Synthesis of akageneite (beta-FeOOH)/reduced graphene oxide nanocomposites for oxidative decomposition of 2-chlorophenol by Fenton-like reaction

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HIGHLIGHTS

- Ak/rGO was successfully prepared by co-precipitating and reduction processes.
- Fe—O—C band inhabited the reduction of graphene oxide.
- Degradation rate of 2-chlorophenol for Ak/rGO increased 2–5 times than that for Ak.
- Higher removal rate is due to the synergy of catalysis and adsorption of Ak/rGO.

GRAPHICAL ABSTRACT

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ABSTRACT

In this work, the composite of reduced graphene oxide and akageneite (Ak/rGO) was synthesised by co-precipitating and reduction processes. The morphological and structural features of the synthesized composites (Ak/rGO) were characterized by XRD, SEM, BET, FTIR, Zeta potential and XPS. The results revealed that (1) beta-FeOOH was successfully loaded on the reduced graphene oxide (rGO); (2) the presence of strong interfacial interactions (Fe—O—C bonds) between rGO and beta-FeOOH was observed; (3) the reduction of graphene oxide may be inhibited in the formation process of beta-FeOOH, producing rGO sheets rather than rGO sphere. In the heterogeneous Fenton-like reaction, the degradation rate constants of 2-chlorophenol (2-CP) increased 2–5 times after the addition of rGO probably due to the Fe—O—C bond. The increase of the content of rGO could contribute to the removal of 2-CP, due to the synergy of catalysis and 2-CP adsorption towards Ak/rGO. In this study, the Ak/rGO composite has exhibited great potential and significant prospects for environmental application.

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1. Introduction

Chlorophenols are aromatic compounds with chlorine, which are widely used in chemical industries, such as pesticides and dyes

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manufactures [1,2], as a consequence, leading to the exposure of chlorophenols in sediment of lakes and rivers [3], aerosols, and hazardous waste [4]. They are toxic and hardly biodegradable due to the stable C–C bond in the chlorinated compounds [5]. Chlorophenols might produce disagreeable taste and odor to drinking water at certain concentrations, causing a potential negative impact on the environment, particularly they have potential carcinogenic and mutagenic activity, damaging livers' physiological processes such as apoptosis and immune response [6,7]. Moreover, they constitute a particular group of priority toxic pollutants listed by the US EPA in the Clean Water Act [2,8].

Conventional methods for removing chlorophenols from wastewater include solvent extraction [9], adsorption [2,10], reverse osmosis [11], and chemical treatment processes [8,12], leading to harmful by-products, solid waste and the increase of disposal and regeneration costs. On the other hand, heterogeneous Fenton reaction, degrading organic contaminants via generating hydroxyl radicals ($\cdot\text{OH}$), has many advantages over the traditional treatment methods, such as no toxic, wide reaction pH range and easy separation. Recently, heterogeneous Fenton reaction has received extensive attention [13–15]. Beta-FeOOH was used as Fenton-like catalyst because of a channels structure parallel to the *c*-axis [16]. Xu et al. [13] reported that methyl orange was removed by beta-FeOOH, but it was low due to weak H_2O_2 -activating ability. Photo-Fenton technology was applied to enhance catalytic degradation rate. Besides Zhao et al. [14] reported that 17 β -estradiol was removed completely by beta-FeOOH resin in presence of H_2O_2 under visible-light irradiation. Among these materials, graphene-based composite material has gained considerable attention due to its excellent electronic properties and high surface area as well as edge reactivity [17]. The nanoparticles loaded on the graphene are not only able to prevent the aggregation of graphene from stacking but also improve the overall catalytic performance owing to the strong synergistic interaction between both components [18,19].

In this paper, the composite structures containing beta-FeOOH and reduced graphene oxide (Ak/rGO) was developed. The Ak/rGO was synthesised by co-precipitation method at low temperature (100 °C). To better understand their structures and functionalities, the composites were extensively characterized by using XRD, FE-SEM, FTIR, BET, Zeta potential and XPS. For the first time, the applicability of the composites in the degradation of 2-chlorophenol (2-CP) was evaluated in a heterogeneous Fenton reaction.

2. Experimental

2.1. Chemicals

Graphite powder (GP, 99.85%–C), sodium hydroxide (NaOH, 99%), hydrogen peroxide (H_2O_2 , 30%), 2-chlorophenol (2-CP, 97%) and *n*-butyl alcohol ($\text{C}_4\text{H}_9\text{OH}$, 98%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 97%) was obtained from J&K Scientific Ltd. All the aqueous solutions were prepared by using ultrapure water (Mill-Q Biocel, 18 M Ω).

2.2. Synthesis of beta-FeOOH(Ak) nanoparticles on reduced graphene oxide (Ak/rGO)

GO was prepared from graphite powder (GP) according to a modified Hummers method [20,21]. In detail, GP (10.0 g) was put to a mixture of concentrated H_2SO_4 and H_3PO_4 (9:1, 360 ml:40 ml). At the same time, KMnO_4 (50.0 g) was added slowly to the above mixture with stirring for 2 h at 35–40 °C. Then the solution was transferred to a 50 °C water bath with a mixing for 24 h, following by

the addition of ice (1 kg) and H_2O_2 (30%, 3 ml). The mixture was centrifuged with 4000 rpm. Then the solid in the bottom was washed with 10% HCl solution 8 times and with ethyl alcohol 8 times respectively. Finally, the collected brown powder was freeze-dried in a vacuum and stored in the ultrapure water.

GO suspension (800 mg, 160 ml) was sonicated in a flask for 2 h. After the addition of the solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.96 g, 20 ml), the pH of the mixture was adjusted to 1.5 following a stirring for 4 h. The urea was added to the above mixture until pH 1.6 with a 10 min stirring, heated at 100 °C of oil bath for 4 h. Last, the solid was centrifuged and washed with the ultrapure water till the pH of the supernatant was about 7.0, storing in the ultrapure water. This product was noted as Ak-20, meaning that the mass ratio of Fe to the mixture was 20%.

Preparation of Ak-40, Ak-60 and Ak-80 products was the same as that of Ak-20. Ak and rGO were obtained without GO or $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ according to the method of the synthesis of Ak-20.

2.3. Fenton-like catalytic oxidation of 2-chlorophenol

Batch experiments were performed in plastic vessels at 298 K. Catalysts and 2-CP were added into the reactors with 20 mL of final solutions with the concentrations of 1 g L⁻¹ and 100 mg L⁻¹, respectively. The pH of initial suspension was adjusted to 4 or 9 by 0.1 M NaOH or HNO_3 . The reaction was initiated by 0.1 M H_2O_2 , and the suspension was vibrated at a speed of 200 r min⁻¹. After different reaction time, the solutions were centrifuged and each supernatant was collected by filtering through 0.22 μm membrane (PVDF). Finally, *n*-butanol (20 μL) was added to the supernatant.

The inductively coupled plasma-atomic emission spectrometry (ICP-AES, Prodidy, Leeman Co.) was used to measure Fe concentration. The concentration of 2-CP in supernatants was determined by using Water 1525 high-performance liquid chromatography (HPLC) equipped with Water 2487 dual λ absorbance detector. A C₁₆ column (4.6 mm $\times$ 150 mm) was used as a separation column. Samples were injected into a 50 μL loop and mobile phase for 2-CP was H_3PO_4 (pH 3.0)-acetonitrile (60:40) with a flow rate of 1 mL min⁻¹. The wavelength was set at 273 nm for 2-CP.

2.4. H_2O_2 degradation

Experiments for degradation of H_2O_2 on the Ak, rGO and Ak-40 without 100 mg L⁻¹ 2-CP were the same with that for degradation of 2-CP. H_2O_2 concentration of the supernatant without *n*-butanol was determined immediately according to potassium titanium (IV) oxalate spectrophotometric method (U-2910, 400 nm) [22].

2.5. Characterization

X-ray diffraction patterns were collected on an X-ray diffractometer (X'Pert PRO MPD) using Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) operating at 40 mV and 40 mA, respectively. Zeta potentials and sizes of catalysts were analyzed by Zetasizer Nano size (Zetasizer 2000, Mastersize 2000, Malvern). Fourier transform infrared spectra were recorded with a FT-IR spectrophotometer (Nicolet 8700, Thermo Fisher Scientific). Raman spectra was recorded from 100 cm⁻¹ to 2000 cm⁻¹ on a high resolution Raman spectrometer (LabRAM HR Evolution, France) using a He–Ne laser (633 nm). Field-emission scanning electron microscope (SEM) (SU-8020, Hitachi Limited) equipped with the energy-dispersive X-ray spectrometer and Transmission electron microscopy (H-7500, Hitachi Limited) and High resolution transmission electron microscope (HRTEM) (JEM 2100F, Japan) were employed to characterize the morphology and crystalline structure of particles. The chemical composition of the catalysts was analyzed by X-ray photoelectron spectroscopy (ESCALAB 250Xi Al Ka, Thermo Fisher Scientific).

Table 1
Chemical composition and surface area of catalysts.

Samples	GO	rGO	Ak-20	Ak-40	Ak-60	Ak-80	Ak
Actual Fe (wt%)	–	0	23.32	32.87	42.75	46.61	54.85
Calculated G (wt%)	–	100	57.48	40.07	22.06	15.02	0
Surface area (m ² /g)	24.83	402.63	148.93	159.30	138.37	83.72	18.65
Pore size (nm)	6.88	2.60	5.30	7.73	10.13	12.26	13.28
Pore volume (cm ³ /g)	0.04	0.26	0.20	0.31	0.35	0.26	0.06

BET surface area of the prepared catalysts was analyzed using a full automatic analyzer (ASAP2020HD88, Micromeritics Instrument Corp.).

3. Results and discussion

3.1. Catalysts characterization

3.1.1. XRD

XRD patterns of all the catalysts are shown in Fig. 1. It can be seen that the as-synthesized beta-FeOOH (Ak) was well crystallized with some feature peaks such as {1 1 0} peak at ca. 11.8°, {2 0 0} peak at ca. 16.8°, {3 1 0} peak at ca. 26.8° and {2 1 1} peak at ca. 36.2° (PDF No.34–1266). Further decrease of Fe content (Table 1) leads to the decrease of different peaks' intensity, indicating that the crystallization of beta-FeOOH could be destroyed due to the addition of rGO (Fig. 2). For instance, no obvious diffraction peaks were observed when 23.32% wt Fe was loaded onto the reduced graphene oxide (Ak-20), except a broad diffraction peak at ca. 24° of reduced graphene oxide itself, indicating the {0 0 2} plane reflection feature of grapheme [21].

3.1.2. SEM and HRTEM

SEM can directly identify the morphologies of catalysts. As shown in Fig. 2, rGO in the presence of beta-FeOOH was nanosheets not spherical nanoparticles. This is probably due to the aggregation of graphene oxide at pH 1.50 with the presence of Fe³⁺ [23]. In addition, beta-FeOOH was nanorods of 500 nm in length and 50 nm in diameter. With the increase of Fe content, more and larger beta-FeOOH nanorods could cover on the rGO nanosheets. The morphology and structure of the GO and Ak/rGO nanocomposites were also observed by HRTEM analysis. In Fig. S1, small dispersed nanorod-like particles were observed to form at the surface of rGO. With the increase of Fe content, nanoparticles grew larger and tended to be aggregated at the surface.

Fig. 1. XRD patterns of catalysts.

3.1.3. Zeta potential

To gain insight into the colloidal solution properties of catalysts, zeta potential and particle size were measured, as demonstrated in Fig. 3. The development of zeta potential as a function of pH reflects the different surface groups in the synthesized materials. For rGO, the surface groups include hydroxyl, epoxide, and strongly acidic carboxyl groups at the edges. rGO shows a negative zeta potential even under acidic conditions (–20 to –25 mV at pH 4.02). As expected, rGO become to more stable as the alkalinity of the solution is increased (~–50 mV at pH 8.07). More interesting is that the rGO with the presence of beta-FeOOH shows a lower zeta potential although the beta-FeOOH has a higher zeta potential (~40 mV at pH 7.04). For example, the zeta potential of the modified rGO with 32.87% Fe (Ak-40) was ~–30 mV and –50 to –55 mV at pH 3.86, 6.5–7.7, respectively. It is probably that beta-FeOOH nanoparticles on the rGO surfaces inhabited the reduction of part GO through masking the surface. Particle size variation is evident for Ak/rGO materials. As shown in Fig. 3b, the particle size is observed at 10 μm for rGO. For beta-FeOOH nanoparticles, there is a large sharp peak at 400 nm and a very small component at 100 nm. In contrast, particle sizes of Ak/rGO samples shift to a larger size distribution. For Ak-20 and Ak-40 samples, there is a broad peak at 300 μm in the particle size. And particle sizes of Ak-60 and Ak-80 samples stabilize at 20–30 μm with a broad distribution. Particle size analysis shows that beta-FeOOH can increase the size of rGO.

3.1.4. BET

As depicted on Fig. 4, Nitrogen adsorption–desorption isotherms of Ak/rGO exhibited a typical type IV with type H3 hysteresis loops. According to the Brunauer–Deming–Deming–Teller (BDDT) classification, it indicated that the composite is a typical mesoporous structure, which may consist of aggregates of platelike particles [24]. As shown in Table 1, the corresponding pore sizes of Ak-20, Ak-40, Ak-60 and Ak-80 are 5.30 nm, 7.73 nm, 10.13 nm and 12.26 nm respectively, confirming that the composites are mainly mesoporous. The specific surface area of Ak/rGO is larger than that of Ak or GO alone but far less than that of rGO, indicating that beta-FeOOH could inhibit the transformation of GO to rGO.

3.1.5. FTIR and Raman

FTIR spectroscopy was used to analyze the functional groups formed in the catalysts, as shown in Fig. 5. The FT-IR spectrum reveals the presence of C=O (1739 cm^{–1}), C–O (1062 cm^{–1}), C–O–C (1229 cm^{–1}), C–OH (1418 cm^{–1}) in the GO samples in Fig. S2. The peak found at 1625 cm^{–1} is a resonance peak that can be assigned to the C–C stretching and absorbed hydroxyl groups in the GO. With the further reduce of GO, the new band at 1577 cm^{–1} appears due to C–C stretching and oxygen functional groups almost disappear apart from C=O (1716 cm^{–1}) and C–O–C (1222 cm^{–1}) [25]. With the increase of the beta-FeOOH content, the peaks intensity of 1716 cm^{–1} and 1222 cm^{–1} decrease. The peak of 1577 cm^{–1} shifts to a higher wavenumber due to the effect of H₂O-bending band at 1620 cm^{–1}. The new peaks form at 1385 cm^{–1} and 696 cm^{–1}. The first band may be relative to the surface Lewis acid sites, and the other one results from Fe–O vibration [26,27]. For the beta-FeOOH, the bands were also observed at 3476 and 1664 cm^{–1}, which can

Fig. 2. SEM of catalysts: beta-FeOOH (dashed box).

Fig. 3. Zeta potential (a) and particles size contribution (b) of catalysts.

Fig. 4. N₂ adsorption-desorption isotherms of catalysts.

Fig. 5. FTIR spectrum of catalysts.

be assigned to the OH-stretching band and the H₂O-bending band [28].

Raman spectroscopy is a powerful tool to characterize carbonaceous materials, particularly for distinguishing ordered and disordered crystal structures of carbon. Fig. 6 shows the Raman spectra of GO, rGO, Ak and Ak/rGO nanocomposites. The Raman spectra of GO displayed a strong G at 1595 cm⁻¹, corresponding to the first-order scattering of the E_{2g} mode as well as a stronger D line at 1330 cm⁻¹, indicating the reduction in size of the in-plane sp² domains, possibly due to the extensive oxidation [29]. The Raman spectrum of the reduced GO also contains both G and D bands (at 1595 and 1330 cm⁻¹, respectively). However, the intensity of D or G band intensity was higher compared to that in GO. These phenomena could be attributed to the significant decrease of the size of the in-plane sp² domains due to oxidation and ultrasonic exfoliation [30]. In addition, the peaks at 215, 279, 394, 592 cm⁻¹ were assigned to beta-FeOOH, and peak intensity of 215, 279, 592 cm⁻¹ decreased with the increase of rGO. This also indicated chemical interaction between beta-FeOOH and rGO.

3.1.6. XPS

The prepared catalysts were then further analyzed using XPS to verify the interaction between beta-FeOOH and rGO. As shown in Fig. S3, the wide scan spectra of catalysts showed photoelectron lines at binding energies of 284.5, 400, 529.8 and 710.8 eV which are ascribed to C1s, N1s, O1s and Fe2p, respectively. The C1s peaks, O1s peaks and Fe2p peaks of catalysts are showed in Fig. 7, the fit results of which are summarized in Table S1. High resolution XPS profiles of C1s, O1s and Fe2p exhibited asymmetric character, indicating the presences of different kinds of surface carbon, oxygen and ferric species on the catalysts. Fig. 7a shows the Fe2p spectra of Ak, Ak-20 and Ak-60. The binding energy peaks for Ak sample at 710.7 and 724.2 eV in the high resolution Fe2p scan corresponded to Fe2p_{3/2} and Fe2p_{1/2}, respectively. With the addition of rGO, the Fe2p peaks shifted to the higher binding energy (i.e., 711.6 eV and 724.8 eV for the Fe2p_{3/2} and Fe2p_{1/2} peaks of Ak-60 sample), indicating the chemical interaction between beta-FeOOH and rGO.

The C1s spectra of catalysts are exhibited in Fig. 7b. The decomposition of the C1s spectrum of catalysts consists

Fig. 6. Raman spectrum of catalysts.

of six components: $C=Csp^2$ (284.6–284.8 eV), $C-Csp^3$ or $C-N$ (285.2–285.9 eV), $C-OH$ and or $C-O-C$ (286.6–286.9 eV), $C=O$ (287.7–288.1 eV), $O-C=O$ (288.6–289.0 eV) and shake-up satellite peaks (291.1–293.1 eV) due to transitions in aromatic rings or carbon in carbonate groups [31]. It is also observed that the binding energy of 285.2–285.9 eV corresponds to $C-C$ or $C-N$ peaks [19,31] indicating that N was doped into the catalysts. Unlike the C1s sig-

nals, the O1s peaks exhibit a difference in Fig. 7c. Further the O1s spectrum of catalysts can be well decomposed into three peaks: the oxygen that binds to Fe ($Fe-O(H)$: 529.3–530.9 eV), the oxygen in carboxylate or carbonyl ($O-C=O$ or $C=O$: 531.5–531.7 eV), the oxygen in the epoxy or hydroxyl ($C-O-C$; $C-OH$: 532.8–533 eV). It should be noticed that the peaks of O1s in Ak-20, Ak-60 samples shifted to a lower binding energy of 529.3 eV ($Fe-O$) in Ak, indicating that the new peak of $Fe-O-C$ at the binding energy of 531.2 eV may be formed on the surface of rGO [31]. Besides, the binding energy of 529.3 eV and 530.9 eV corresponds to $Fe-O$ and $Fe-OH$ [32].

3.2. Fenton-like catalytic oxidation of 2-chlorophenol

In order to test the catalytic performance of Ak/rGO, the Fenton-like oxidation of 2-chlorophenol was employed as a typical action. The degradation of 2-CP under different experimental conditions was evaluated. As shown in Fig. 8a, 2-CP removal efficiency by using catalysts in the presence of 100 mM H_2O_2 were measured at initial pH 4.0 within 72 h. 2-CP removal efficiency could achieve to 88% with the addition of beta- $FeOOH$, which demonstrated a linear relationship with time. The degradation of 2-CP was compared by using the Ak/rGO. For instance, 2-CP removal efficiency was 67% by using similar dosage of Ak-80 in 24 h. Almost all of 2-CP was removed for Ak-20, Ak-40 and Ak-60 in 16 h. In contrast, removal of 2-CP is decreased at initial pH 9.0 (Fig. 8b). Particularly, only 33% 2-CP was removed for beta- $FeOOH$ because the release iron and OH radical could be decreased [33]. However, Ak-20 and Ak-40 showed a little change in 2-CP removal, because of the rGO content. If the

Fig. 7. XPS curve fit of Fe2p (a), C1s (b) and O1s (c) spectra.

Fig. 8. Removal of 2-CP on the Ak/rGO (1 g L^{-1} catalyst, 100 mg L^{-1} 2-CP, $100 \text{ mM H}_2\text{O}_2$): (a) initial pH 4.0, (b) initial pH 9.0.

Fig. 9. Dynamic process of 2-CP on the catalysts at initial pH 4.0 (a) and pH 9.0 (b).

dosage was the same, 2-CP removal efficiency reached almost same as 75% with H_2O_2 at initial pH 4.0 or 9.0. This is likely due to the adsorption, as shown in Fig. S4. This means that the rGO could help the degradation of 2-CP through adsorption and thereby improving the reaction rate.

3.3. Mechanism analysis

3.3.1. Released iron concentration

To gain insight of the Fenton-like oxidation of 2-chlorophenol, the concentrations of soluble Fe produced from the proton-promoted dissolution of beta-FeOOH were examined, which could activate the Fenton reaction [34,35]. According to Fig. S5, more soluble irons are from Ak/rGO rather than beta-FeOOH at initial pH 4.0 or 9.0. This result indicates that the presence of rGO could accelerate the Fenton reaction.

3.3.2. Kinetic equation

The experimental results for the degradation rate of 2-CP at initial pH 4.0 or 9.0 were described by pseudo first order kinetics, as shown in Fig. 9. From Table S2, where the curve fit results were summarized, the 2-CP oxidation rate at initial pH 4.0 is 2–3 times higher than that at initial pH 9.0. The decrease of the decomposition rate at higher pH was attributed to the precipitation of Fe(III) and the reduction of H_2O_2 life [36]. With the increase of rGO content, oxidation rates of 2-CP increase exponentially (i.e., oxidation rates

Fig. 10. Degradation of H_2O_2 onto the Ak, rGO and Ak-40.

of 2-CP for Ak-20 is almost 10 times than that for Ak), implying that the catalytic activity was enhanced by the introduction of rGO.

3.3.3. H_2O_2 degradation

Degradation of H_2O_2 on the Ak, Ak-40 and rGO without 2-CP is exhibited in Fig. 10. Many researchers [33] observe that OH radical is proportional to H_2O_2 . Compared with Ak, H_2O_2 degradation on Ak-40 increased significantly whether initial pH as 4.0 or 9.0.

Fig. 11. 2-CP removal via Synergy of reduced graphene oxide and beta-FeOOH.

Besides, degradation of H_2O_2 onto the rGO was much lower and almost can be neglected. This indicates that certain active site on the Ak/rGO contributes to H_2O_2 degradation, producing more OH radical.

3.3.4. Synergism of rGO and beta-FeOOH

Furthermore, the degradation of 2-CP by a physical mixture of beta-FeOOH and rGO in the presence of H_2O_2 was modeled, providing that (1) not interfering with the reactions between them; (2) a model parameters producing from the degradation of 2-CP on the beta-FeOOH and rGO, respectively.

$$(a) R.E.(rGO) = 75\% \times rGO\text{content}$$

$$(b) R.E.(A.k) = 5.56 + 1.18 \times \text{Time}(h)(\text{initialpH}4.0, R^2 = 0.9973)$$

$$R.E.(A.k) = 10.33 + 0.31 \times \text{Time}(h)(\text{initialpH}9.0, R^2 = 0.9980, \text{Time} > 6h) \quad (c)$$

$$\text{TotalR.E.} = R.E.(rGO) + R.E.(Ak) \times (1 - rGO\text{content}) \quad (d)$$

In Eq. (a), rGO contents are 57.48%, 40.07%, 22.06%, 15.02% for Ak-20, Ak-40, Ak-60, Ak-80, respectively, where 75% is assumed as removal efficiency of 2-CP at initial pH 4.0 or 9.0 due to 2-CP removal range from 71% to 78%. As shown in Fig. 11, 2-CP removal efficiency on the composite is increased significantly. For example, 2-CP removal difference between Ak-20 and corresponding

Fig. 12. Removal of 2-CP onto the catalysts after 72 h.

mixture rises with the increase of reaction time, reaching 40% and 36% at initial pH 4.0 and 9.0. By comparison, the catalytic activity of Ak/rGO composites were higher than that of mixture, suggesting that there might be a synergy effect in the composite, thereby enhancing the relative rates of mass transfer to reactive sites and chemical reaction at reactive sites. In addition, synergy of beta-FeOOH and rGO for Ak-40, Ak-60 and Ak-80 is quite significant, as seen in Fig. 12.

Based on the information obtained above, a possible reaction mechanism of Ak/rGO toward the reduction of 2-CP is proposed in Fig. S6. The mechanisms involved in the Fenton-like oxidation of organic compounds could be explained by considering both the reactions in solution and at the beta-FeOOH surface. As reported by other researchers [33,37], the first step in the heterogeneous reaction is the surface complexation of H_2O_2 to Fe(III) forming $\text{Fe}^{\text{III}}\text{H}_2\text{O}_2$, leading to the formation of $\bullet\text{OH}$ radicals in solution (Eqs. (1)–(4)), which degrades 2-CP (Eq. (11)). In the bulk solution, dissolved iron from beta-FeOOH initiates the decomposition of H_2O_2 through a chain reaction (Eqs. (5)–(10)) to produce $\bullet\text{OH}$, which degrades 2-CP (Eq. (11)). At the same time, adsorption has important pole in the process of 2-CP degradation.

4. Conclusions

In summary, Ak/rGO composites were prepared by a facile co-precipitation method. The presence of rGO prevented the beta-FeOOH NP from aggregating and enabled them to distribute uniformly on the surface of the rGO sheets, activating the reactive sites. Furthermore, Ak/rGO composites showed efficient catalytic activity for the reduction of 2-CP at acid or alkaline conditions. On the basis of iron leaching, H_2O_2 degradation and comparison of model, Ak/rGO composites can produce more OH radical to enhance 2-CP degradation, implying that using graphene as a host material for catalysts to accomplish synthetic transformations has great potential and far-reaching prospects for environmental application.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2016.01.011>.

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