) and Cu(II), which can activate H_2O_2 to produce $^{\cdot}OH$ and $O_2^{-\cdot}$.

1. Introduction

Humic acids (HA) are acid-insoluble components of humic substances (HS), which are derived from the humification of plants, animal debris and microfauna [1]. They are major components of natural organic matter (NOM) and are widely present in water, soil and sediment. Although HA are non-toxic compounds, due to the diversification of sources, their functional groups can be combined with other organic

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http://dx.doi.org/10.1016/j.cej.2017.08.008
Received 9 May 2017; Received in revised form 1 August 2017; Accepted 2 August 2017

and inorganic materials to form new contaminants [2,3]. For example, HA can form complex compounds with trace metals [4,5] and react with chlorine to produce trihalomethanes (THMs) and haloacetic acids (HAAs), which are strictly controlled in drinking water [6,7]. In water treatment, coagulation [8] and membrane filtration [9] are practical methods to remove HA. However, these methods only transfer HA, causing secondary pollution (sludge and membrane pollution). To avoid these adverse effects, the application of advanced oxidation processes (AOPs) has attracted more attention. These are based on the generation of hydroxyl radicals ($^{\cdot}OH$) with a redox potential of 1.8–2.7 V [10,11]. Their non-selective oxidation and high efficiency for the degradation of HA have already been shown [12–18]. However, the application of AOPs is still limited by its narrow working pH range [2], the high cost of oxidants [15] and the complexity of catalyst preparation [1,12].

Microwave (MW)-enhanced AOPs have been demonstrated as a promising technology for the efficient treatment of organic wastewater [19–23]. The application is based on increasing $^{\cdot}OH$ formation, decreasing activation energy and selective heating of MW [24–27]. To improve the MW thermal effect, activated carbon (AC) is usually used in MW-enhanced AOPs for their excellent MW-absorbing property. Under MW irradiation, hotspots are generated on AC, and the organic pollutants in aqueous solution can be adsorbed and degraded through reactions catalysed by AC [28,29]. However, the application of AC suffers from nonselective adsorption and low catalytic functions, and AC alone in an amorphous state is not suitable for a continuous-mode wastewater treatment process.

Recently, transition metals, or their oxides, loaded on AC as a heterogeneous Fenton-like catalyst have shown higher oxidation rates and wider working pH ranges [30–35]. However, until now, no work has reported microwave-induced metal oxide-supported AC catalytic degradation of organic pollutants in aqueous solution. In this study, to investigate the feasibility of free radical generation in an aqueous solution using MW energy as the sole energy source and a transition metal oxide-supported AC as the catalyst as well as to determine the factors associated with its generation, a transition metal oxide-supported AC catalyst (CuO-Co_3O_4@AC) for advanced oxidation of HA under microwave irradiation was investigated, and the synergetic effects of hydrogen peroxide among MW, AC and metal oxides are discussed. This is expected to be a rapid and effective technology for the complete degradation of organic pollutants in wastewater.

2. Materials and methods

2.1. Chemicals

Activated carbon (AC) was purchased from Yineng Activated Carbon Co., Ltd (Dongguan, China), HNO_3, $NaHCO_3$, NaCl, $Cu(NO_3)_2 \cdot 3H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$, chloroform (CF) and *tert*-butyl alcohol (TBA) were purchased from Titan Scientific Co., Ltd. (Shanghai, China). H_2O_2 (30%) was obtained from Guangzhou Chemical Reagent Factory, humic acid (HA) and 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) were purchased from Macklin Biochemical Co., Ltd. (Shanghai, China). All chemicals were of analytical grade and were used as received, and all solutions were prepared with deionized water.

2.2. Preparation of catalyst

The catalyst (CuO-Co_3O_4@AC) was prepared using a simple dip-calcination method. AC (20–40 mesh) was pre-activated with 2 M HNO_3 solution at 60 °C for 8 h and filtered and washed until the pH of the filtrate was stable, followed by drying at 105 °C for 24 h. Next, 15 g AC (after activation) was added into 200 mL mixed solution containing 0.075 mol/L of Cu^{2+} and 0.075 mol/L of Co^{2+}. The mixture was rapidly mechanically agitated at 80 °C for 6 h. Afterwards, the catalyst was washed with distilled water and calcined in a muffle (TXCS9, pyramid, China) at 400 °C for 2-h to obtain the catalyst.

2.3. Characterization of catalyst

The structure of the catalyst was characterized with an X-ray diffractometer (Ultima IV, Japan) using Cu Kα radiation at 40 kV and 100 mA. The FTIR spectra of samples were measured using a Nicolet iS10 FTIR Spectrophotometer (Nicolet, USA) with KBr pellets. X-ray photoelectron spectroscopy (PHI X-tool, Japan) was conducted to determine the chemical species of cobalt and copper. The X-ray source was Al Kα with 15 kV and 51 W.

2.4. Degradation procedures

Batch degradation experiments of HA were performed in a 500 mL flask containing 200 mL of a HA solution (100 mg/L). HA solution was obtained by diluting the stock solution which was prepared by adding 1 g solid HA into 1 L deionized water and adjusting the pH to 10.0 with 1 M NaOH. The flask was placed in a microwave chemical reactor (MCR-3, Henan, China) with a frequency of 2,450 MHz and a nominative maximum output power of 800 W. The initial pH was adjusted by appropriate amounts of 0.1 M H_2SO_4 or 0.1 M NaOH. Thereafter, appropriate dosages of catalyst and H_2O_2 were added, and the degradation reaction was carried out for an hour at a constant temperature under microwave control.

To explore the effect of natural common inorganic salts on the degradation efficiency of the oxidation system, various concentrations of HCO_3^- and Cl^- were added before the degradation reaction. Quenching experiments for free radicals were also conducted by adding various concentrations of TBA or CF before the degradation reaction.

During the experimental run, solution samples were withdrawn from the reactor at selected intervals and immediately cooled in an ice-water bath to monitor UV_{254} and TOC change. All samples were filtered prior to analysis.

2.5. EPR studies

Electron Paramagnetic Resonance spectrometry (EPR) A200-9.5/12 (Bruker, Germany) was used to determine the species of free radical. DMPO was used as a spin-trapping agent in experiments. A mixture (at pH 7.0 ± 0.2) containing 45 mM DMPO, 9.8 mM H_2O_2 and 0.5 g/L catalyst initiated the reaction with MW. After 5 min reaction, samples were removed with a capillary and analysed at room temperature.

EPR measured parameters: field sweep 100 G, microwave frequency 9.824 GHz, microwave power 6.78 mW, modulation amplitude 1 G, conversion time 40 ms, time constant 10.24 ms.

2.6. Analysis

HA removal was analysed by measuring the absorbance at 254 nm (UV_{254}) and total organic carbon (TOC). UV_{254} was measured by UV–vis spectrophotometer (Pro-752, Lengguang, China). The degree of mineralization of HA was analysed with a TOC analyser (TOC-V CPH, Shimadzu, Japan). The pH values were determined using a pH meter (PHS-3C). The concentration of metal ions was monitored by flame atom absorption spectrometry (AAS) Z2000 (Hitachi, Japan).

3. Results and discussion

3.1. XRD analysis of catalyst

The XRD patterns of CuO-Co_3O_4@AC and activated AC are displayed in Fig. 1. The peaks at $2\theta = 31.3°$, 36.8°, 44.8°, 59.5° and 65.2° are attributed to the lattice planes of Co_3O_4, which corresponded to (2 2 0), (3 1 1), (4 0 0), (5 1 1) and (4 4 0) of the Co_3O_4 phase, respectively [36,37]. The peaks at $2\theta = 35.5°$ (1 1 1) and 38.5° (2 0 0)