Applied Catalysis A, General 544 (2017) 10–20

Contents lists available at ScienceDirect

Applied Catalysis A, General

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

Efficient transformation in characteristics of cations supported-reduced graphene oxide nanocomposites for the destruction of trichloroethane

Usman Farooq[a], Muhammad Danish[a,b], Shuguang Lu[a,*], Mark L. Brusseau[c], Muhammmad Naqvi[d], Xiaro Fu[a,c], Xiang Zhang[a], Qian Sui[a], Zhaofu Qiu[a]

[a] State Environmental Protection Key Laboratory of Environmental Risk Assessment and Control on Chemical Process, East China University of Science and Technology, Shanghai 200237, China
[b] Department of Chemical Engineering, NFC Institute of Engineering and Technology, Multan 59030, Pakistan
[c] Soil, Water and Environmental Science Department, School of Earth and Environmental Sciences, The University of Arizona, 429 Shantz Bldg., Tucson, AZ 85721, United States
[d] Department of Energy,Building and Environment, Mälardalen University, Västerås 72123, Sweden

ARTICLE INFO

Keywords:
Chemical reduction
Solvo-thermal
Graphene supported nanocomposites
TCA degradation
Groundwater remediation

ABSTRACT

Experiments were conducted to investigate the use of graphene-oxide supported metallic nanocomposites for improving the degradation of trichloroethane (TCA) by sodium percarbonate (SPC). Two methods of production, chemical reduction (CR) and solvo-thermal (ST), were tested for preparation of single (Fe) and binary (Fe-Cu) nanocomposites supported by reduced graphene oxide (rGO). A variety of analytical techniques including N_2 adsorption Brunauer-Emmett-Teller (BET), x-ray diffraction (XRD), fourier-transfrom infrared spectroscopy (FTIR), and transmisison electron microscopy (TEM) were applied to characterize the physicochemical and microstructural properties of the synthesized nanocomposites. The characterization indicated that the CR method produced nanocomposites that comprised only mesoporous structure. Conversely, both micro and mesoporous structures were present for samples produced with the ST method. The synthesized single and bimetallic composites produced from the ST method showed higher surface areas, i.e. 93.6 m^2/g and 119.2 m^2/g as compared to the ones synthesized via the CR method, i.e. 13.8 m^2/g and 38.0 m^2/g respectively. The results of FTIR and XRD analyses confirmed that the ST method produced highly crystalline nanocomposites. SEM and TEM analysis validated that metallic particles with definite morphology well distributed on the surface of rGO. X-ray photoelectron spectroscopy (XPS) analysis confirmed the homogeneity nanocomposites and occurrence of variation in copper oxidation states during degradation process. EDS mapping validate the homogeneous distribution of Cu and Fe at reduced graphene oxide surface. The Fe-Cu/rGO (ST) activated SPC system effectively degraded TCA (92%) in 2.5 h at low nanocomposite dose compared to the Fe-Cu/rGO (CR) and only Fe, for which the maximum degradation efficiencies achieved were 81% and 34%. In conclusion, excellent catalytic characteristics were observed for the ST-synthesized single and bimetallic (Fe/rGO, Fe-Cu/rGO) catalysts. These catalysts were successful in improving the degradation of TCA via activated SPC.

1. Introduction

Trichloroethane (TCA) has been extensively used for a wide variety of industrial purposes including metal degreasing, textile manufacturing, and adhesive production, and it is identified as a major groundwater pollutant. The presence of TCA is of particular concern due to its recalcitrant properties and risk to human health from long-term exposures. Among various groundwater remediation techniques, advanced oxidation processes (AOP) are considered as one of the most effective for treating recalcitrant contaminants [1]. The Fenton-based AOP is a favorable and efficient method for the treatment of a variety of organic compounds, such as organic solvents, pesticides, personal care products, pharmaceuticals, and synthetic dyes [2]. Recently, sodium percarbonate (SPC) has achieved considerable attention as an efficient, selective, and environmentally friendly reagent for Fenton-based AOP [3,4].

The conventional homogeneous Fenton process destroys the organic contaminants by generating highly reactive species from the reaction of Fe^{2+}/Fe^{3+} with hydrogen peroxide (H_2O_2). However, there are several drawbacks such as: (i) production of large quantities of iron salts as

* Corresponding author.
E-mail address: lvshuguang@ecust.edu.cn (S. Lu).

http://dx.doi.org/10.1016/j.apcata.2017.07.007
Received 13 April 2017; Received in revised form 19 June 2017; Accepted 6 July 2017
Available online 08 July 2017
0926-860X/

effluent, (ii) additional steps required to separate the sludge, (iii) generation of strong acidic conditions that inhibits the catalyst activity [5]. To address these issues, heterogeneous-catalysis technology is being investigated as a substitute for homogeneous-reaction based AOP with desire to provide extended stability over a wider pH range and improve recycling and reuse ability [6]. In previous studies, several organic pollutants have been treated by Fenton-based AOP using nano zero valent iron (nZVI) and iron minerals in heterogeneous catalysis to activate H_2O_2 for the generation of reactive hydroxyl radicals (OH·) [7–10]. For example, Fe-pillared clay was studied as a heterogeneous composite for the effective degradation of cinnamic acid [11]. Doong and Hussain et al. studied the effectiveness of nanoscale iron as a reductant for the dechlorination of organic solvents [12,13].

Concerted efforts have been made to enhance the activity of heterogeneous Fenton catalysts by introducing a second metal. These bimetallic nanocomposites have been also used for the degradation of organic pollutants in groundwater [14]. Luadthong et al. used copper-ferrite/spinal-oxide catalyst for methnolysis of palm oil [15]. Porous Fe-Ni oxide nano sheets have been studied as a catalyst for groundwater contaminant treatment [16]. Nano zero valent Fe/Cu have been used by Zhu et al. for the remediation of chromium in soil [17]. Doping iron oxides with metallic elements, e.g. Ce, Ti, Co, Zr and Mn, to prepare bimetallic catalysts is a current focus of research in Fenton chemistry [18].

One limitation assocaited with the use of nanocomposites is that these nanoparticles tend to agglomerate and aggregate, which can lead to deterioration of the catalyst performance [19]. To address this problem, the metallic particles can be distributed on solid supports. Carbon based materials such as graphene could be an alternative solid support since the graphene has large surface area with high delocalized π-stacking interaction that could immobilize nanoparticles and could enhance the catalytic activity [20]. In addition, the use of carbon materials as a support is promising owing to their excellent stability under both acidic and alkaline conditions.

To the best of our knowledge, the degradation of TCA using single and bimetallic catalyst supported on rGO, and the comparison of their effectiveness via different synthesis routes have not yet been reported. In the present study, the single and bimetallic (Fe and Fe-Cu) heterogeneous nanocomposites supported on rGO were synthesized. TCA was selected as a model chlorinated organic compound to investigate the catalytic activity of the synthesized composites. Sodium percarbonate (SPC) was used as the oxidant for the TCA degradation. The aim of this work is to delineate the effects of synthesis methods on the characteristics and activity of the heterogeneous composites, and to determine their overll effeciveness in improving Fenton-based AOP.

2. Materials and methods

2.1. Materials and chemicals

The TCA and the graphite powder were purchased from Aladdin Corporation (Shanghai, China). The potassium permanganate ($KMnO_4$), hydrochloric acid (HCl, 37%), sulfuric acid (H_2SO_4, 99%), ethylene glycol (EG), sodium acetate anhydride (NaAc), hydrogen peroxide (H_2O_2, 30% wt.), and *n*-hexane were obtained from Shanghai Lingfeng Reagent Co. Ltd. China. The sodium borohydride ($NaBH_4$, 99.5%), sodium percarbonate (SPC, 98%), ferrous sulfate hydrate ($FeSO_4{\cdot}7H_2O$, 99%), sodium nitrate ($NaNO_3$, 98%), ethanol (99.8%), copper sulfate hydrate ($CuSO_4{\cdot}5H_2O$, 99%) were acquired from Acros Organics (Shanghai, China). The stock solution of TCA was prepared separately using ultra-pure milli-Q water. To adjust the pH, 0.1 M NaOH and 0.1 M H_2SO_4 were used. The reagents used were not further purified, whereas the deionized water in all experiments was purified by milli-Q ultrapure process (Classic DI, ELGA, 102 Marlow, UK).

2.2. Preparation of nanocomposites

Two methods will be tested for producing the nanocomposite materials, chemical reduction and solvo-thermal. Huang et al. synthesized iron nanoparticles by a chemical reduction method using sodium borohydride as reducing agent [21]. Nano-size copper particles have been synthesized using chemical reduction of $CuSO_4$ and the effect of different parameters on size and shape and catalytic efficiency were studied [22]. Das et al. studied the role of reducing agent in formation of Zn-Se nano rods using the CR method [23]. Comparatively, the ST technique is an inexpensive, low temperature and scalable technology. The ST method produces homogeneous dispersed metallic particles with various shapes, nano sizes and effective catalytic performances. Wang et al. reported ST synthesized Fe doped CeO_2 nano sheets with best activity towards oxidation of dichloroethane [24]. Single and bimetallic nano-sized particles, hollow spheres with definite morphology and high crystallinity have been synthesized through the ST method using ethylene glycol for the removal of chlorinated compounds [25–27].

2.2.1. Preparation of composites via solvo-thermal method

Graphene oxide (GO) was prepared by the method reported in our previous studies [4]. GO supported iron-copper composite was synthesized by ST procedure. The Fe-Cu/rGO (ST) catalyst was prepared using 0.5 g of GO mixed with 120 ml of ethylene glycol (EG) in a round bottom flask. The solution was sonicated for 4 h to ensure the nano sheet formation of GO [28]. 1.0 g of ferrous sulfate hydrate, 0.030 g of copper sulfate hydrate and 2.0 g of sodium acetate anhydrous were mixed to the sonicated solution. The mixture was stirred normally using magnetic stirrer for one hour to ensure the homogenous mixing. The solution was transferred to Teflon lined stainless steel auto clave and heated at 200 °C for 6 h. The obtained solution was naturally cooled and was centrifuged and blackish precipitates recovered, washed with ethanol several times to remove the impurities, finally the sample was dried in vacuum drier at 60 °C for 12 h. Similarly single metal Fe/rGO (ST) catalyst was prepared using the same method and sequence except the addition of copper precursor.

2.2.2. Synthesis of composites using chemical reduction route

The wet chemical reduction method was used for the synthesis of graphene supported iron composite. In this method, 0.5 g of GO and 1.6 g of ferrous sulfate hydrate were mixed in 150 ml of ultra-pure water in a round bottom flask. The mixture was sonicated for 1 h to make it homogenous. The pH of solution was continously adjusted to 4 to avoid possible oxidation of the metal. The homogenous solution was continued to mix for couple of hours using magnetic stirrer to ensure the exchange of ferrous ions on the surface of GO. 1.0 M sodium borohydride was added in the solution drop wise as the reducing agent for iron particles on the surface of GO. The addition of $NaBH_4$ started to form blackish particles in the suspension and the particles were separated by filtration after completion of reaction. The solid catalyst obtained was washed three times, first with deionized water and then with ethanol to remove the traces of impurities. The sample was vacuum dried at 60 °C overnight. The synthesized composite was designated as Fe/rGO (CR). A copper-iron bimetal catalyst supported by rGO [Fe-Cu/rGO (CR)] was prepared using the CR method, by adding 0.048 g of $CuSO_4{\cdot}5H_2O$ along with the iron precursor. The iron and copper reduction occurs after the addition of $NaBH_4$ as expressed in Eqs. (1)–(2).

$$Fe^{2+} + 2BH_4^- + 6H_2O \rightarrow Fe^0 + 2B(OH)_3 + 7H_2 \quad (1)$$

$$Cu^{2+} + 2BH_4^- + 6H_2O \rightarrow Cu^0 + 2B(OH)_3 + 7H_2 \quad (2)$$

2.3. Experimental procedure

The standard solution (0.15 mM concentration) of TCA was