Synthesis of nitrogen-doped carbon nanotubes-FePO₄ composite from phosphate residue and its application as effective Fenton-like catalyst for dye degradation

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ABSTRACT

Phosphate residue is regarded as a hazardous waste, which could potentially create significant environmental and health problems if it is not properly treated and disposed of. In this study, nitrogen-doped carbon nanotubes-FePO₄ (NCNTs-FePO₄) composite was successfully synthesized from phosphate residue, and its application as an effective catalyst was explored. Firstly, an effective method was developed to recover FePO₄ from phosphate residue, achieving an impressive FePO₄ mass recovery rate of 98.14%. Then, the NCNTs-FePO₄ catalyst was synthesized from the recovered FePO₄ by two main reactions, including surface modification and chemical vapor deposition. Finally, the synthesized NCNTs-FePO₄ was applied to photo-degrade 15 mg/L Rhodamine B (RhB) in a Fenton-like system. The results showed that 98.9% of RhB could be degraded in 60 min, closely following the pseudo-first-order kinetics model. It was found that even after six consecutive cycles, NCNTs-FePO₄ still retained a high catalytic capacity (> 50%). Moreover, •OH radicals participating in the RhB degradation process were evidenced using quenching experiments and electron paramagnetic resonance analysis, and a rational mechanism was proposed. It was demonstrated that the materials synthesized from hazardous phosphate residue can be used as an effective catalyst for dye removal.

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Introduction

Phosphate residue is formed after metal surface phosphorization and is regarded as hazardous waste due to its strong acidity, high phosphorus content and the presence of some heavy metal ions in the sludge from the phosphating solution (Juchi and Huang, 2010; Kuo, 2012; Narayanan, 2005; Petschel, 1996). Additionally, the accumulation of metals and excess PO₄³⁻ from phosphate residue can easily cause soil acidification and water eutrophication, resulting in serious environmental pollution (Lurling and van Oosterhout, 2013; Li et al., 2010; Meinkmann et al., 2015). The conventional methods for treating the phosphate residue are landfill, and solidification and vitrification, which are expensive and
environmentally unfriendly, as a large amount of energy is consumed (Dogan and Karpuzcu, 2010; Meinikmann et al., 2015; Reeve, 2007; Xiao et al., 2008). More importantly, the useful metals contained in the sludge are discarded. Therefore, it is important that a more reliable and economical strategy be developed to recover the major components of phosphate residue. Yue et al. (2014) recently regulated the composition of phosphate residue by adding hydrochloric acid to change the pH value, as the components exhibited different phase states as a function of pH. When the pH value is 1–3, the FePO4 remains in the solid phase while other phosphates including Zn3(PO4)2 and Ca3(PO4)2 are dissolved. However, this leaching process using hydrochloric acid has a very low throughput. Thus, it is imperative to select a suitable acid for the leaching process. Considering the redox potential and the simplicity of the extraction process, phosphoric acid (H3PO4) could be used (Molina-Sabio et al., 1995; Shamsuddin et al., 2016).

On the other hand, the organic waste produced in industrial processes has been another significant environment and health issue. The Fenton-like catalytic process, as a green remediation technology used to degrade dyes using various catalysts, has drawn intensive attention (Khataee and Zarei, 2011; Sheydaei et al., 2014; Wang et al., 2005). In such a process, the transition metal (Fe, Mn, etc.) is considered an effective catalyst for generation of radicals, such as $\text{OH, O}_2^\cdot$, $\cdot\text{OOH}$, which can decompose organics into water, CO2 and easily degradable compounds. So far, a variety of heterogeneous iron-based materials have been widely used in Fenton-like technology due to their abundant resources, high catalytic activity and possibility of recycling after reaction (Cruz et al., 2017). Moreover, as the major component of phosphate residue, iron phosphate has many advantages in catalysis (Fedorková et al., 2010; Guo et al., 2015), water purification (Hamayun et al., 2014), electrochemical performance (Jegal et al., 2013; Yue et al., 2014) and environmental compatibility (Jiang and Jiang, 2012; Liu et al., 2008). For these reasons, it would be very powerful if the materials collected from waste residues could be used to remediate other environmental concerns. For example, Lin et al. (2010) fabricated silica-supported FePO4 catalysts for oxidative bromination of methane and achieved 50% methane removal. Nevertheless, the catalytic activity of FePO4 in the Fenton-like process is quite low, because the reduction reaction from Fe(III) to Fe(II) is limited by its kinetics, which need to be improved by utilization of ultraviolet (UV) light combined with carbon-based materials (Jung et al., 2012; Li et al., 2012; Nitoi et al., 2013; Peng et al., 2017).

Carbon-based materials, such as nitrogen-doped carbon nanotubes (NCNTs) (Wang et al., 2011; Yao et al., 2016a), graphene (Liu et al., 2013) and graphitic carbon nitride (Li et al., 2017; Ma et al., 2017), have recently been demonstrated to be promising Fenton-like catalysts, which have been used to efficiently improve the adsorption and catalytic performance in organics removal due to their high specific surface and excellent capability for electron transfer. Iron encapsulated in boron and nitrogen co-doped carbon nanotubes showed an increased activity as a catalyst in oxidative degradation of various organics (Yao et al., 2016b). It has been demonstrated that heteroatom doping (oxygen, nitrogen and sulfate) bonded and concentrated on the edges of the carbon layers results in the formation of unsaturated carbon atoms and defects at the edge of the carbon planes (Duan et al., 2015a, 2015b; Hlekelele et al., 2016). These sites with a high concentration of unpaired electrons play a key role in promoting the recycling of Fe(III)/Fe(II), thereby accelerating the production of $\cdot\text{OH}$ from $\text{H}_2\text{O}_2$.

Inspired by the above aspects, we explored an effective method to recover FePO4 from phosphate residue and further synthesize nitrogen-doped carbon nanotubes by the chemical vapor deposition method. To the best of our knowledge, such an approach has not been reported in any previous publications. The synthesized NCNTs-FePO4 composite has shown strong catalytic capability to remove organic dye in aqueous solution.

1. Materials and methods

1.1. Materials

Phosphate residue was supplied by an auto components company in Zhejiang, China. Na2CO3 (analytical reagent (AR), ≥ 99.8%), hydrogen peroxide (AR, ≥ 30%), hydrofluoric acid (AR, ≥ 40%), phosphoric acid (AR, ≥ 85%) and diethylamine (AR, 99%) were obtained from Sinopharm Chemical Reagent Co. Ltd., of Shanghai, China. Rhodamine B (Rhb) (AR, ≥ 95%) was purchased from Sigma Aldrich Co., USA. Other chemicals used in the present work were of analytical grade and used without further purification. Deionized water was produced by an ultrapure water system (UPT-I-60L, Super Pure Technology Corporation, China).

1.2. Catalyst preparation

The procedures used to prepare the catalyst with unique properties included the removal of impurities, the surface modification of purified samples, the synthesis of nitrogen-doped carbon nanotubes, and the removal of amorphous carbon.

Specifically, 20 g phosphate residue and 2 g H3PO4 were mixed with 20 g deionized water in a beaker at pH 2.31. After stirring for 8 hr, the product was filtered and washed with deionized water until the pH reached 7, then dried at 80°C overnight. In order to ensure the purity of the sample, this purification process was repeated three times to remove zinc and calcium phosphate. To provide active Fe and enable the fabrication of NCNTs on the surface of the FePO4, 10 g of Na2CO3 and 20 g purified FePO4 were added simultaneously to deionized water with continuous stirring at room temperature for 6 hr to form a yellow suspension. The resulting solid was filtered and washed using deionized water until the pH value of the filtrate was about 7, and then dried at 80°C for 12 hr. The pretreated FePO4 was heated to 800°C at 20°C/min in N2 atmosphere in the furnace. Diethylamine was then flowed into the system as a C/N precursor at 10 mg/min for 2 hr (Hlekelele et al., 2016). After that, a black product was obtained when the reactor was cooled to room temperature. The obtained sample was washed three times by 10% HF solution and then dried at 105°C overnight. The final product was labeled as NCNTs-FePO4.
1.3. Catalytic performance tests of catalyst

The photo-Fenton-like degradation reaction was carried out with a catalyst dosage of 2.0 g/L, \( \text{H}_2\text{O}_2 \) concentration of 10 mmol/L and initial RhB concentration of 15 mg/L. At designated intervals, samples of the solution were collected and immediately centrifuged to monitor the degradation efficiency by ultraviolet and visible spectrophotometry (UV–vis) (UV-2550, Shimadzu Corporation, Japan) (Guo et al., 2015). The reaction rate \((k)\) was calculated by the pseudo-first-order kinetic model, as shown in Eq. (1) (De Laat and Gallard, 1999):

\[
k = (\ln C_0 - \ln C)/t
\]

where, \( C_0 \) (mg/L) and \( C \) (mg/L) are the initial and final RhB concentrations, respectively; \( t \) (min) is the reaction time. Additionally, the synergetic index (SI) of the catalyst was evaluated using the following equation (Ai et al., 2014):

\[
\text{SI} = k_{\text{OH}}/(k_{\text{H}} + k_{\text{OM}})
\]

where \( k \) is the rate constant, \( U, M \) and \( H \) represent ultraviolet light, catalyst and hydrogen peroxide, respectively.

All degradation experiments were performed in a photochemical reactor (XPA-7, Xujie Electromechanical Plant, China) stirred at 200 r/min. A 500 W ultraviolet lamp was chosen as the light source. After Fenton-like degradation of the organics, the NCNTs-FePO\(_4\) catalyst was collected with a magnet and then reused. Since the amount of released iron ions is a key parameter in catalyst evaluation, the concentration of iron ions in solution was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES) (ICAP 6000, Thermo Corporation, USA).

2. Results and discussion

2.1. Recovery of FePO\(_4\) from phosphate residue

The composition of the phosphate residue is mainly consisted of FePO\(_4\), Zn\(_3\)(PO\(_4\))\(_2\) and Ca\(_3\)(PO\(_4\))\(_2\). In the acid leaching process, the purity and morphology of the obtained FePO\(_4\) strongly depend on the acid leaching time. XRD patterns (Appendix A Fig. S1) revealed that the diffraction patterns of samples can easily be ascribed to the monoclinic FePO\(_4\)-\(2\text{H}_2\text{O}\) phase (PDF#3-0666). The sharp and narrow diffraction peaks of the samples indicate that the material has excellent crystallinity (Zhou et al., 2017). A comparison between samples with different acid leaching times showed strong intensity for the (002) and (122) diffraction peaks, which suggests that the hydrous FePO\(_4\) recovered from the phosphate residue after three cycles of acid leaching is well-crystallized with scarcely any impurities, and can be expected to be applied in many fields.

The SEM images of the FePO\(_4\) recovered from the phosphate residue also confirmed that the acid leaching treatment was successful. It can be clearly seen from Appendix A Fig. S2d and e that the sample after triple acid leaching exhibited a uniform granular morphology with only a few exceptions, which could be due to vestigial Zn\(_3\)(PO\(_4\))\(_2\) in the sample, and the main diffraction peak (131) in the XRD pattern also confirmed this hypothesis (Appendix A Fig. S1). However, some defects were observed on the surface of the samples after quadruple acid leaching (Appendix A Fig. S2f), indicating that further corrosion occurred on the surface of FePO\(_4\) with more exposure to acid solution, which could result in low yield of FePO\(_4\). To compare the chemical composition of purified and raw samples, XRF analysis was undertaken and the results are presented in Table 1 (calculated from Appendix A Table S1). The mass percentage of valuable FePO\(_4\) increased...
from 68.70% to 98.14% (Appendix A Eq. (S1)), while the \( \text{Zn}_3(\text{PO}_4)_2 \) decreased from 20.05% to 1.1% and \( \text{Ca}_3(\text{PO}_4)_2 \) decreased from 9.3% to 0.5%. The removal efficiency of impurities was 94.06%. In brief, the purified sample was mainly composed of \( \text{FePO}_4 \), which could be further used to prepare the NCNTs-\( \text{FePO}_4 \) catalyst.

2.2. Morphology and structure of the prepared catalyst

The morphology and structure of as-synthesized NCNTs-\( \text{FePO}_4 \) were characterized by SEM and TEM. Fig. 1a–b reveals that bamboo-like nitrogen-doped carbon nanotubes were successfully synthesized on the surface of \( \text{FePO}_4 \). The outer diameter of the tubes is in the range of 50–200 nm with a wall-thickness of between 15 and 25 nm, more than 5 times larger than the CNTs in a previous study (Kang et al., 2017). It is very likely that small \( \text{FePO}_4 \) particles are encapsulated into the carbon layer, which will roll up to form NCNTs, increasing the particle size of the final product. The bamboo-like structure and interlayer spacing of 0.34 nm in the nitrogen-doped carbon nanotubes (Fig. 1c–d) are attributed to the introduction of nitrogen into the graphitic structure, forming \( \text{C} = \text{N} \) bonds by altering the nanotube surface from a straight cylinder geometry (Fan et al., 2015; Hleklele et al., 2016). Moreover, a propensity for unsaturated carbon atoms and high concentration of unpaired electrons were resulted from this heterogeneous surface, which could enhance the electron-donor capability and then favor some catalysis (Bach and Semiat, 2011; He et al., 2016).

A comparison between the XRD patterns of the NCNTs-\( \text{FePO}_4 \) composite and the pristine \( \text{FePO}_4 \cdot 2\text{H}_2\text{O} \) is shown in Fig. 2. The NCNTs-\( \text{FePO}_4 \) showed a similar XRD pattern to \( \text{FePO}_4 \cdot 2\text{H}_2\text{O} \), suggesting that the introduced NCNTs have no noticeable effect on the crystal structure of \( \text{FePO}_4 \). However, two new peaks appeared at 26.1° and 43.4° corresponding to the typical (002) and (101) planes of NCNTs, respectively (Yao et al., 2016a). In addition, the intensity of \( \text{FePO}_4 \cdot 2\text{H}_2\text{O} \) peaks became weaker, confirming that NCNTs were successfully synthesized on the \( \text{FePO}_4 \), which is consistent with the SEM results.

The specific surface areas of the phosphate residue, purified sample and NCNTs-\( \text{FePO}_4 \) are presented in Table 2. The specific surface area increased from 5.8616 to 24.4163 m²/g.

<table>
<thead>
<tr>
<th>Samples</th>
<th>( \text{FePO}_4 ) (wt.%)</th>
<th>( \text{Zn}_3(\text{PO}_4)_2 ) (wt.%)</th>
<th>( \text{Ca}_3(\text{PO}_4)_2 ) (wt.%)</th>
<th>Others (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphate residue</td>
<td>68.70</td>
<td>20.05</td>
<td>9.30</td>
<td>1.95</td>
</tr>
<tr>
<td>Purified sample</td>
<td>98.14</td>
<td>1.1</td>
<td>0.5</td>
<td>0.26</td>
</tr>
</tbody>
</table>
after the introduction of NCNTs into FePO₄ compared to the untreated sample. It is worth noting that the low BET values of the three samples compared to those in a previous paper (Huang et al., 2017) may be attributed to the presence of too many impurities in the phosphate residue as well as residual H₃PO₄, the fact that the recovered FePO₄ was purified from slag instead of being chemically synthesized, and that the NCNTs-FePO₄ sample in this study is mainly composed of FePO₄ and a handful of the NCNTs in quantity, respectively. However, the NCNTs-FePO₄ material still showed great catalytic performance in the degradation of organics, as shown in the next section.

2.3. Catalytic evaluation

The catalytic performance of NCNTs-FePO₄ was tested using RhB as a model contaminant under different conditions. As can be seen from Fig. 3a, the degradation efficiency of RhB is 34.3% under UV irradiation for 120 min, suggesting that ultraviolet light facilitates the RhB degradation (Zhang et al., 2015). For the UV/NCNTs-FePO₄ system, the degradation efficiency of RhB increased to 39.4%, but this was lower than that of the UV/H₂O₂ (64.9%) system, indicating that H₂O₂ benefits the dye removal process by generating free radicals under UV due to its high oxidizing power (E°(•OH/H₂O) = 1.9–2.7 V). More significantly, the concentration of RhB was decreased by 81.2% when NCNTs-FePO₄ and H₂O₂ were used together, suggesting that more radicals were generated from H₂O₂ by the NCNTs-FePO₄ catalyst. Therefore, NCNTs-FePO₄ coupled with H₂O₂ is an effective system for the degradation of organic pollutants. Furthermore, the RhB was completely degraded in the UV/NCNTs-FePO₄/H₂O₂ system within 120 min, which was almost twice the removal rate achieved by UV/H₂O₂, indicating that the NCNTs-FePO₄ catalyst played a critical role in the Fenton-like process.

To quantify the effects of NCNTs-FePO₄ and H₂O₂ under ultraviolet light, the pseudo-first-order kinetic constant k and synergetic index SI were calculated. Comparing different systems (Fig. 3b), the rate constant (k) of the UV/NCNTs-FePO₄/H₂O₂ system (0.073 min⁻¹) was 10 times higher than that of the UV/NCNTs-FePO₄ system (0.0064 min⁻¹) and 5 times higher than that of the NCNTs-FePO₄/H₂O₂ system (0.014 min⁻¹). Moreover, the SI value of the UV/NCNTs-FePO₄/H₂O₂ system was calculated as 3.60, much greater than that of UV/FePO₄/H₂O₂.
These results suggest that the introduction of NCNTs on the FePO₄ surface could dramatically enhance the degradation of RhB, which will be further discussed in the following section. In these systems, the concentration of dissolved ions was detected by ICP-AES. The iron leaching was negligible compared to the iron content in the catalyst, showing that the activation of the H₂O₂ oxidant on the catalyst surface is mainly heterogeneous rather than homogeneous. The leaching of other metal ions, including zinc, cadmium and manganese, remained below 1 mg/kg, which is acceptable according to European Union (EU) and USA discharge standards (<2 mg/kg) (Ma et al., 2017).

Further investigations were implemented to clarify the effects of reaction parameters on the photo-degradation. To quantify the effect of different parameters in the UV/NCNTs-FePO₄/H₂O₂ system, the kinetic curves for RhB photodegradation were fitted to the pseudo-first order model. The effect of NCNTs-FePO₄ dosage on the degradation efficiency of RhB is presented in Fig. 4a. The RhB removal within 60 min reached up to 81.6%, 98.9%, and 91.5%, for catalyst dosages of 1.0, 2.0, and 3.0 g/L, respectively. The kinetic rate constant increased from 0.027 to 0.073 min⁻¹ when the NCNTs-FePO₄ dosage was increased from 1.0 to 2.0 g/L, suggesting that a larger amount of catalyst would facilitate the generation of •OH radicals. However, the degradation rate of RhB did not increase significantly when the catalyst dosage was increased to 3 g/L, because of the obstruction of UV irradiation by the catalyst. Fig. 4b shows the importance of the effect of H₂O₂ dosage in the Fenton-like reaction. The degradation efficiency of RhB was increased as the H₂O₂ concentration changed from 5 to 10 mmol/L, which was ascribed to the generation of more •OH radicals from H₂O₂. However, only a slight decrease in the degradation rate was observed when the H₂O₂ dosage was further increased to 15 mmol/L, due to the fact that H₂O₂ works as a scavenger of the highly potent •OH radicals at high concentrations (Cruz et al., 2017).

The pH is another significant parameter in the Fenton-like system. As can be seen in Fig. 4c, the RhB removal reaction showed different behavior when the pH was increased from 2.15 to 10.14. RhB was removed completely in 120 min when the pH increased from 2.15 to 6.21, as more oxidant species such as •OH radicals were generated, which could degrade organics more effectively. At basic pH (8.04–10.14), a decrease in degradation efficiency of RhB was observed, which was attributed to the disproportional reaction of H₂O₂, leading to lower •OH production. Fig. 4d clearly shows the variation in the ultraviolet and visible spectral (UV–vis) changes of RhB under optimum conditions. Unless otherwise stated, reaction conditions were 2.0 g/L NCNTs-FePO₄, 15 mg/L RhB, and 10 mmol/L H₂O₂ without pH adjustment.
of the UV–vis spectrum of RhB with increasing reaction time in the UV/NCNTs-FePO4/H2O2 system. The intensity of adsorption peaks appearing at 552 nm decreased greatly in the second 5 min during the Fenton-like oxidation.

The stability and recyclability of NCNTs-FePO4 catalysts was evaluated in successive experiments. As shown in Fig. 5a, the RhB degradation declined after the first cycle, but 54% removal efficiency still remained after 6 cycles, and the reaction rate constant declined greatly from 0.073 to 0.0062 min⁻¹ (Fig. 5b). This could possibly be ascribed to chemical and structural changes to the NCNTs-FePO4 surface, including the adsorption of intermediates and the coverage of active surface sites by organics (Yao et al., 2016b). FTIR characterization of NCNTs-FePO4 further confirmed the excellent chemical stability of the catalyst. As presented in Fig. 6a, the catalysts showed similar FTIR spectra before and after cyclic utilization. These results suggested that NCNTs-FePO4 was an effective and stable catalyst for the heterogeneous Fenton-like process. In addition, NCNTs-FePO4 dispersed in a water solution can be conveniently separated and collected by a magnet (Fig. 6b).

2.4. Proposed mechanisms

To identify the hydroxyl radicals as major active oxygen species involved in the UV/NCNTs-FePO4/H2O2 system, tert-butanol (TBA) was selected as the radical quencher due to its high reactivity toward •OH ($k_{•OH} = 3.8 \times 10^8 - 7.6 \times 10^8$ L/(mol·sec)). As shown in Fig. 7a, without a quenching agent, about 99% of RhB was degraded in 90 min. However, the removal of RhB was obviously decreased at different concentrations of TBA, indicating that a large amount of •OH radicals were generated in the Fenton-like system. It should be noted that even after the addition of TBA with an equivalent volume of H2O2, about 9% RhB removal can still be achieved. From this we deduced that only a low removal rate (9%) could be achieved by ultraviolet light (Zhang et al., 2015).

The EPR technique, which can be used to investigate the evolution of active radicals generated during the reaction, further confirmed the existence of hydroxyl radicals. The EPR spectra (Fig. 7b) displayed a typical 4-fold peak with an intensity ratio of 1:2:2:1, which can be ascribed to the DMPO•OH adduct. Moreover, the special signals of DMPO•OH measured after
5 min varied a great deal in quenching experiments, indicating that •OH radicals played a key role in RhB degradation.

For a better understanding of the degradation mechanism of organic contaminants, XPS analysis of the as-synthesized NCNTs-FePO₄ catalysts was carried out. The survey scan spectrum of NCNTs-FePO₄ before and after RhB degradation is presented in Fig. 8a with the characteristic peaks of C, O, P, N, and Fe. Furthermore, the Fe 2p spectrum (Fig. 8b) was

![Graph](image1)

Fig. 7 – (a) Catalytic degradation of RhB by UV/NCNTs-FePO₄/H₂O₂ system and (b) electron paramagnetic resonance (EPR) spectrum of 5,5-dimethylpyrrolone-oxide-•OH (DMPO-•OH) with different concentrations of tert-butanol (TBA).

![Graph](image2)

![Graph](image3)

![Graph](image4)

![Graph](image5)

Fig. 8 – (a) X-ray photoelectron spectroscopy (XPS) survey, (b) Fe 2p XPS spectra, (c) N1s XPS spectra and (d) C1s XPS spectra of NCNTs-FePO₄ before and after RhB removal.
deconvoluted into two peaks at 714.1 and 727.2 eV with two satellite signals at 718.6 and 731.5 eV, respectively. In contrast, the binding energy showed a slight shift of 1 eV (from 714.1 to 713.1 eV) after reaction. This negative shift can be attributed to the increased electron density on the Fe(III) due to the electron donation from the lone pair of electrons in NCNTs, indicating that some Fe(III) could be transformed to Fe(II) in the heterogeneous Fenton-like process (Yao et al., 2016a). The N ls spectrum (Fig. 8c) of samples was fitted to three components, assigned to pyridinic N (397.7 eV), graphitic N (401.0 eV) and oxidized N (406.5 eV), respectively, similar to previous reports (Wang et al., 2011; Pan and Bao, 2008). Pyridinic N has been recognized as a catalytically active site for oxygen reduction (Raziq et al., 2016). Additionally, the active N species including graphitic N and oxidized N are generally regarded as important factors for the facilitation of photo-Fenton-like reactions due to the greater amount of active sites formed by nitrogen doping (Peng et al., 2017). It was also found that the binding energies of pyridinic N, graphitic N and oxidized N become lower after the catalytic degradation, which could likely be attributed to the electronegativity of nitrogen atoms. Another significant change in the XPS results involved the C ls spectra. As shown in Fig. 8d, the C ls signals exhibited a peak-shift from lower to higher binding energy after the catalytic reaction. This shift suggested that some electrons could be transferred from graphitic domains in the NCNTs. Based on the above results, we deduced that the NCNTs functioned as an electron-transfer medium to donate electrons for Fe(III) reduction, which could further accelerate the recycling of Fe(III)/Fe(II) and produce high catalytic activity in the Fenton-like system. To gain a deeper understanding of how NCNTs provided higher activity for accelerating the recycling of Fe(III)/Fe(II), a cyclic voltammetry test was conducted as reported by Ma et al. (2017). As shown in Fig. 9, a reduction peak was clearly observed at about −0.58 V, and NCNTs-FePO₄ showed a much higher reduction current (33.36 μA). This difference suggested that the Fe(III) is prone to being reduced to Fe(II) by NCNTs, because the carbon nanotubes exhibited high electron-transfer performance in the redox reaction (Peng et al., 2017; Yao et al., 2016a).

To facilitate the identification of all paths for the RhB removal reaction, a possible mechanism was proposed, as illustrated in Fig. 10. The reaction starts with the redox cycle of Fe(III)/Fe(II) (as shown in the interior reaction), initiated by partial electron transfer from NCNTs. Subsequently the formed Fe(II) will catalyze the traditional Fenton reaction to produce the unbound oxidant •OH, and Fe(II) was restored to Fe(III). Finally, the generated •OH radical attacks RhB in the solution to yield CO₂, H₂O and small molecules. Therefore, the NCNTs-FePO₄ catalyst showed outstanding catalytic performance in the Fenton-like reaction.

3. Conclusions

In this study, an effective phosphate residue recovery method was proposed, which could effectively purify 98.14% of FePO₄ and be used to fabricate a heterogeneous photo-Fenton-like catalyst. It was found that NCNTs-FePO₄ has good catalytic performance in RhB degradation in combination with UV and H₂O₂. The kinetic studies indicated that the catalyst dosage, H₂O₂ dosage, and pH have a great influence on RhB oxidative degradation. The stability and recyclability results showed
that the catalytic activity of NCNTs-FePO₄ declined after the first cycle, but a removal efficiency of 54% still remained after 6 cycles. EPR results demonstrated the evolution of active radicals during the reaction, and •OH is believed to be the primary radical in the Fenton-like process. XPS and CV curve results provide a further insight into the electron transfer between Fe(III) and NCNTs. This study not only showed that phosphate residue can be effectively recovered, but also demonstrated that a promising catalyst can be fabricated for the removal of organic pollutants.

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Appendix A. Supplementary data

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