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Heterogeneous electro-Fenton oxidation of p-nitrophenol with a reusable fluffy clump steel wire

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ABSTRACT

A heterogeneous electro-Fenton system with fluffy clump steel wire (FCSW) was described for the degradation of p-nitrophenol (p-NP) in water. The influences of the initial pH, initial concentration of FCSW, applied current density on the p-NP, and total organic carbon (TOC) removal percentages were investigated. Compared with the homogeneous electro-Fenton process, the presence of the FCSW catalyst significantly improved the degradation efficiency, the p-NP removal percentages could reach 94.31% after 60 min under the appropriate operating conditions that initial pH value of 3.0, initial FCSW concentration of 3.0 g/L, current density of 3.0 mA/cm^2, and the TOC removal percentages could reach 78.96% after 180 min. Aromatic intermediates and carboxylic acids had been identified by chromatographic techniques, and a plausible reaction pathway for p-NP mineralization by heterogeneous electro-Fenton process with FCSW was proposed. The catalytic reusability of FCSW was ultimately evaluated for the repeated use, and the degradation ratio of p-NP could be maintained steadily at 89–96% during 10 cycles, as well as the minimal variations of its structure and composition.

Keywords: Fluffy clump steel wire; Heterogeneous electro-Fenton oxidation; p-nitrophenol; Reaction pathway; Catalytic reusability

1. Introduction

Nowadays, a large amount of toxic and refractory pollutants have been emerged in industrial effluents and natural water with the rapid development of industry. Nitro phenols (NPs), a class of priority pollutants listed by the US Environmental Protection Agency [1,2], have been widely used as the precursors or intermediates in the synthesis of insecticides, leather preservatives, synthetic dyes, pharmaceuticals, plastics, industrial solvents, and so on [3–5]. They can enter the natural environment through the effluents discharged from factories and pose serious risks to the ecosystem and human health because of their high toxicity, poor biological degradability, and persistence [6,7]. To address the pollution of industrial wastewater by NPs, many efforts have been paid on developing various available treatment processes in the past decades including the advanced oxidation processes

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(AOPs), such as Fenton-like oxidation [8–11], photocatalytic oxidation [12,13], and electrocatalytic oxidation methods [14–18]. AOPs are based on the *in situ* generation of highly reactive and non-selective hydroxyl radicals ($\cdot$OH), which is the second strongest oxidants (oxidation potential is 2.87 V, only being surpassed by fluorine) [19] by means of chemical, photochemical, or electrochemical methods.

Among these AOPs, the electro-Fenton oxidation method seems to be more efficient, economical and environmentally friendly, because H_2O_2 can be continuously produced *in situ* from the two-electron reduction of the injected O_2 at the cathode in acidic medium (Eq. (1)), and then generates $\cdot$OH with the dissolved Fe^{2+} in solution by Eq. (2) [20,21]. Furthermore, Fe^{2+} can be recycled by different reduction processes, which involve H_2O_2 or organic intermediate radicals, as well as the direct reduction of Fe^{3+} on the cathode [22], so the addition of Fe^{2+} and the formation of Fe sludge are much smaller than they are in the traditional Fenton method. Nevertheless, the dissolved iron in the ultimate degradation solution cannot be reused and requires subsequent removal from water, and the narrow pH range of treated water (2–4) [23–25] restricts the electro-Fenton process from a wide application.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{1}$$

$$H_2O_2 + Fe^{2+} + H^+ \rightarrow Fe^{3+} + \cdot OH + H_2O \tag{2}$$

To overcome the above disadvantages of homogeneous electro-Fenton process, the heterogeneous electro-Fenton systems, where the soluble Fe^{2+} is replaced by Fe-containing solids, such as nano-zero valent iron [26], Fe-based metal oxides [27–29], Fe alginate gel beads [30], and $AlSi_2Fe_6$ [31], have been recently developed. Different catalysts used in the heterogeneous electro-Fenton systems have shown high catalytic activities for degrading organic pollutants with minimal iron leaching and have a wider pH operating range. However, the development of such catalysts is limited by the complicated preparation process and expensive raw materials, which in turn suppress practical application of the heterogeneous electro-Fenton process. Therefore, it is of great importance to seek availability and cost-effective catalysts for the electro-Fenton systems.

In this study, a novel catalyst, fluffy clump steel wire (FCSW) containing both Fe and other elements with magnetic property would be evaluated for the heterogeneous electro-Fenton degradation of NPs. There are several virtues in FCSW which may offer remarkable advantages for the electro-Fenton process in wastewater, e.g. (i) it contains Fe which might play an important role as an electron donor to initiate the Fenton reaction according to the classical Haber-Weiss mechanism [29], (ii) the other elements in the FCSW such as Cu, which have similar redox properties to Fe, can also efficiently produce $\cdot$OH with H_2O_2 (Eq. (3)) and could work over a broader pH range than the Fe-based redox system [32–34], (iii) it is available easily and cheap because it is widely used for cleaning the dirt settled onto surfaces in China, and (iv) it is convenient separation from solution by external magnetic field. This work focuses on the degradation efficiency and mechanism of FCSW as a heterogeneous electro-Fenton catalyst in the degradation of p-NP. The efficiency was studied through the degradation of p-NP under different operation parameters including initial pH, initial concentration of FCSW and applied current density. The degradation pathway was elucidated by detecting the oxidation by-products with high performance liquid chromatography (HPLC) method. Ultimately, the reusability of FCSW was also conducted in the repeated degradation of p-NP under ideal operational conditions.

$$Cu(I) + H_2O_2 + H^+ \rightarrow Cu(II) + \cdot OH + H_2O \tag{3}$$

2. Experimental

2.1. Materials and reagents

The FCSW was taken from the used steel wool of family. FCSW was immersed in acetone and 1% hydrochloric acid for 20 min in turn, then washed with distilled water for several times before use. The multi-walled carbon nanotubes (MWCNTs) were obtained from Beijing DK nanotechnology Co. Ltd (China) with purity >98%, outer diameter (O.D.) of 10–20 nm, and length of 10–30 μm. All other chemicals used in this study were purchased from Sinopharm Chemical Reagent Co. Ltd, China. All chemicals were higher than analytical grade and were used without further purification. Deionized water (18.2 mΩ/cm) was obtained from a Millipore Milli-Q system and used in all the experiments.

2.2. Description of reaction system

Electro-Fenton oxidation experiments were carried out by batch processes in a three-dimensional (3-D) system and the apparatus was mainly consisted of a DC power supply, a heat-gathering style magnetic stirrer, and a glass reactor (Fig. 1). A fabricated PbO_2

electrode [18] was used as anode and a gas diffusion electrode (GDE), which immobilized MWCNTs onto graphite surface [35] was used as cathode, respectively. The anode and the cathode were positioned vertically and parallel to each other at a distance of 3 cm. An appropriate concentration of FCSW as heterogeneous catalyst was filled into the reactor between the anode and the cathode. Air was continuously bubbled onto the cathode at a flow rate of 0.2 L/min through a glass aeration pipe. The pH was adjusted to the desired value by H_2SO_4 or NaOH. 0.05 M Na_2SO_4 was used as a supporting electrolyte. The reaction temperature was maintained at 298 ± 1 K during all the experimental runs. Samples were drawn from the solution at predetermined time intervals and filtered immediately through 0.45 μm membrane filters for analysis. Three independent tests were conducted for each condition, and the error was within ±5% of each test.

2.3. Analysis and characterization

The concentration variation of p-NP during the degradation process was monitored by measuring the absorbance at 400 nm under pH > 11 (adjusted by adding the proper quantity of NaOH) with a UV–vis spectrophotometer (TU-1810, PERSEE, China) [36]. The pH value was obtained on a pH-meter (HI2213, HANNA, China). The concentration of total iron released during the electro-Fenton degradation of p-NP was detected by an atomic absorption spectroscopy (AA-680, Shimadzu, Japan). The total organic carbon (TOC) concentration was measured with a TOC analyzer (ELAB, China).

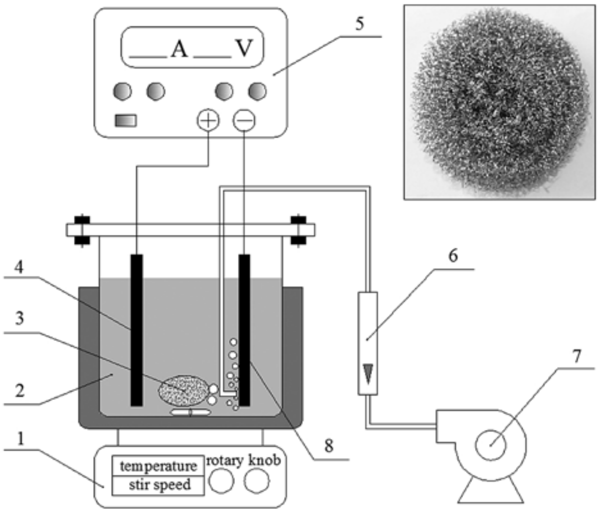

Fig. 1. Schematic diagram of the heterogeneous electro-Fenton oxidation equipment (the inset is the photographs of catalyst): (1) magnetic stirrer; (2) glass reactor; (3) catalyst FCSW; (4) anode; (5) DC power supply; (6) glass rotameter; (7) air pump; (8) cathode.

The concentration of H_2O_2 was monitored by spectrophotometer at 400 nm using the potassium titanium (IV) oxalate method [37]. The current efficiency (CE) of H_2O_2 production was calculated by Eq. (4).

$$\mathrm{CE} = \frac{nFC_{\mathrm{H_2O_2}}V}{\int_0^t I\,dt} \times 100\% \tag{4}$$

where n is the number of electrons transferred for oxygen reduction to H_2O_2, F is the Faraday constant (96,486 C mol/L), C_{H2O2} is the concentration of H_2O_2 formed (mol/L), V is the bulk volume (L), I is the current (A), and t is the time (s).

The determination of intermediates during the oxidation degradation of p-NP was carried out on high-performance liquid chromatography (HPLC, Shimadzu, Japan). The mobile phase was a mixed solution containing 60% (volume fraction) methanol, and 39.8% water and 0.2% concentrated H_3PO_4. The separation was performed using an Agilent TC-C18 column (150 mm × 4.6 mm, 5 μm) at the column temperature of 30°C and at a flow rate of 1.0 mL/min. A UV detector was used with the wavelength set at 265 nm. Intermediates were characterized by comparing the retention time of the standard compounds.

Scanning electron microscopy coupled with energy-dispersive X-ray spectrometry (SEM/EDX) was performed on a FEI Quanta 450 scanning electron microscope. An acceleration electron voltage of 20 keV was applied to obtain the SEM images and the composition of FCSW.

3. Results and discussion

3.1. H_2O_2 accumulation

Since H_2O_2 is the important factor of an electro-Fenton process, it is necessary to identify the H_2O_2 production capacity of this prepared GDE. Because of good conductivity and low price, graphite electrode was selected as the supporting material, and the MWCNTs with high specific surface area were immobilized on it to provide more active sites. The effects of initial pH and current density on H_2O_2 production were investigated, and the results were shown in Fig. 2(a) and (b). It indicated that the H_2O_2 accumulation increased, but the CE decreased with time under all experimental conditions. The amount of H_2O_2 production increased with increasing initial pH from 1.0 to 3.0, then decreased with pH from 3.0 to 7.0, and the CE was similar with the H_2O_2 accumulation. After 60 min of electrolysis, there were maximum values of the amount of H_2O_2 production and CE were 3.338 mmol/L and 59.64%, respectively, at pH 3.0. These results can be explained from that there exist two side reactions at the cathode: the reduction of H_2O_2 to H_2O (Eq. (5)) and hydrogen (H_2) gas evolution (Eq. (6)) [35], which decrease the electrogenerated H_2O_2 in the medium at lower pH values (pH < 3.0), and when pH is above 3.0, the electrogeneration of H_2O_2 decreases due to the decrease in proton concentration.

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \qquad (5)$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad (6)$$

The H_2O_2 accumulation increased with the increasing current density from 1.0 to 3.0 mA/cm^2, and then decreased slightly at the current density of 5.0 mA/cm^2, but the CE decreased when the current density increased from 1.0 to 5.0 mA/cm^2. After 60 min electrolysis, the concentration of H_2O_2 at the current density of 1.0, 3.0, 5.0 mA/cm^2 were 1.718, 3.018, 2.743 mmol/L, and CE were 92.09, 53.92, 29.41%, respectively. With the increase in current density, the competitive reactions such as H_2O production process (Eq. (7)) and decomposition of H_2O_2 itself (Eq. (8)) were improved, which might lead to the CE decrease [38]. Even so, the prepared GDE is still an excellent cathode material for H_2O_2 production, and thus it is potential to be used in electro-Fenton process.

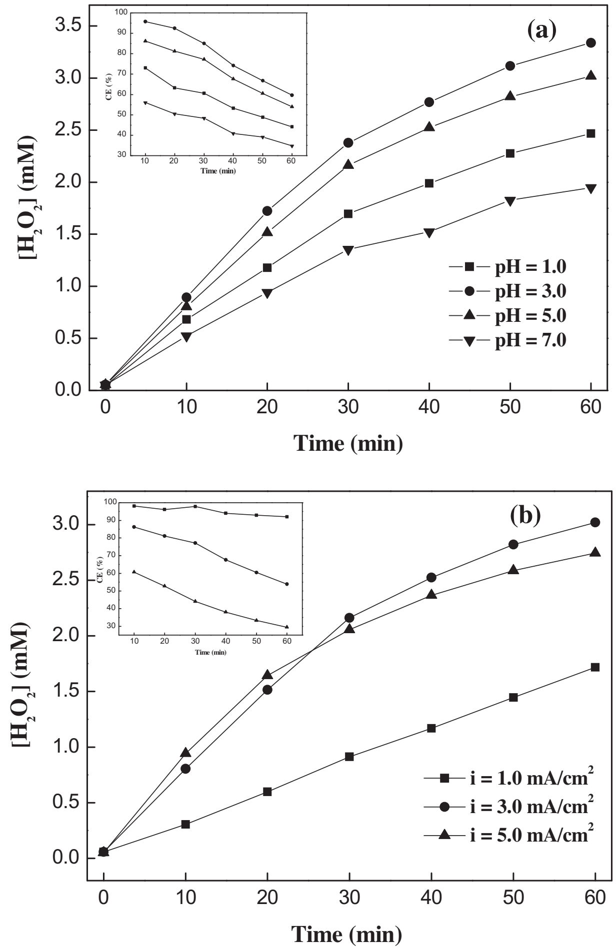

Fig. 2. Effects of initial pH (a) and current density (b) on H_2O_2 production (insets were the corresponding variations of CE). Conditions: $[Na_2SO_4] = 0.05$ mol/L, air flow = 0.2 L/min, $T = 298$ K.

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad (7)$$

$$H_2O_2 \rightarrow HO_2^{\bullet} + H^+ + e^- \qquad (8)$$

3.2. Characteristics of catalyst FCSW

The catalyst FCSW is composed of steel wire which was randomly aggregated, interlaced distributed, and occluded with each other by point-to-point and line-to-line contacts, forming a three-dimensional reticulated metal backbone (the inset of Fig. 1). The SEM micrograph of the unused FCSW is exhibited in Fig. 3(a). A smooth surface with little corrosion pit could be seen on the image, which indicates that the FCSW is stable in a natural environment. The energy dispersive spectrometric (EDS) mapping of the unused FCSW is shown in Fig. 3(c), and the corresponding elementary composition of FCSW can be seen in Table 1. Several kinds of metallic elements contained in the FCSW could be observed on the EDS, and Fe was the major element, where content was about 74.89%. Besides, the carbon and oxygen elements could also be observed on the EDS, and the contents of carbon and oxygen elements were 10.68 and 2.34%, respectively. It can be inferred that the FCSW is mainly composed of single metals, as well as a minor amount of metallic oxides and metallic carbides. To validate the catalytic performance of FCSW in the electro-Fenton system, 1.0 g FCSW was put into the acid solution of pH 3.0, and 3.79 mg/L iron ions were leached into the solution after 3 h. So the FCSW has the ability of catalyzing reduction of H_2O_2 to $^{\bullet}OH$.

3.3. Influence factors in p-NP degradation

3.3.1. Influence of initial pH value

Solution pH value plays a critical role on the efficacy of Fenton and Fenton-like reactions, which directly affects not only the synthesis of H_2O_2, but also

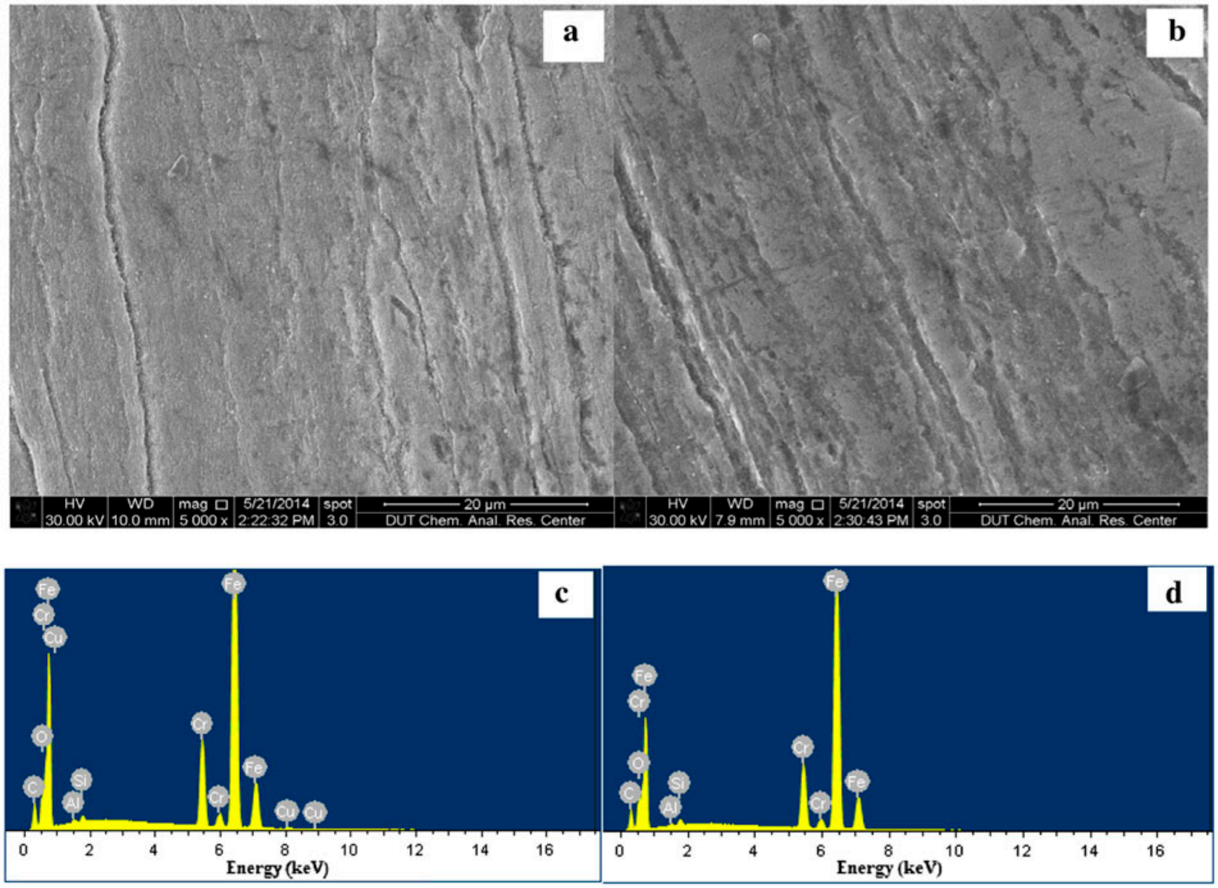

Fig. 3. SEM micrograph and EDS of FCSW. (a) and (c) unused; (b) and (d) after being used for 10 cycles.

Table 1
Elemental compositions of the catalyst FCSW

	Wt (%)	
Elemental composition	Unused	After used for 10 cycles[a]
C	10.68	10.85
O	2.34	3.32
Al	0.21	0.22
Si	0.40	0.43
Cr	11.12	11.25
Fe	74.89	73.93
Cu	0.36	–

[a] Reaction conditions: $[\text{p-NP}]_0$ = 50 mg/L, pH 5.0, [FCSW] = 3.0 g/L, current density = 3.0 mA/cm^2, $[\text{Na}_2\text{SO}_4]$ = 0.05 mol/L, air flow = 0.2 L/min, T = 298 K, reaction time = 60 min.

the regeneration of Fe^{2+}, and the appropriate pH for Fenton and Fenton-like process is generally reported to be around 3.0 [39]. Fig. 4(a) and (b) plotted the p-NP and TOC removal percentage of heterogeneous electro-Fenton oxidation with FCSW catalyst at initial pH range from 1.0 to 7.0, respectively. As shown in Fig. 4(a), the p-NP removal percentage kept at a high level in a wide pH range (1.0–5.0), and the highest p-NP removal percentage was obtained at pH 3.0 (97.76% after 60 min). When the pH value increased to 7.0, a quick decline of the p-NP removal percentage was observed (87.79% after 60 min). The trend of TOC removal percentage was similar to the p-NP removal percentage (Fig. 4(b)), the maximum value of 85.56% after 180 min was obtained at pH 3.0, while falling to 60.67% after 180 min at pH 7.0.

To demonstrate the effectiveness of the catalyst FCSW, the concentration of leached iron ions was measured using atomic absorption spectroscopy technology. When pH was 1.0, 3.0, 5.0, and 7.0, the concentration of leached iron ions were 7.51, 3.02, 1.43, and 0.97 mg/L, respectively. The experiments of homogeneous electro-Fenton oxidation under the same conditions were performed for comparison with the heterogeneous electro-Fenton oxidation using the same concentration of iron ions that were leached out from the catalyst (the insets of Fig. 4). Obviously, in the

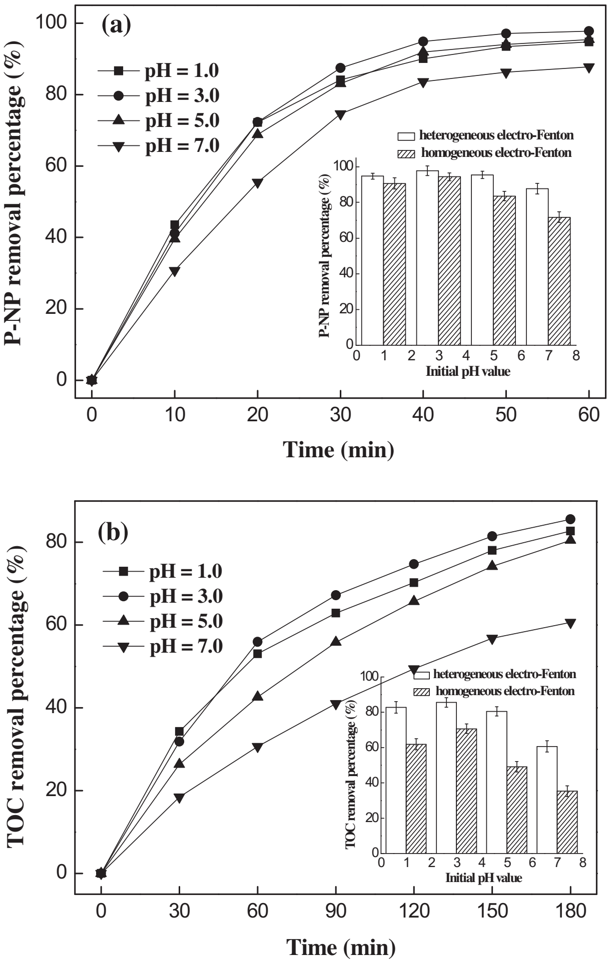

Fig. 4. Effect of initial pH on p-NP degradation: variations of (a) p-NP removal percentage and (b) TOC removal percentage with time during electro-Fenton oxidation; Insets in Fig. 4: comparisons of (a) p-NP removal percentage and (b) TOC removal percentage between the heterogeneous electro-Fenton and homogeneous electro-Fenton at different pH. Conditions: [p-NP] = 50 mg/L, current density = 3.0 mA/cm^2, [FCSW] = 5.0 g/L, [Na_2SO_4] = 0.05 mol/L, air flow = 0.2 L/min, T = 298 K.

experimental pH range, the p-NP and TOC removal percentages by heterogeneous electro-Fenton process were all higher than the homogeneous electro-Fenton process, e.g. when pH was 5.0, the p-NP and the TOC removal percentages of homogeneous electro-Fenton process were 78.54 and 45.17%, which were 16.89 and 35.32% lower than in the heterogeneous electro-Fenton system. Although the same amount of iron ions existed in homogeneous electro-Fenton process, the p-NP and the TOC removal percentages were slightly higher than that in the electrochemical system without catalyst (As shown in Fig. 5, the p-NP and the TOC removal percentages were 74.41 and 40.49%, respectively). This phenomenon might be explained from the facts: (i) because of the addition of elements Cr, Cu, etc., the FCSW had better corrosion resistance than pure iron [40,41], which resulted a smaller iron leaching rate, and thus the concentration of Fe^{2+} in solution was maintained the best ratio with H_2O_2 according to Eq. (2) and avoided iron precipitates at higher pH values, (ii) The copper species containing in FCSW had higher activity of catalyzing H_2O_2 to produce $^{\cdot}OH$ (the reaction rate is 1×10^4 M^{-1} s^{-1}) than the Fe(II)–H_2O_2 system (the reaction rate is 76 M^{-1} s^{-1}), and the reaction was less restricted by pH [32–34]. Therefore, the FCSW had excellent catalytic activity and a broad pH application range, and the initial pH value of 5.0 was selected for the subsequent experimental study.

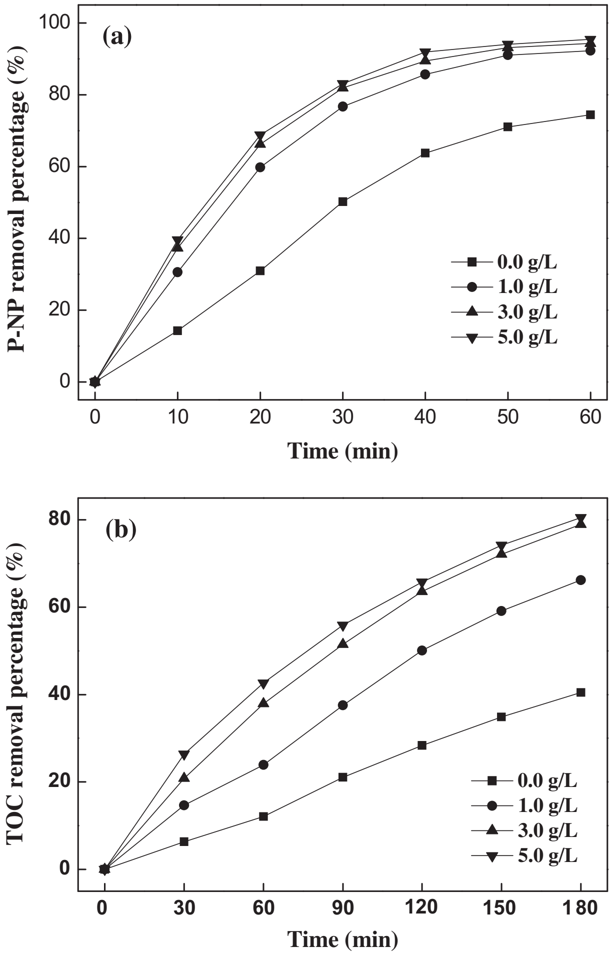

Fig. 5. Effect of initial FCSW concentration on p-NP degradation: variations of (a) p-NP removal percentage and (b) TOC removal percentage with time during electro-Fenton oxidation. Conditions: [p-NP] = 50 mg/L, pH 5.0, current density = 3.0 mA/cm^2, [Na_2SO_4] = 0.05 mol/L, air flow = 0.2 L/min, T = 298 K.

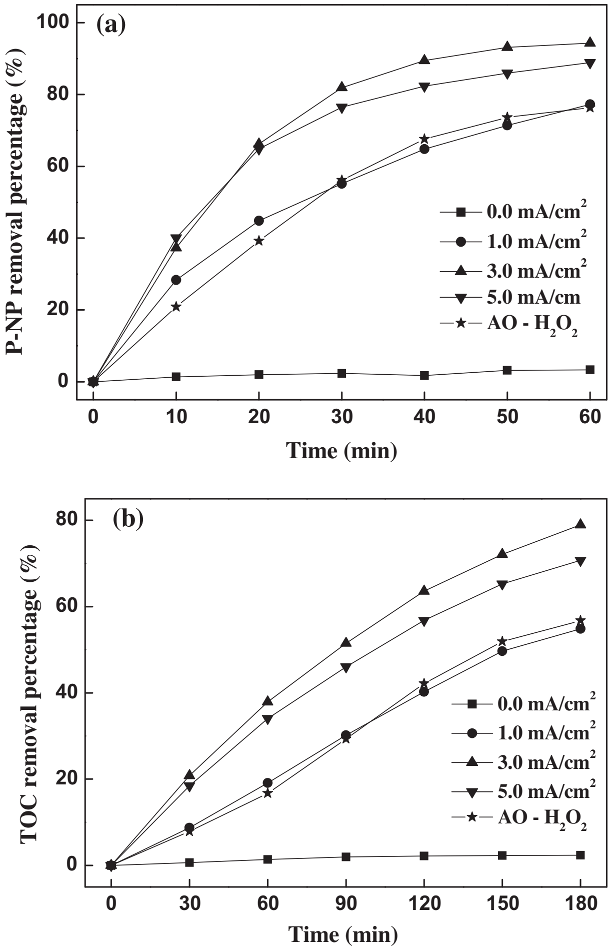

Fig. 6. Effect of current density on p-NP degradation: variations of (a) p-NP removal percentage and (b) TOC removal percentage with time during electro-Fenton oxidation. Conditions: [p-NP] = 50 mg/L, pH 5.0, [FCSW] = 3.0 g/L, $[Na_2SO_4]$ = 0.05 mol/L, air flow = 0.2 L/min, T = 298 K.

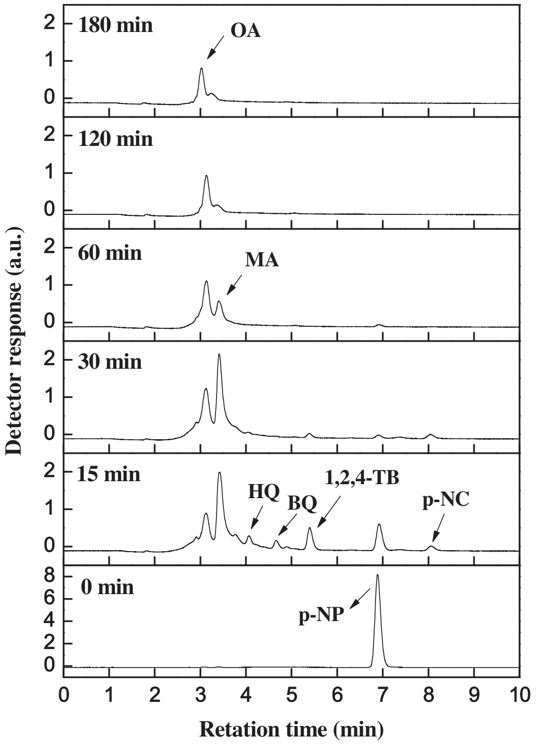

Fig. 7. HPLC chromatogram of p-NP solution treated with heterogeneous electro-Fenton process. (Conditions: [p-NP] = 50 mg/L, pH 5.0, [FCSW] = 3.0 g/L, current density = 3.0 mA/cm^2, $[Na_2SO_4]$ = 0.05 mol/L, air flow = 0.2 L/min, T = 298 K).

3.3.2. *Influence of initial FCSW concentration*

Fig. 5 illustrates the p-NP degradation at conditions of initial pH value of 5.0, current density of 3.0 mA/cm^2 with various initial concentration of FCSW. Notably, when no catalyst was added into the system, the degradation of p-NP was relatively slow, e.g. the p-NP removal percentage was 74.41% after 60 min and the TOC removal percentage was 40.49% after 180 min. The addition of FCSW significantly enhanced the degradation of p-NP because the FCSW acted as catalyst to accelerate the decomposition of H_2O_2 into $^{\cdot}OH$. When the initial FCSW concentration was increased from 1.0 to 3.0 g/L, the p-NP removal percentage was increased from 92.28 to 94.31%, and the TOC removal percentage was greatly increased from 66.21 to 78.96%. However, the improvement of the p-NP and TOC removal percentages were not obvious when the initial FCSW concentration increased from 3.0 to 5.0 g/L. This trend was mostly due to the fact that the degradation of p-NP was attributed H_2O_2, O_2 and $^{\cdot}OH$ generated on the anode with no catalyst in the electro-Fenton system. When the catalyst FCSW was added to form a 3-D system, the number of active sites increased, resulting in the improvement of the p-NP degradation. However, when the initial FCSW concentration was higher than 3.0 g/L, the degradation efficiency of p-NP was limited by the concentration of H_2O_2 reduced on the cathode. So the initial FCSW concentration of 3.0 g/L was selected for the subsequent experimental study.

3.3.3. *Influence of current density*

The current density determines the anodic oxidation and the formation of H_2O_2, which is an important parameter in electro-Fenton system. In order to investigate the catalytic activity of FCSW in

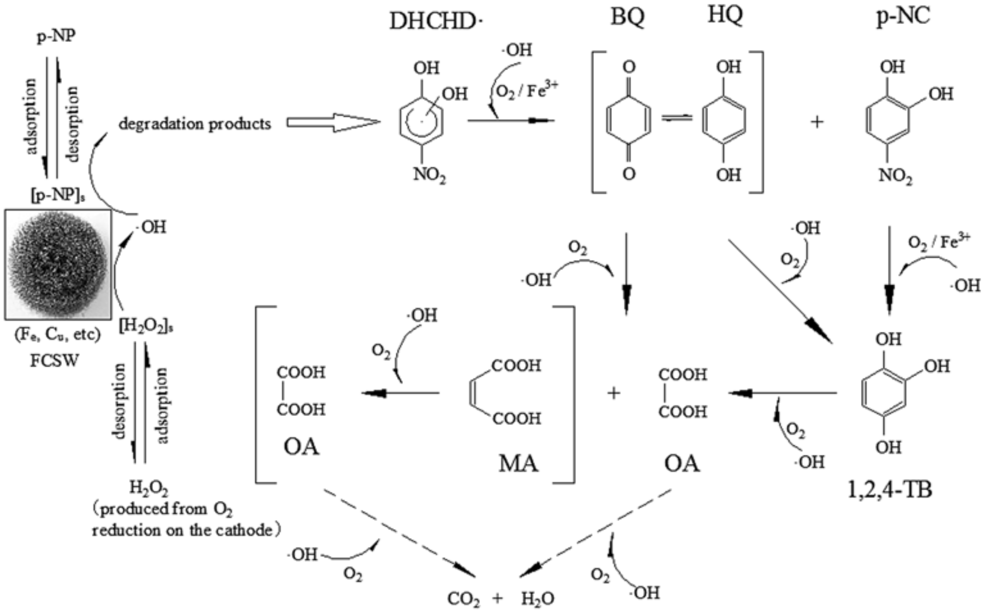

Fig. 8. Proposed reaction pathway of the degradation of p-NP by heterogeneous electro-Fenton with FCSW.

electro-Fenton system, electro-Fenton oxidation at the current density from 0.0 to 5.0 mA/cm^2, as well as the single anodic oxidation with electro-generated H_2O_2 at the current density of 5.0 mA/cm^2 (AO-H_2O_2) were studied. The experimental results are depicted in Fig. 6. If no current was applied in the system, the p-NP removal percentage at 60 min and the TOC removal percentage at 180 min were only 3.31 and 2.38%, respectively. So the adsorption of electrodes and catalyst FCSW in this study can be negligible. When the applied current density increased from 1.0 to 3.0 mA/cm^2, the p-NP removal percentage increased from 77.29 to 94.31% after 60 min, and the TOC removal percentage increased from 54.83 to 78.96% after 180 min. However, the p-NP and TOC removal percentages were declined to 88.88 and 70.72% when the current density was further increased to 5.0 mA/cm^2. It was attributed to the increased production of H_2O_2 (Fig. 2(b)) which resulted in larger amount of ·OH with iron and copper species, and the ·OH from anodic oxidation would also be promoted with increasing current density. But when the current density was further increased beyond the optimum value, although the anodic oxidation was stronger at higher current density (Figs. 5 and 6), the production of H_2O_2 decreased because of the side reactions (Eqs. (7) and (8)) [38], and eventually lead to the total amount of ·OH decreasing. Therefore, the current density of 3.0 mA/cm^2 was selected for the subsequent experimental study.

3.4. The degradation mechanism of p-NP

HPLC was used to explore the possible p-NP degradation mechanism on the catalyst FCSW. All the identified compounds were unequivocally identified by comparing the retention time of the standard compounds. Fig. 7 gives the changes of the HPLC chromatograms of p-NP degradation solution with time. The aromatic by-products (p-nitrocatechol, hydroquinone, benzoquinone, and 1,2,4-trihydroxybenzene) and the aliphatic by-products (maleic acid and oxalic acids) were detected during the process of heterogeneous electro-Fenton oxidation of p-NP. So it can be inferred that main reactions are successively electrophilic addition of hydroxyl radical on the aromatic ring leading to the formation of polyhydroxylated benzene derivatives. The concentrations of these compounds are accumulated to the maximum in the first 15 min, and then slowly decreased till totally disappearance at 60 min.

Based on the identified major aromatic intermediates, the possible degradation scheme of p-NP by FCSW heterogeneous catalyzed electro-Fenton process was proposed (Fig. 8). Firstly, ·OH was generated by the catalytic decomposition of absorbed hydrogen peroxide (produced from the reduction of O_2 near the cathode) on the FCSW surface, and the also absorbed p-NP was transformed to dihydroxycyclohexadienyl radical (DHCHD·) by the attack of ·OH. Then because of the mesomeric electro donor

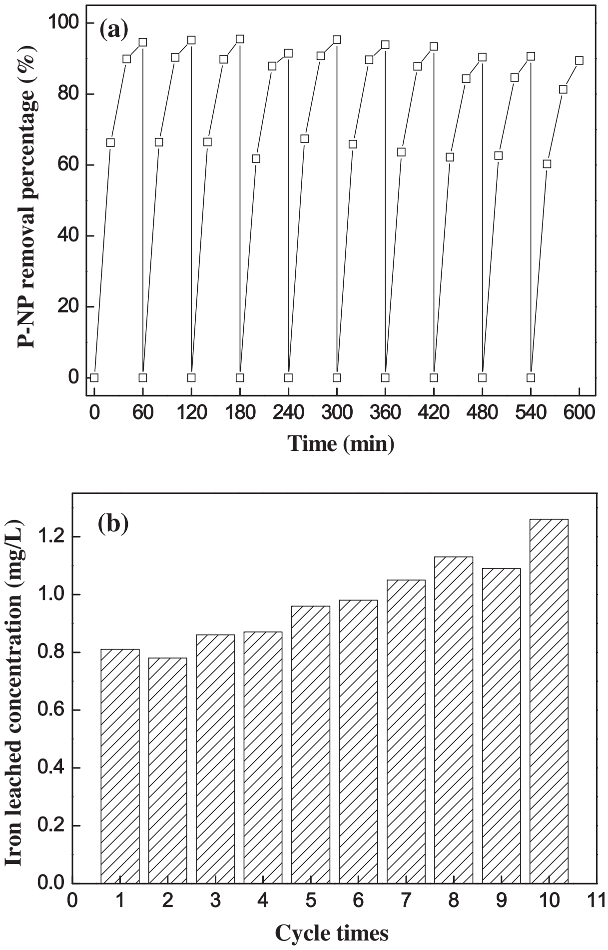

Fig. 9. Cyclic performance of FCSW in the heterogeneous electro-Fenton process: (a) p-NP removal percentage vs. cycle times and (b) variations of the concentration of leached iron ion in every cycle. Conditions: [p-NP] = 50 mg/L, pH 5.0, [FCSW] = 3.0 g/L, current density = 3.0 mA/cm^2, [Na_2SO_4] = 0.05 mol/L, air flow = 0.2 L/min, T = 298 K.

character of the hydroxyl group (–OH) on the benzene ring, $^{\cdot}OH$ tends to attack on the ortho- and para- positions [10], so DHCHD$^{\cdot}$ was oxidized to hydroquinone (HQ), benzoquinone (BQ), and p-nitrocatechol (p-NC) quickly in the presence of oxidants such as O_2 and Fe^{3+}. And the formation of 1,2,4-trihydroxybenzene (1,2,4-TB) from the further oxidation of HQ and p-NC due to the electrophilic attack of $^{\cdot}OH$ on HQ and the ipso-attack of $^{\cdot}OH$ on the $-NO_2$ of p-NC. Finally, the aromatic intermediates could further reaction with $^{\cdot}OH$ to form short chain carboxylic acids such as maleic acid (MA), fumaric acid (FA), and oxalic acid (OA), which were then mineralized to CO_2 and H_2O.

3.5. Catalytic stability of FCSW

The reusability of FCSW catalyst was ultimately evaluated for the repeated degradation of p-NP under the above optimized conditions. A magnet was used to separate the FCSW from the solution after each treatment. Then the separated FCSW was rinsed with deioned water for three times and added again to the fresh p-NP solution. This process was repeated for 10 times. Fig. 9(a) depicted the performance of p-NP removal after 60 min treatment in every cycle, and the results showed that the removal percentage of p-NP degradation could be kept at a relatively stable value from 89 to 96% during 10 cycles using the recycled FCSW. Besides, Fig. 9(b) shows that the concentration of leached iron ion in all runs, and there was about 1.0 mg/L iron ion leaching to the solution in every cycle, which indicated that the dissolution of FCSW was slight. At the same time, the elementary composition (Table 1), the SEM image and energy dispersive spectrometric (EDS) mapping of the FCSW used for 10 cycles (Fig. 3(b) and (d)) all exhibited a high stability except a little amount of Fe and Cu leaching. Although 10 cycles are not long enough to evaluate the long-term performance, we could preliminarily deduce that the FCSW catalyst has a certain potential for sustainable use in the heterogeneous electro-Fenton process.

4. Conclusions

The reusability of catalyst and operating pH range are two common limiting factors for the wide application of electro-Fenton process, and the development of heterogeneous electro-Fenton catalyst with high pH adaptability is of practical importance. In this work, a novel catalyst FCSW was used as a heterogeneous catalyst for electro-Fenton degradation of p-NP, and its performance was examined by varying different operating parameters. Compared with the homogeneous electro-Fenton process, the heterogeneous electro-Fenton process with FCSW catalyst exhibited higher degradation efficiency and had broader operating pH range. The possible degradation mechanism of p-NP catalytic degradation process with FCSW was explored by the technology of HPLC. Furthermore, the results of stability and reusability of FCSW demonstrated that this novel heterogeneous catalyst had a good application prospect in the electro-Fenton treatment of wastewater.

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