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

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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 N₂ 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 m²/g and 119.2 m²/g as compared to the ones synthesized via the CR method, i.e. 13.8 m²/g and 38.0 m²/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 longterm 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 $\text{Fe}^{2+}/\text{Fe}^{3+}$ with hydrogen peroxide (H_2O_2). However, there are several drawbacks such as: (i) production of large quantities of iron salts as 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 ($\text{OH}^\bullet$) [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 copperferrite/spinel-oxide catalyst for methanolysis of palm oil [15]. Porous FeNi 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 associated 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 overall effectiveness 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 ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 99%), sodium nitrate (NaNO_3 , 98%), ethanol (99.8%), copper sulfate hydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 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 ultra-pure 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 autoclave 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 hour to make it homogenous. The pH of solution was continuously adjusted to 4 to avoid possible oxidation of the metal. Then the homogenous solution was mixed again for 30 min using magnetic stirrer to ensure the 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 NaBH₄ 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 CuSO₄·5H₂O along with the iron precursor. The iron and copper reduction occurs after the addition of NaBH₄ as expressed in Eqs. 1–2.

2.3. Experimental procedure

The standard solution (0.15 mM concentration) of TCA was prepared by allowing pure aqueous phase liquid TCA to equilibrate with milli-Q highly pure water in the absence of light for one hour under moderate stirring. The solution of nanocomposite and contaminant without addition of oxidant was stirred continuously for 45–60 min to achieve adsorption-desorption equilibrium. The degradation experiments were carried out in a cylindrical jacketed reactor having two openings at the top, one as sampler and the other for the input.

The glass reactor has inner diameter 6.0 cm and height 9.0 cm. A temperature water bath (DC Ningbo, China) was used to circulate the water in the external jacket of the reactor and maintain temperature at $25 \pm 0.5^\circ\text{C}$ during all experiments. The required amount of reagents and catalysts was added sequentially in the reactor containing TCA and the magnetic stirrer with Teflon coating was used to ensure the homogeneous mixing of the reagents. The samples were withdrawn from the sampler opening of the reactor after required intervals and *n*-hexane was mixed immediately before the analysis. All experiments were performed in duplicate and the average value was reported.

2.4. Characterization of nanocomposites

The morphology and surface characteristics of the synthesized catalysts were characterized by scanning electron microscope (SEM, JSM-630LV, Tokyo, Japan) and transmission electron microscope and EDS mapping (TEM, JEM-2100 electron microscope operated at an accelerating voltage at 200 kV). The phase identification and the crystal structure of catalysts were tested by x-ray diffraction (XRD) with a Rigaku D/max diffractometer (2550 VB/PC; $\text{CuK}\alpha$ ($\lambda = 0.154$ nm radiation)). The operating current and voltage were 40 mA and 40 kV respectively, in the 2θ range from 5° to 80° at scanning speed of 5° min^{-1} . The key phases were recognized by matching the diffraction lines with reference patterns in the Joint Committee of Powder Diffraction Standards (JCPDS) standard cards. The BET surface area, total pore volume, particle size and pore size of the prepared catalysts were determined with nitrogen adsorption desorption isotherms at 77 K using Micromeritics Tristar-3000 Analyzer Quantasorb Jr. Instrument (Quantachrome Co. UK). Prior to measurements, all composites were degassed at 200°C for 2 h in N_2 atmosphere. Fourier transformation infrared spectroscopy (FTIR) of the composites was conducted using a Nicolet 6700 (Thermo Fisher Scientific, $4000\text{--}400 \text{ cm}^{-1}$) with a scan no. 32 and spectral resolution of 4 cm^{-1} . The surface characteristics of synthesized nanocomposites were evaluated by X-ray photoelectron spectroscopy (XPS) having ESCALAB 250Xi instrument with an $\text{Al-K}\alpha$ radiation source at an energy step size of 0.05 eV for high resolution XPS spectrum. The stoichiometric concentrations of the prepared samples were verified by energy dispersive x-ray spectroscopy (EDS), employing an AMETEX instrument with silicon drift detector (SDD).

2.5. Analytical methods

The samples for TCA (1.0 ml) were collected at desired intervals and extracted with 1.0 ml of *n*-hexane and stirred vigorously using a vortex stirrer for 3–5 min, followed by ~5 min of quiescence to ensure the separation. The extracts were transferred to GC vial by plastic dropper. The concentration of TCA was analyzed by gas chromatography (Agilent GC 7890A, Palo Alto, 209 CA, USA) with auto sampler (Agilent 7693), an electron capture detector (ECD) and a DB-VRX column with $1.4 \mu\text{m}$ thickness, $250 \mu\text{m}$ inner diameter and 60 m length. The detector, oven and injector temperature were fixed at 260°C , 75°C and 250°C respectively. Electron spin resonance (ESR) spectra was measured by EMX-8/2.7C, Bruker, Germany with Microwave Bridge (conversion time, 40.96 ms, microwave frequency 9.866 GHz, field sweep 100 G, time constant 163.84 ms, microwave power 2.016 mW, modulation amplitude 1 G and number of scans, The pH measured using pH meter (Mettler-Toledo DELTA 320, Greifensee, Switzerland).

3. Results and discussion

3.1. XRD analysis

The composites were analyzed using x-ray diffraction (XRD) as shown in Fig. 1. The sharp and broadest peak at 2θ of 10.9° clearly indicates that the graphite powder totally exfoliated to GO. The diffraction peak disappeared and a new broad peak appeared at approximately 24° , which shows reduction of GO by EG or NaBH_4 [29,30]. The characteristic peak of monoclinic tenorite CuO was observed at 35.49° (0 0 2) in the case of Fe-Cu/rGO (CR) and Fe-Cu/rGO (ST) catalysts, in agreement with JCPDS No. 45-0937 [31]. This clearly indicated the presence of Cu on the rGO. The representative peaks of Fe-Cu/rGO (CR) catalyst were observed at $2\theta = 35.64^\circ, 44.58^\circ, 57.07^\circ$ and 62.77° indexed as (3 1 1), (4 0 0), (5 1 1) and (4 4 0), respectively. These peaks suggest cuprospinel (CuFe_2O_4) crystals having face centered cubic crystal lattice, in agreement with JCPDS # 25-0283. CuFe_2O_4 belongs to spinel type ferrites having the same structure but slightly different physico-chemical properties due to the presence of copper [32]. The characteristics reflections become more prominent to Cu-ferrite phase at $2\theta = 18.27^\circ, 30.05^\circ, 35.39^\circ, 37.02^\circ, 43.02^\circ, 53.36^\circ, 56.89^\circ, 62.47^\circ$ and 73.89° when the ST technique was applied for the synthesis of catalyst. The relative intensity and position of peaks are in agreement with other researchers [33] and JCPDS # 73-2317.

The appearance of additional peaks with increased intensity for the material produced using the ST technique indicates that Fe-Cu particles successfully embedded on the rGO sheet. The broadness of peaks may be due to strong structural dimensions and transformation to smaller crystalline size of Fe-Cu/rGO (ST) catalyst [34], consistent with the BET and TEM analyses to be discussed below. The lattice constant, d-spacing and crystal size of the prepared catalysts are shown in Table 1. The lattice constant slightly increased from $8.34 \text{ \AA}$ to $8.40 \text{ \AA}$ due to change of face center cubic crystals of cuprospinel to cubic crystal of copper iron. The d spacing was calculated by Bragg's equation (Eq. (3))

$$n\lambda = 2d \sin \theta \quad (3)$$

Where

λ = X-ray wavelength = 0.154 nm d = interlayer spacing (nm)

θ = Bragg diffraction angle (deg.)

It is evident that diffraction peaks shifted towards low angle due to the heat treatment induced in the ST synthesis that increased the interlayer spacing of the sample [35]. The shift might be due to the increase in copper contents observed in the EDS analysis. The increase in d-spacing also validated the penetration of nano particles into the surface of GO results expansion [36]. The high intensity of peaks reflected high crystallinity of the Fe-Cu particles. Scherer's equation (Eq. (4)) was used to calculate the crystal size of prepared catalysts using the most intense peaks found in each XRD pattern.

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (4)$$

Where D is crystal size (nm), K = 0.90 is the Scherer's constant, λ the x-ray wavelength, β the peak width of half-maximum (FWHM), and θ the Bragg diffraction angle.

It was observed (Table 1) that catalysts synthesized using the ST technique have lower crystal size as compared to CR catalysts.

In single metal composite supported on rGO, similar behavior was observed. The peaks in Fe/rGO (CR) observed at 35.63°, 43.28°, 57.27° and 62.94° confirmed the presence of maghemite (γ -Fe₂O₃) crystals (JCPDS # 39-1346). When the composite was synthesized by the ST method, the characteristic peaks were observed at 30.09°, 35.42°, 43.05°, 53.39°, 57.15° and 62.61° indexed as (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) respectively that confirmed the presence of magnetite (Fe₃O₄) cubic crystals (JCPDS # 19-0629) with cubic spinel structure [33]. It has been observed that the peaks shifted towards lower Bragg angle when such samples are converted to crystalline magnetite due to heating [37]. The comparison of the XRD peaks of γ -Fe₂O₃ (Fe/rGO (CR)) and crystalline Fe₃O₄ (Fe/rGO (ST)) showed that latter were much broader, indicating that the particle size of crystalline Fe₃O₄ was smaller than that of γ -Fe₂O₃ [38]. It was also confirmed by BET analysis, as discussed later. Maghemite is considered an Fe (II) deficient magnetite according to its chemical formula. The Fe₃O₄ and γ -Fe₂O₃ differs in the presence of cationic vacancies within the octahedral sites, and the vacancies only depend on the catalyst preparation methods [39]. Thus formation of magnetite in the ST method favors degradation efficiency due to availability of more Fe (II). The noticeable and prominent appearance of peaks confirmed that iron oxides are well dispersed at the surface of rGO. The increase in interlayer spacing and smaller crystal size were also observed for the Fe/rGO (ST) catalyst.

3.2. Textural characterization

The influence of preparation methods on the textural properties of synthesized nanocomposites were characterized by nitrogen adsorption-desorption measurements (Table 2). It was observed that all isotherms follow the IUPAC type IV classification along with hysteresis type H3, a characteristic of micro-mesoporous material [40]. Nitrogen filling occurs approximately at P/P₀ = 0.40–0.80 due to the capillary condensation occurring in pores, reflecting a high uniformity of mesopores. The beginning of the linear middle section of the isotherm denotes the completion of monolayer adsorption and the beginning of multilayer behavior [35]. The sorption process varies depending on the size of pores that increase from micro to meso, and concomitantly the relative pressure needed to fill the pores will also increase. The nanocomposites synthesized by the ST method showed higher adsorption at low pressure, indicating a large specific micropore volume (Fig. 3) compared to the CR nanocomposites (Fig. 2). The significantly larger slope of adsorption-desorption isotherms of the ST synthesized composites is consistent with the larger specific surface area due to the small pore and particle size that is consistent with the TEM results.

The micropore domain is considered to be comprised of pores with diameters of less than 2 nm, whereas the mesopores comprise diameters between 2 nm and 50 nm [41,42]. The pore size distribution curves [Fig. 2 & 3 (insets)] of synthesized materials, calculated by the Barrett-Joyner-Halenda (BJH) method using desorption branches verifies the existence of a wide range of pore sizes. The Fe/rGO (ST) material appears to consist solely of mesopores, whereas the Fe-Cu/rGO (ST) material comprises both micro and mesoporous structure. The porous structure in the ST synthesized composites enhances the oxidation efficiency by enhancing available active sites, and promote generation of radicals, which eventually stimulate degradation [43].

Inspection of Table 2 reveals that surface area is appreciably greater for the nanocomposites synthesized using the ST method compared to the CR technique. In the case of the single metal CR catalyst, surface area of 13.77 m²/g, pore volume of 0.042 cm³/g, pore size of 12.41 nm and particle size of 435 nm were observed. While for the ST technique, surface area, pore volume, pore size and particle size were 93.65 m²/g, 0.196 cm³/g, 8.38 nm and 64 nm respectively. The results indicate that the mesoporous structure of catalyst was remarkably affected by calcination temperature and reducing agent that increased the surface area [5]. The Fe-Cu/rGO (CR) and Fe/rGO (ST) had surface areas of 38.05 m²/g and 119.25 m²/g, respectively. An increase in surface area was also observed after addition of a second metal in already prepared single metal catalyst through the CR or the ST methods [3,19]. The particle size reduced from 157 nm to 50 nm when Fe-Cu/rGO synthesized by CR and ST methods, respectively, showing consistency with the TEM results discussed in the next section.

3.3. Surface morphology

The morphology and surface characteristic of single and bimetallic catalyst supported on rGO were obtained using SEM and TEM images. The smooth surface of rGO was evident as depicted in TEM images. The formation of wrinkle type structure along with aggregation was observed in the CR synthesized Fe/rGO composite (Fig. 4a). Whereas, the ST synthesized nanocomposite had spherical shaped particles uniformly distributed on the surface of rGO as shown in Fig. 4b. The measurement of particle size distribution indicated that particle diameters range from 60 to 85 nm. In Fe-Cu/rGO (CR), the TEM image verified cauliflower-shaped structures with symmetrical distribution of iron copper particles (Fig. 4c). The planar, porous, chain, and wrinkle shapes along with core shell structure were observed at close magnification of the image as shown in Fig. 4d (inset) in the ST synthesized Fe-Cu/rGO nanocomposite. The particle size was 50 nm, having core 42 nm and shell 4 nm. The size of particles observed in TEM images are in close agreement with XRD and BET results. The SEM images shown in Fig. 5a & b of single metal catalysts clearly indicate well-distributed particles of smaller size particles in the ST synthesized material compared with the CR nanocomposite. The Fe-Cu/rGO (ST) catalyst showed spherical metallic particles (light spots) uniformly dispersed at rGO (Fig. 5d). The homogeneity of Fe-Cu nanocomposites was further verified by EDS mapping (Fig. S1).

The elemental analysis of rGO supported Fe and Fe-Cu catalysts was performed using energy dispersive x-ray spectroscopy (EDS) as shown in Fig. 6a & b. It is evident that

significant amount of iron was present along with copper. The Fe/rGO and Fe/Cu ratios determined from EDS analysis are similar to the prepared stoichiometric compositions.

3.4. X-ray photoelectron spectroscopy

The performed XPS analysis of solvo-thermally prepared composite provided the information of surface composition, showing the presence of metallic species with an atomic ratio of 9.34 for Fe to Cu that is well in consistent to the performed EDS analysis showing 9.83, that infers the overall composite homogeneity as shown in Table 2. Whereas, the presence of graphene oxide in its reduced form is validated due to the observed asymmetrical behavior, towards higher binding energy of C 1s peak at 284.8 eV. Upon deconvolution the C 1s spectra, a low intense peak was generated at a higher binding energy value of 1.2 eV from the main peak, of CeC, as the characteristic peak for CeO (Fig. S2). This low intense peak is attributed to partially oxidized graphene or partially reduced graphene oxide, where the later usually has a high intense peak at this binding energy value as reported in the earlier studies [44]. The metallic components of the composite had the binding energy values of their characteristic peaks, for Fe 2p_{3/2} and Cu 2p_{3/2} at 711.4 eV and 933.1 eV, respectively, as shown in Fig. 7. The oxidation states of +3 and +2 were designated to Fe 2p_{3/2} and Cu 2p_{3/2} that are well in agreement to the previously reported works on copper ferrite graphene hybrids [45,46]. On comparing the XPS spectra of metallic constituents as prepared and on being recovered from degradation process, there appeared no change for Fe 2p_{3/2} but Cu 2p_{3/2} possessed further broadening of characteristic peak. This appearance resulted was due to the rise in intensity of peak at 934.9 eV for Cu 2p_{3/2}, evident after deconvolution of obtained spectra and was attributed to the occurred variation in copper oxidation state during the degradation process. Furthermore, the above presented comparative analysis of Cu 2p_{3/2} elucidated the core side presence of copper as the confronting specie during degradation [47].

3.5. FTIR spectroscopy

FTIR spectroscopy was used for identification and quantification of functional groups associated with constituents such as oxides and oxyhydroxides in a given sample. The FTIR spectra of different synthesized samples were recorded between 4000 cm⁻¹ and 400 cm⁻¹. A broad absorption peak between 3550 cm⁻¹ and 3350 cm⁻¹ observed in the spectrums of all catalysts is attributed to OH-stretching vibrations of hydroxyl groups and water molecules [48]. A strong band at 1640 cm⁻¹ can be associated to hydroxyl bending vibrations. The sharp band observed in all samples between 670 and 640 cm⁻¹ was assigned with the lattice vibrations [49].

The FTIR spectra of single metal catalyst synthesized on rGO is shown in Fig. 8. It is noted that the spectrum shoulder in Fe/rGO (CR) at 650 cm⁻¹ and 750 cm⁻¹ indicate the presence of maghemite [50]. Moreover, the spectrum clearly reveals a large and intense peak at 3430 cm⁻¹ that can be assigned to hydroxyl stretching of adsorbed water molecules or surface OH groups. In Fe/rGO (ST), the shift of peak from 650 cm⁻¹ to 570 cm⁻¹ clearly indicates that maghemite converted to magnetite. The OH stretching peak at 3430 cm⁻¹ became broader for the ST synthesized nanocomposite. The presence of broad bands at 1630 cm⁻¹ and 1550 cm⁻¹ is attributed to COOH and C=O stretching respectively, indicating the functionalization

of magnetite nanoparticles with carboxylic and/or hydroxyl groups of reduced graphene oxide.

The FTIR spectra of bimetallic catalysts (Fig. 8 inset) indicates two absorption peaks at 585 cm^{-1} and 420 cm^{-1} . According to the geometrical configuration of metallic oxides, the peak at 585 cm^{-1} is due to the vibrations of Fe-O complexes [4], and 420 cm^{-1} is due to Cu-O complexes to form CuFe_2O_4 spinel structure [51]. The peak at 3440 cm^{-1} characterizes the presence of OH functional group. The broadness of OH peak and sharpness of Fe-O band indicates the abundance of Fe oxides in the ST synthesized catalysts. Additional bands at 1385 cm^{-1} and 1109 cm^{-1} can be assigned to the carbonate stretching vibrations. The existence of carbonate specie in synthesized samples suggested by IR bands at 1540, 1380 and 1116 cm^{-1} is due to the carbonation of iron oxides/hydroxides by atmosphere CO_2 [52].

The FTIR spectra suggested that the samples, i.e. Fe/rGO (CR) and Fe/rGO (ST), consisted of maghemite and magnetite crystalline phases, respectively, and indicates formation of CuFe_2O_4 spinel structure, which is in agreement with the XRD results.

3.6. Catalytic performance

The catalytic activity of nanocomposites prepared by different routes was investigated for the degradation of TCA and the results were compared to control experiments conducted in the absence of catalyst and oxidant SPC. All experiments were performed at 0.15 mM TCA concentration. The removal of TCA caused by adsorption was measured before the assessment of TCA degradation. The adsorption-desorption equilibria was achieved between TCA and prepared nanocomposites by stirring all reagents vigorously for one hour without addition of SPC as shown in Fig. 9. There was no significance difference observed in the next hour (Fig. 10) that confirmed the achievement of equilibrium. The TCA adsorption on rGO alone was investigated and 18% adsorption rate was achieved. The adsorption of TCA was observed to be 20%, 25%, 22% and 28% using Fe/rGO (CR), Fe/rGO (ST), Fe-Cu/rGO (CR) and Fe-Cu/rGO (ST), respectively. The higher adsorption capacity of the ST synthesized catalysts may be associated to the higher surface area and larger pore volume [3,5].

The catalytic activity of the Fe-nanocomposites was investigated using catalyst doses of 0.2, 0.4, 0.6, 0.8 and 1.0 g/L. The Fe/rGO (CR) achieved a maximum degradation of 77.5% at 1.0 g/L dose. Minimal increase in the TCA degradation (77%–77.5%) was observed from 0.8 to 1.0 g/L. (Fig. 11a). The ST synthesized Fe/rGO nanocomposite showed higher efficiency (90%) at the 0.8 g/L dose (Fig. 11b) but at 1.0 g/L, the degradation decreased to 77%. At lower catalyst dosages of 0.4 and 0.6 g/L, low contaminant removal efficiency was observed for both the ST and CR synthesized nanocomposites.

For the bimetallic nanocomposites, a TCA degradation efficiency of 81% was achieved at 0.6 g/L catalyst [Fe-Cu/rGO (CR)] dose (Fig. 12a). Whereas Fe-Cu/rGO (ST) nanocomposite showed the highest efficiency (92%) at a dose of 0.4 g/L as shown in Fig. 12b. The Fe-Cu/rGO (CR) composite achieved 37.8%, 65.2%, 74.8% and 72.8% TCA degradation efficiency at 0.2, 0.4, 0.8 and 1.0 g/L catalyst doses respectively. However the

ST-synthesized bimetallic catalyst attained higher degradation efficiencies of 81.7% (0.2 g/L), 79.1% (0.6 g/L), 77.6% (0.8 g/L) and 75.1% (1.0 g/L).

The decrease in the catalytic performance observed at higher doses could be due to greater OH radical production at higher concentrations of catalyst. These may act as scavengers due to its higher reaction rate constant ($5.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) than OH $\cdot$ generation rate constant ($76 \text{ M}^{-1}\text{s}^{-1}$) as shown in Eqs. (5)–(6). A number of side reactions could also occur in the system that reduces the degradation efficiency [53]. Fe (II) reacts with OH $\cdot$ and produces Fe (III) and OH $^-$ with a rate constant of $3.0 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ (Eq. (7)). The superoxide radicals produced also reacts with other ions and radicals produced in the system and forms various by-products (Eqs. (9)–(10)) [54]. The reaction rate constant of TCA and OH is found to be $7.82 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ [55]. It has been observed that the side reactions occurred in the process have higher reaction rate constant than rate constant of OH $\cdot$ with TCA. This may lead to a decrease in TCA degradation efficiency [54]. Experiments were also performed to analyse the effect of SPC doses (20, 25, 30 and 35 mM) on TCA destruction as shown in Figs. 13 and 14. It was observed that the nanocomposites show lower efficiency for removal of TCA at the SPC concentration above and below 30 mM, which could be due to the consumption of H₂O₂ by OH $\cdot$ and some additional products produced during the process (Eq. (8)). The enhancement in the degradation of TCA using Fe-Cu than single metallic samples are due to the combined effects of bimetals owing to enhancement in physical and chemical characteristics, which have been also investigated in various studies [19,56,57]. Furthermore, the formation of intermediates and final products was investigated by GC–MS analysis. The analysis confirmed the noticeable concentration of dichloroethane (DCA) and chloroethene (CA) intermediates products that further transformed to chloride ions, carbondioxide and water as end products (Fig. S3). The dechlorination process elucidated an increase in chloride ions concentration during degradation of TCA (Fig. S4). Assuming that complete dechlorination process produced 3 mol of Cl $^-$ from 1 mol of TCA. The measured Cl $^-$ concentration in our study was 56% of the theoretical yield which is consistent with previously reported results [58].

4. Conclusions

In this study, single (Fe) and bimetallic (Fe-Cu) nanocomposite catalysts supported on rGO were tested for SPC-based TCA degradation. The materials were produced with two methods, chemical reduction and solvo-thermal. The ST approach produced Fe/rGO and Fe-Cu/rGO catalysts with larger specific surface areas and high particle dispersion, exhibiting higher catalytic activity for TCA degradation compared to the catalysts prepared by the CR method.

The eminent appearance of peaks in XRD analysis of ST synthesized composites affirmed transformation to highly crystalline structure and small crystalline size compared to CR nanocomposite. The magnitude of spectrums in FTIR revealed abundance of Fe-oxides in ST synthesized nanocomposites. The combined SEM, TEM, BET and EDS mapping results expressed the superior catalytic performance of ST synthesized nanocomposites which was due to the well distribution of nano particles and formation of definite crystal structures. The higher surface areas confirmed the availability of more active sites for the generation of reactive oxygen species (ROS) in SPC system. Moreover, XPS spectra confirmed the occurrence in variation in oxidation states of copper during the degradation process. GC-MS analysis elucidated DCA and CA as intermediates products. In conclusion, the ST-synthesized Fe-Cu@rGO nanocomposite provided improved degradation of TCA in the SPC activated system, and shows significant potential in heterogeneous catalysis applications for AOP treatment of contaminants in water.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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References

1. Antonopoulou M, Evgenidou E, Lambropoulou D, Konstantinou I. Water Res. 2014; 53:215–234. [PubMed: 24525070]
2. Wang J, Liu C, Tong L, Li J, Luo R, Qi J, Li Y, Wang L. RSC Adv. 2015; 5:69593–69605.
3. Danish M, Gu X, Lu S, Brusseau ML, Ahmad A, Naqvi M, Farooq U, Zaman WQ, Fu X, Miao Z. Appl. Catal. A. 2017; 531:177–186.

4. Farooq U, Danish M, Lu S, Naqvi M, Gu X, Fu X, Zhang X, Nasir M. *Res. Chem. Intermed.* 2016;1–18.
5. Wang Y, Zhao H, Zhao G. *Appl. Catal. A.* 2015; 164:396–406.
6. Yu L, Chen J, Liang Z, Xu W, Chen L, Ye D. *Sep. Purif. Technol.* 2016; 171:80–87.
7. Danish M, Gu X, Lu S, Zhang X, Fu X, Xue Y, Miao Z, Ahmad A, Naqvi M, Qureshi AS. *Water Air Soil Pollut.* 2016; 227:1–14.
8. Danish M, Gu X, Lu S, Xu M, Zhang X, Fu X, Xue Y, Miao Z, Naqvi M, Nasir M. *Res. Chem. Intermed.* 2016; 42:6959–6973.
9. Ahmad A, Gu X, Li L, Lv S, Xu Y, Guo X. *Environ. Sci. Pollut. Res.* 2015; 22:17876–17885.
10. Danish M, Gu X, Lu S, Naqvi M. *Environ. Sci. Pollut. Res.* 2016; 13:13298–13307.
11. Tabet D, Saidi M, Houari M, Pichat P, Khalaf H. *Chem. Eng. J.* 2012; 203:269–276.
12. Doong R, Lai Y. *Chemosphere.* 2006; 64:371–378. [PubMed: 16466778]
13. Lee JP, Chen D, Li X, Yoo S, Bottomley LA, El-Sayed MA, Park S, Liu M. *Nanoscale.* 2013; 5:11620–11624. [PubMed: 24126702]
14. Luadthong C, Khemthong P, Nualpaeng W, Faungnawakij K. *Appl. Catal. A.* 2016; 525:68–75.
15. Long X, Ma Z, Yu H, Gao X, Pan X, Chen X, Yang S, Yi Z. *J. Mater Chem A.* 2016; 4:14939–14943.
16. Zhu F, Li L, Ma S, Shang Z. *Chem. Eng. J.* 2016; 302:663–669.
17. Fu F, Cheng Z, Lu J. *RSC Adv.* 2015; 5:85395–85409.
18. Danish M, Gu X, Lu S, Ahmad A, Naqvi M, Farooq U, Zhang X, Fu X, Miao Z, Xue Y. *Chem. Eng. J.* 2017; 308:396–407.
19. Julkapli NM, Bagheri S. *Int. J. Hydrogen Energy.* 2015; 40:948–979.
20. Huang KC, Ehrman SH. *Langmuir.* 2007; 23:1419–1426. [PubMed: 17241068]
21. Zhang QL, Yang ZM, Ding BJ, Lan XZ, Guo YJ, Nonferr T. *Metal Soc.* 2010; 20:s240–s244.
22. Das TK, Bhattacharya R, Manna A, Saha S. *Eur. Phys. J. Appl. Phys.* 2010; 51:30605.
23. Wang W, Zhu Q, Dai Q, Wang X. *Chem. Eng. J.* 2017; 307:1037–1046.
24. Mishra D, Arora R, Lahiri S, Amritphale SS, Chandra N. *Prot. Met.* 2014; 50:628–631.
25. Hernández-Uresti D, Martínez-de la Cruz A, Torres-Martínez L. *Ceram. Int.* 2016; 42:3096–3103.
26. Li W, Qiao X, Zheng Q, Zhang T. *J. Alloy Compd.* 2011; 509:6206–6211.
27. Durge R, Kshirsagar RV, Tambe P. *Procedia Eng.* 2014; 97:1457–1465.
28. Zang X, Sun C, Dai Z, Yang J, Dong X. *J. Alloy Compd.* 2017; 691:144–150.
29. Zou Y, Wang Y. *ACS Nano.* 2011; 5:8108–8114. [PubMed: 21939228]
30. Ning W, Shen H, Liu H. *Appl. Catal. A.* 2001; 211:153–157.
31. Ristic M, Hannover B, Popovic S, Music S, Bajraktaraj N. *Mater. Sci. Eng. B.* 2000; 77:73–82.
32. Chen F, Xie S, Zhang J, Liu R. *Mater. Lett.* 2013; 112:177–179.
33. Albuquerque AS, Tolentino MV, Ardisson JD, Moura FC, de Mendonça R, Macedo WA. *Ceram. Int.* 2012; 38:2225–2231.
34. Lawrence G, Baskar AV, El-Newehy MH, Cha WS, Al-Deyab SS, Vinu A. *Sci. Technol. Adv. Mater.* 2015; 16:024806. [PubMed: 27877767]
35. Saad L, Riad M, Serb J. *Chem. Soc.* 2008; 73:997–1009.
36. Cao X, Prozorov R, Koltypin Y, Kataby G, Felner I, Gedanken A. *J. Mater. Res.* 1997; 12:402–406.
37. Cao X, Koltypin Y, Prozorov R, Kataby G, Gedanken A. *J. Mater. Chem.* 1997; 7:2447–2451.
38. Laurent S, Forge D, Port M, Roch A, Robic C, Vander Elst L, Muller RN. *Chem. Rev.* 2008; 108:2064–2110. [PubMed: 18543879]
39. Sing KS. *Pure Appl. Chem.* 1985; 57:603–619.
40. Kierlik E, Monson P, Rosinberg M, Tarjus G, Phys J. *Condens. Matter.* 2002; 14:9295.
41. Voigt EM, Tomlinson R. *Can. J. Chem.* 1955; 33:215–231.
42. Zang XX, Sun CC, Dai ZY, Yang J, Dong XC. *J. Alloy Compd.* 2017; 691:144–150.
43. Blanton TN, Majumdar D. *Power Diff.* 2013; 28:68–71.

44. Fu Y, Chen Q, He M, Wan Y, Sun X, Xia H, Wang X. *Ind. Eng. Chem. Res.* 2012; 51:11700–11709.
46. Zhang W, Quan B, Lee C, Park SK, Li X, Choi E, Diao G, Piao Y. *ACS Appl. Mater. Interfaces.* 2015; 7:2404–2414. [PubMed: 25584805]
47. Nedkov I, Vandenberghe RE, Marinova T, Thailhades P, Merodiiska T, Avramova I. *Appl. Surf. Sci.* 2006; 253:2589–2596.
48. Oulego P, Villa-García MA, Laca A, Diaz M. *Dalton Trans.* 2016; 45:9446–9459. [PubMed: 27187786]
49. Prasad P, Prasad KS, Chaitanya VK, Babu E, Sreedhar B, Murthy SR. *J. Asian Earth Sci.* 2006; 27:503–511.
50. Daou T, Greneche J, Pourroy G, Buathong S, Derory A, Ulhaq-Bouillet C, Donnio B, Guillon D, Begin-Colin S. *Chem. Mater.* 2008; 20:5869–5875.
51. Selvan RK, Augustin C, Berchmans LJ, Saraswathi R. *Mater. Res. Bull.* 2003; 38:41–54.
52. Su C, Suarez DL. *Clays Clay Miner.* 1997; 45:814–825.
53. Miao Z, Gu X, Lu S, Dionysiou DD, Al-Abed SR, Zang X, Wu X, Qiu Z, Sui Q, Danish M. *Chem. Eng. J.* 2015; 275:53–62.
54. Miao Z, Gu X, Lu S, Brusseau ML, Yan N, Qiu Z, Sui Q, Hazard J. *Mater.* 2015; 300:530–537.
55. Nelson L, Shanahan I, Sidebottom HW, Treacy J, Nielsen OJ. *Chem J. Kinet.* 1990; 22:577–590.
56. Singh AK, Qiang X. *Chem. Catal. Chem.* 2013; 5:652–676.
57. Mohan B, Park KH. *A. Appl Catal.* 2016; 519:78–84.
58. Gu X, Lu S, Li L, Qiu Z, Sui Q, Lin K, Luo Q. *Ind. Eng. Chem. Res.* 2011; 50:11029–11036.

Fig. 1.
X-ray diffraction (XRD) of GO, Fe/rGO (CR), Fe/rGO (ST), Fe-Cu/rGO (CR) and Fe-Cu/rGO (ST).

Fig. 2. N₂ adsorption-desorption isotherms of single metal supported rGO nanocomposites [Fe/rGO (CR) and Fe/rGO (ST)], particle size distribution (inset) curve of Fe/rGO (ST).

Fig. 3. N₂ adsorption-desorption isotherms of Fe-Cu/rGO (CR) and Fe-Cu/rGO (ST), particle size distribution curve of Fe-Cu/rGO (ST) catalyst (inset).

Fig. 4. TEM images of a) Fe/rGO (CR), b) Fe/rGO (ST), c) Fe-Cu/rGO (CR), and d) Fe-Cu/rGO (ST) and core shell formation (inset).

Fig. 5.
SEM analysis of prepared nanocomposites a) Fe/rGO (CR), b) Fe/rGO (ST), c) Fe-Cu/rGO (CR), and d) Fe-Cu/rGO (ST).

Fig. 6. Energy dispersion spectroscopy (EDS) of a) Fe/rGO (ST), and Fe-Cu/rGO (ST).

Fig. 7. XPS spectra of a) Fe 2p_{3/2} and b) Cu 2p_{3/2} for Fe-Cu/rGO (ST) nanocomposites before and after use.

Fig. 8. Fourier transformation infrared (FTIR) of Fe/rGO (CR) and Fe/rGO (ST) nanocomposites, FTIR of Fe-Cu/rGO (CR) and Fe-Cu/rGO (ST) (inset).

Fig. 9.
The kinetic adsorption-desorption equilibrium of TCA on GO, Fe/rGO (CR), Fe/rGO (ST), Fe-Cu/rGO (CR) and Fe-Cu/rGO (ST), and SPC only. [nanocomposites] = 0.8 g/L.

Fig. 10.

The adsorption-desorption equilibrium of TCE on various catalysts with respect to time profile. [nanocomposite] = 0.8 g/L.

Fig. 11.

Effect of catalyst doses on TCA degradation, a) $[TCA]_0 = 0.15$ mM, $[SPC] = 30$ mM for Fe/rGO (CR), and b) $[TCA]_0 = 0.15$ mM, $[SPC] = 30$ mM for Fe/rGO (ST).

Fig. 12.

Effect of catalyst doses on TCA degradation, a) $[TCA]_0 = 0.15$ mM, $[SPC] = 30$ mM for Fe-Cu/rGO (CR), and b) $[TCA]_0 = 0.15$ mM, $[SPC] = 30$ mM for Fe-Cu/rGO (ST).

Fig. 13.

Effect of SPC doses on TCA degradation, a) $[TCA]_0 = 0.15$ mM, $[Fe/rGO (CR)] = 0.8$ g/L,
 b) $[TCA]_0 = 0.15$ mM, $[Fe/rGO (ST)] = 0.8$ g/L.

Fig. 14.

Effect of SPC doses on TCA degradation, a) $[TCA]_0 = 0.15$ mM, $[Fe-Cu/rGO (CR)] = 0.6$ g/L, b) $[TCA]_0 = 0.15$ mM, $[Fe-Cu/rGO (ST)] = 0.4$ g/L.

Table 1
XRD analysis of nanocomposites prepared by chemical reduction (CR) and solvothermal (ST) processes.

Sample	2 θ (deg.)	d-spacing (nm)	Lattice parameter (Å)	FWHM (deg.)	Crystallite size (nm)
Fe/rGO (CR)	35.63	0.2517		0.417	
	43.28	0.2088	8.34	0.535	20.91
	57.27	0.1607		0.193	
	62.94	0.1475		0.131	
Fe/rGO (ST)	30.09	0.2967		0.761	
	35.42	0.2530		0.875	
	43.05	0.2099	8.38	0.957	9.95
	53.39	0.1716		0.949	
Fe-Cu/rGO (CR)	57.02	0.1610		1.212	
	62.61	0.1482		1.054	
	35.64	0.2517		0.455	
	44.58	0.2030	8.29	0.070	19.16
Fe-Cu/rGO (ST)	57.07	0.1612		0.482	
	62.77	0.1479		0.035	
	18.27	0.4851		0.259	
	30.05	0.2967		0.498	
Fe-Cu/rGO (ST)	35.39	0.2532		0.503	
	43.02	0.2109	8.39	0.617	17.32
	53.36	0.1714		0.584	
	56.89	0.1615		0.609	
Fe-Cu/rGO (ST)	62.47	0.1486		0.619	
	73.89	0.1280		0.603	

Table 2

Physicochemical properties of synthesized nanocomposites

Sample	Surface area (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)	Particle size (nm)	Fe contents (wt%)	Cu contents (wt%)
Fe/rGO (CR)	13.77	12.41	0.0427	435.12	50.67	-
Fe/rGO (ST)	93.65	8.37	0.1960	64.06	51.12	-
Fe-Cu/rGO (CR)	38.05	14.27	0.1357	157.68	53.44	4.42
Fe-Cu/rGO (ST)	119.25	11.34	0.3382	50	50.04	5.78