Peroxymonosulfate enhanced photoelectrocatalytic degradation of phenol activated by Co_3O_4 loaded carbon fiber cathode

Shanshan Liu^{a,b}, Xu Zhao^{a,*}, Yanbin Wang^a, Huixin Shao^{a,b}, Meng Qiao^a, Yan Wang^a, Shen Zhao^a

^a Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

^b University of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

In this paper, a photoelectrocatalytic (PEC) system consisting of $\gamma\text{-Bi}_2\text{MoO}_6$ anode and Co_3O_4 loaded carbon fiber paper ($\text{Co}_3\text{O}_4/\text{CFP}$) cathode prepared by a hydrothermal method was established and used to degrade phenol. In order to enhance the PEC degradation efficiency of phenol, peroxymonosulfate (PMS) was introduced into this system. At an applied bias of 1.5 V, the removal efficiency of 10 mg/L phenol was increased from 6% to 100% with 2 mM PMS addition into the PEC process. The degradation rate constant of phenol was also increased to be 0.0496 min^{-1} . Effects of PMS concentration, applied bias and initial pH were investigated. Based on the ESR analysis, sulfate radicals ($\text{SO}_4^{\cdot-}$) and hydroxyl radicals ($\text{HO}^{\cdot}$) were proved to be the dominant oxidizing species for phenol degradation in the combined system. The PMS was activated to generate $\text{SO}_4^{\cdot-}$ by loaded Co_3O_4 , in which photogenerated-electrons accelerated the cobalt cycle process on the cathode. As a result, Co leaching was largely inhibited. The stability of the PEC system for organics degradation was exhibited.

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1. Introduction

Advanced oxidation processes (AOPs) are considered as one of the most active and promising research topics in the wastewater treatment field [1]. Generated active radicals with high redox potential, such as hydroxyl radicals ($\text{HO}^{\cdot}$), are responsible for the elimination and mineralization of refractory organics [2]. The most representative techniques are the Fenton reaction and its derivative processes. However, the strict requirement for pH and generation of large amounts of sludge both limit its range of application [3]. Recently, advanced oxidation technology based on sulfate radicals ($\text{SO}_4^{\cdot-}$, SR-AOPs) is reported as the most promising alternative process for Fenton reactions [4]. Sulfate radicals, with a high oxidation potential of 2.5–3.1 V, can be produced by activation of peroxymonosulfate (PMS) or persulfate (PS) through UV [5], heat [6], transition metals [7], base [8], photogenerated electron [9], carbon materials [10], or organics [11].

Among these methods, homogeneous activation of PMS by cobalt ions (Co(II)/PMS) has a better efficiency than other couples over a wide pH range (2)–(9) [12]. Early in 1987, Manivannan and Maruthamuthu reported the kinetics of aqueous polymerization of acrylonitrile initiated by the Co(II)/PMS reactions [13].

Although Co/PMS couple has been proven to be efficient for contaminant degradation, the cobalt ions in aqueous solution still causes health concerns due to the toxicity [14]. Therefore, the cobalt ions have to be removed carefully. In order to avoid this, Ren et al. tested four magnetic ferrosphenel and found that CoFe_2O_4 posed the highest activity towards PMS activation, which can be separated easily by magnet [15]. It was also reported that Co_3O_4 with a structure of Co^{2+} and Co^{3+} ions exhibited a good performance in activating PMS [16]. Recently, many researches focus on the preparation of Co_3O_4 particle with nanostructure and the construction of the supported Co_3O_4 system [17]. Ding et al. reported that a $\text{Co}_3\text{O}_4\text{-Bi}_2\text{O}_3$ composite oxide showed a strong catalytic activity towards PMS for efficient degradation of dyes and organic pollutants [4]. In addition, MnO_2 , SiO_2 and ZnO were also used as support materials to enhance the catalytic efficiency and reduce the cobalt leaching [18–20].

Nowadays, photoelectrocatalysis (PEC) which combines electrochemical oxidation and photocatalysis technique using a semiconductor electrode has shown a great potential for organic contaminants removal [21,22]. For the sake of energy conservation and efficiency improvement, further increasing the PEC efficiency for the organic degradation is desired. Most of previous studies focus on the enhancement of photocatalytic activities or visible light response of the photoanode [23,24]. But the cathode in the same system has not been paid a sufficient attention. Above two techniques are considered to be combined to enhance the organic

* Corresponding author at: P.O. Box 2871, 18 Shuangqing Road, Haidian District, Beijing 100085, China.

E-mail address: zhaoxu@rcees.ac.cn (X. Zhao).

degradation process. Previous studies are more concentrated on the discussion of oxidant addition. Therefore, the connection point between PEC system and PMS oxidation process should be further clarified.

Herein, Co_3O_4 particles were loaded onto the carbon fiber paper ($\text{Co}_3\text{O}_4/\text{CFP}$) via a facile hydrothermal process [25]. The prepared $\text{Co}_3\text{O}_4/\text{CFP}$ was used as a cathode in the PEC system to activate PMS for the generation of active radicals. Efficient degradation of phenol was achieved in this PEC system under visible light irradiation. PMS was activated by the $\text{Co}_3\text{O}_4/\text{CFP}$ cathode and the active radicals such as $\text{HO}^\cdot$ and $\text{SO}_4^{\cdot-}$ were produced, which were responsible for the enhanced removal of phenol. Meantime, the dissolved cobalt ions were reduced via the electrochemical cathodic reduction. The activation mechanism was proposed in details.

2. Experimental section

2.1. Chemicals

Carbon fiber paper (CFP) was obtained from Shanghai Hesen electric Co., Ltd. Indium-tin oxide (ITO) glass was purchased from Jingweite electronics Co., Ltd. Bismuth(III) nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 99%), molybdenum oxide (MoO_3 , 99.5%), diethylenetriaminepentaacetic acid ($\text{C}_{14}\text{H}_{23}\text{N}_3\text{O}_{10}$, 99.0 + %), diethanolamine ($\text{C}_4\text{H}_{11}\text{NO}_2$, 98–102%), phenol ($\text{C}_6\text{H}_5\text{OH}$, 99.98%), 2,4-dichlorophenol ($\text{C}_6\text{H}_4\text{Cl}_2\text{O}$, 99%), *p*-nitrophenol ($\text{C}_6\text{H}_5\text{NO}_3$, $\geq 99.0\%$), bisphenol A ($\text{C}_{15}\text{H}_{16}\text{O}_2$, $\geq 99.0\%$), ethanol (EtOH) and *tert*-butanol (TBA) were purchased from Sinopharm Chemical Reagent Co., Ltd. Diclofenac sodium ($\text{C}_{14}\text{H}_{10}\text{Cl}_2\text{NNaO}_2$, 98%) was procured from TOKYO Chemical Industry Co., Ltd. Sodium perchlorate (NaClO_4) and Potassium peroxydisulfate (Oxone, $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$) were bought from Aladdin Chemistry Co., Ltd. China.

All reagents were at least analytical grade and used without further purification. All solutions were prepared with Milli-Q water ($\rho = 18.2 \text{ M}\Omega \cdot \text{cm}$).

2.2. Fabrication of $\text{Co}_3\text{O}_4/\text{CFP}$ cathode and PEC experiments

Before used, the CFP was firstly immersed in the 0.3% (w/w) Triton X-100 solution for 24 h and then cleaned with ultrapure water for 2 h. This procedure removed the paper surface dust effectively and lowered the material hydrophobicity simultaneously. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and NaOH were dissolved in 40 mL H_2O . The pretreated CFP and precursor solution were put into the reactor, then heated at 180°C for 5 h and cooled to room temperature [26]. Finally, the $\text{Co}_3\text{O}_4/\text{CFP}$ was washed with water to remove excess particles and dried under 60°C .

All experiments were performed in a rectangular quartz reactor with phenol solution (120 mL, 10 mg/L). The PEC reaction was driven by an electrochemical workstation (CHI 660E; Shanghai Chenhua Instruments Co., Ltd, Shanghai, China) connected with a working photoelectrode (the $\gamma\text{-Bi}_2\text{MoO}_6$ film deposited onto the Indium-tin oxide glass, 13 cm^2), a counter electrode ($\text{Co}_3\text{O}_4/\text{CFP}$, 6 cm^2) and a reference electrode (saturated calomel electrode, SCE). $\gamma\text{-Bi}_2\text{MoO}_6$ film was deposited on the ITO glass as our previous work reported [27]. The visible light source was from a Xe lamp (PLS-SXE300; Beijing Perfect Light Co., Ltd, Beijing, China) with a UV cutoff filter ($\lambda > 420 \text{ nm}$). The initial pH (pH_0) adjustments were achieved by addition of H_2SO_4 (0.1 M) or NaOH (0.1 M).

2.3. Analytical method

Phenol samples were taken from the PEC reactor at different time and then immediately mixed with methanol to quench active

radicals. The concentrations of phenol were measured using high performance liquid chromatography (HPLC; Shimadzu LC-20AT, Tokyo, Japan) equipped with a C18 ($250 \text{ mm} \times 4.6 \text{ mm} \times 5 \mu\text{m}$) reversed-phase column (GL Sciences Inc., Tokyo, Japan) and a UV detector. The mobile phase consisted of 30% acetonitrile and 70% H_2O with a flow rate of 1.0 mL/min. The maximum adsorption wavelength was selected as 270 nm.

The surface morphology of the $\text{Co}_3\text{O}_4/\text{CFP}$ cathode was characterized by field emission-scanning electron microscope (FE-SEM; HITACHI SU8020, Tokyo, Japan). The X-ray diffraction (XRD) analysis was recorded on an X-ray diffractometer (X'Pert Pro MPD) with a $\text{Cu K}\alpha$ radiation. X-ray photoelectron spectroscopy (XPS) was measured on ESCALAB 250Xi (Thermo Fisher Scientific).

The mineralization degree of phenol was quantified with an Elemental vario TOC analyzer (Germany). The leached metal ions were measured by inductively coupled plasma-optical emission spectrometer (ICP-OES, Optima 8300, PerkinElmer, America). For the involved active radicals, experiments were conducted on Bruker A300-10/12 (Germany) using DMPO as trapping agent.

3. Results and discussion

3.1. Characterizations of the $\text{Co}_3\text{O}_4/\text{CFP}$ electrode

The surface morphology of CFP and prepared $\text{Co}_3\text{O}_4/\text{CFP}$ electrodes were firstly characterized by SEM. As shown in Fig. 1, the original CFP electrode is consisted of uniform fibers (Fig. 1(a) and (c)) and the major element is C (Fig. 1(e)). After loading, the Co_3O_4 particles are distributed evenly throughout the fibers and most of them shows eight (1 1 1) planes with an octahedral structure (Fig. 1(b) and (d)). The loading of Co_3O_4 does not change the main fiber structure of CFP, indicating the stability of carbon substrate. XRD patterns of the CFP and $\text{Co}_3\text{O}_4/\text{CFP}$ electrodes are presented in Fig. 2. Before loading, only peak at $2\theta = 26.5^\circ$ is identified. After loading, all the characteristic diffraction peaks at 19.08° , 31.35° , 36.91° , 59.45° and 65.30° can be assigned to Co_3O_4 (JCPDS: 43-1003). No other impurity diffraction peaks are detected, indicating the high purity of the prepared electrode. Above characterization results of the prepared electrode demonstrated the even distribution of Co_3O_4 particles on the CFP electrode.

3.2. PMS enhanced degradation of phenol in PEC process

The degradation efficiency of phenol in different systems was compared. As shown in Fig. 3(a), no phenol is degraded with single CFP and PMS within 2 h (black line). Previous studies have reported that carbon materials, such as activated carbon fiber, can activate PMS. Yang et al. proposed that the basic site on the surface of ACF may be the active site for the PMS decomposition with the generation of active radicals [28]. But, in our system, the CFP, as a kind of carbon material, does not show the capacity towards PMS activation. In the individual PEC process with $\gamma\text{-Bi}_2\text{MoO}_6$ photoanode and CFP cathode, only 4.4% phenol is removed under visible light irradiation with an applied bias of 1.5 V. But when 2 mM PMS is added into this PEC system, a removal ratio of 16.6% is observed. The increase is caused by the PMS activation induced by the electron transferred to the cathode. Zeng et al. proved the increasing current density can promote the cathodic activation of PS in the PEC process [9]. Furthermore, the prepared $\text{Co}_3\text{O}_4/\text{CFP}$ electrode is used with the addition of PMS and 79.4% removal ratio of phenol is observed. But in the PEC process with $\gamma\text{-Bi}_2\text{MoO}_6$ anode and $\text{Co}_3\text{O}_4/\text{CFP}$ cathode with the applied bias of 1.5 V, the phenol can be totally removed within 90 min under visible light irradiation. Fig. 3(b) shows more intuitively about the high perfor-

Fig. 1. SEM images (a–d) and EDS analysis (e and f) of the CFP electrode and fresh Co₃O₄/CFP electrode.

mance of this system towards PMS activation and phenol removal from the view of kinetic rate constant. In PEC system with the Co₃O₄/CFP cathode and PMS addition, the pseudo-first-order kinetic rate constant is 0.0496 min^{−1}, indicating the faster reaction rate. In addition to phenol, different recalcitrant organic pollutants have been also degraded in this system, including 2,4-dichlorophenol (2,4-DCP), diclofenac sodium (DCF), bisphenol A (BPA), p-nitrophenol (*p*-NP). As shown in Fig. 3(c), all of the target contaminants could be effectively degraded and the pseudo-first-order kinetic rate constants are 0.0295, 0.0379, 0.0634, 0.0095 and 0.0146 min^{−1}, respectively.

3.3. The influence of various parameters

The following condition experiments were conducted using the prepared Co₃O₄/CFP electrode as cathode and γ-Bi₂MoO₆ as photoanode. The effect of PMS concentration on the phenol degrada-

tion was investigated firstly. As shown in Fig. 4(a), the phenol removal efficiency increases with the added PMS amount. From 0.2 to 2.0 mM, the removal ratio is increased from 19.4% to 100% within 2 h. This result is attributed to that more PMS can react quickly with loaded Co₃O₄ and generate more active radicals [29].

And it is proved that phenol degradation in the PEC process with PMS addition follows a pseudo-first-order reaction kinetics equation. As shown in Fig. 4(b), the rate constants are 0.0017, 0.0027, 0.0079, 0.0146 and 0.0496 min^{−1}, corresponding to PMS concentration from 0.2 to 2.0 mM. Moreover, an exponential relationship could be established between k (min^{−1}) and PMS concentration over the range of 0.2 to 2.0 mM. The equation is $y = 0.0008e^{2.0706x}$ with a correlation coefficient of 0.966. This strong relationship demonstrates that the PMS concentration is the key influencing component of phenol degradation in this system. As shown in Fig. 4(c), when PMS concentration is increased from 1 to 2 mM in the solution, TOC removal ratio is increased

Fig. 2. XRD patterns of the CFP electrode and fresh $\text{Co}_3\text{O}_4/\text{CFP}$ electrode.

from 6% to 21.9%. It is demonstrated that phenol can be degraded more thoroughly in the PEC process with an increasing addition of PMS.

The influence of the applied bias on the phenol degradation efficiency was also examined. As shown in Fig. 5(a), the phenol removal ratio increases with the increase of the applied bias. Corresponded to the applied bias from 0 to 2 V, the pseudo-first-order rate constants are 0.0013, 0.0052, 0.0091, 0.0146 and 0.0292 min^{-1} , respectively. It can be deduced that the phenol degradation efficiency is significantly affected by the applied bias. It was known that the increase of the applied bias in the PEC system within a certain range is beneficial to the efficient separation between photogenerated holes and electrons; therefore the oxidation capacity of the photoanode is increased [30]. Moreover, considering the loaded Co_3O_4 on the cathode and PMS in the solution, the photogenerated electrons may promote the reduction of Co^{3+} to Co^{2+} . In most PMS activation cases, the process of Co^{3+} reduction is completed by HSO_5^- [31]. When the Co_3O_4 particles are loaded on the cathode, the Co^{3+} can receive an electron from both HSO_5^- and photogenerated electrons transferred to the cathode. The acceleration of $\text{Co}^{3+}/\text{Co}^{2+}$ cycle may be beneficial to PMS activation process and further increases the phenol degradation. In brief, the increased bias potential can improve the oxidation capacity of both two electrodes in the PEC system. Furthermore, the total Co concentration in the solution after the reaction was determined by ICP-OES. When the applied bias is increased, the Co concentration is dramatically decreased from 1.2390 mg/L at the applied bias of 0 V to 0.2275 mg/L. This result indicates the cathodic reduction in the combined system is favorable to reduce Co leaching in the solution.

The effect of the initial pH on phenol removal was presented in Fig. 6. It can be seen that as initial pH increases from 6.2 to 11.0, the degradation efficiency is 85.1%, 30.2% and 36.6%, respectively. The rate constants are 0.0146, 0.0030 and 0.0039 min^{-1} , respectively. In the acid condition, H_2O can be oxidized into $\text{HO}^\bullet$ by $\text{SO}_4^{\cdot-}$ and/or HSO_5^- at a moderate rate (Eqs. (1) and (2)) [32]. The presence of both $\text{SO}_4^{\cdot-}$ and $\text{HO}^\bullet$ leads to a relatively high degradation efficiency. But when the solution pH is increased to be 9.0, the removal ratio of phenol is only 30.2%. At this time, the OH^- would scavenge the $\text{SO}_4^{\cdot-}$ and the dominant active radicals become the $\text{HO}^\bullet$ with weaker oxidation property [33]. Hence, the degradation efficiency of phenol decreased dramatically. With further increasing pH to 11.0, the removal ratio is raised again. Qi et al. have reported that PMS can be activated by base [34]. Therefore in our

Fig. 3. Degradation efficiency of phenol (a), kinetic rate constants (b) in different catalytic systems; degradation efficiency of different pollutants in the combined system (c) within 120 min. Conditions: [Phenol] = 10 mg/L; applied bias, 1.5 V; [PMS] = 2.0 mM; pH_0 , 6.2.

system, at pH 11.0, the OH^- activated the PMS, leading to the generation of active radicals for phenol degradation. Above results demonstrate that the solution pH has a significant influence on the removal efficiency in this system. As shown in Fig. 6(b), the cobalt leaching is also decreased with the pH_0 increase. Besides, the solution pH value also decreases during the reaction as shown in Fig. 6(c). This acidification process occurred mainly at the beginning of reaction was due to the property of Oxone [35].

Fig. 4. Effect of PMS concentration on the phenol removal (a), kinetic rate constants (b) and removal ratio of TOC (c). Conditions: [Phenol] = 10 mg/L; applied bias, 1.5 V; pH₀, 6.2.

3.4. Involved active radicals

Two radical scavengers have been added to our system, including 0.75 M *tert*-butyl alcohol (TBA) for scavenging HO[•] and 0.75 M

Fig. 5. Effect of applied bias on the phenol removal (a), kinetic rate constants (b) and leached cobalt concentration (c) in PEC system. Conditions: [Phenol] = 10 mg/L; [PMS] = 1.5 mM; pH₀, 6.2.

ethanol (EtOH) for scavenging both SO₄^{•-} and HO[•]. It can be seen from Fig. 7(a) that both TBA and EtOH could inhibit the degradation of phenol. With 0.75 M TBA and 0.75 M EtOH, the degradation efficiency is 63.1% and 52.6%, respectively. Hence, the inhibition performance for the degradation of phenol revealed that both HO[•] and SO₄^{•-} existed in the system.

To confirm the reactive species involved in the combined system, ESR analyses with DMPO as spin trap agent were also conducted. As shown in Fig. 7(b), both SO₄^{•-} and HO[•] signals are observed, indicating the generation of SO₄^{•-} and HO[•] radicals.

Fig. 6. Effect of initial pH values on the phenol removal (a), leached cobalt concentration (b) and pH value variation during the reaction (c). Conditions: [Phenol] = 10 mg/L; applied bias, 1.5 V; [PMS] = 1.5 mM.

Furthermore, the signal intensity of generated active radicals nearby the cathode and anode were investigated. It can be concluded that the radicals' concentration around the cathode is obviously larger than those near the anode. The active radicals generated around the anode could be attributed to the reaction between holes on the photoanode and H₂O as illustrated in Eq. (3) [36]. The ESR results suggest that most of active radicals generated in the system are concentrated nearby the cathode.

Fig. 7. Effect of radical scavengers on the degradation of phenol (a). comparison of ESR spectrum in bulk solution, at the anode and at the cathode in the combined system (b); comparison of ESR spectrum at the cathode under different applied bias (c). Conditions: [PMS] = 20 mM; pH₀, 6.2.

It is largely reported that UV irradiation could activate PS or PMS [9,37]. But in our case, the light source is visible light and it cannot activate PMS effectively. Some researchers have reported that the photogenerated electron could activate PMS. For instance, g-C₃N₄ was used in heterogeneous activation for PMS and this couple could degrade AO7 in 30 min [38]. Hazime et al. reported that PS played an electron scavenger role and promoted the radicals

Fig. 8. Linear sweep voltammetry curves of different concentration of persulfate at CFP (a) and Co_3O_4 /CFP (b) cathode.

generation at the same time [39]. But in this case, the phenol degradation efficiency is limited with the CFP cathode without Co_3O_4 particles loading in the PEC reaction. Therefore, the PMS activation effect induced by photogenerated electrons is limited in this system; instead, PMS could be efficiently activated by the loaded Co_3O_4 on the CFP in this system and $\text{SO}_4^{\cdot-}$ and $\text{HO}^{\cdot}$ are generated. As shown in Fig. 7(c), as the applied bias increases, the concentration of free radicals increases. More free radicals are beneficial to the degradation of contaminant, indicating that the electrons transferred to the cathode are beneficial to the PMS activation by the loaded Co_3O_4 particles. In summary, it can be concluded from the ESR analysis results that free radicals are simultaneously generated both from the $\gamma\text{-Bi}_2\text{MoO}_6$ photoanode and the prepared Co_3O_4 /CFP cathode, leading to an enhanced degradation efficiency of phenol.

3.5. A proposed PMS enhanced reaction process

In our case, the $\text{SO}_4^{\cdot-}$ and $\text{HO}^{\cdot}$ radicals were determined as the main oxidizing species for phenol degradation. The generation of active radicals stemmed from not only the PEC reaction, but also the PMS activation process. Therefore, a degradation mechanism of phenol in this combined system was put forward as following equations:

In PEC system:

In PMS activation process:

Degradation process:

Fig. 9. SEM images (a and b) and EDS analysis (c) of the Co_3O_4 /CFP electrode after using.

In the conventional PEC process, the equations shown in Eqs. (4) and (5) were the main reactions for generating oxidizing species. But the degradation results demonstrate that the phenol removal was limited in the individual PEC system. In the current PEC system with Co_3O_4 /CFP cathode, phenol can be efficiently degraded with the PMS addition. The linear sweep voltammetry (LSV) curves were investigated by examining the Co_3O_4 /CFP electrode with different PMS concentrations. As shown in Fig. 8, it can be observed that the current increases as the increasing PMS concentration,

Fig. 10. Comparison of XRD pattern (a), XPS full scan spectra (b), XPS Co 2p spectra (c) and Raman spectroscopic analysis (d) of Co₃O₄/CFP electrode before and after using.

Fig. 11. The residual of phenol in three successive cycles. Conditions: [Phenol] = 10 mg/L; applied bias, 1.5 V; pH₀, 6.2; [PMS] = 1.5 mM.

indicating the stronger interaction between PMS and the prepared Co₃O₄/CFP electrode. The activation mechanism for PMS was illustrated by Eqs. (6)–(10). Sulfate radicals were produced from HSO₅⁻ along with the oxidation process between Co²⁺ and Co³⁺, which was shown in Eq. (7). In the previous studies, it was agreed that the reduction of Co³⁺ to Co²⁺ was achieved by HSO₅⁻. But in our case, the Co₃O₄ particles were loaded on the cathode and it could

receive electrons from the photoanode via the circuit simply. As shown in Eq. (10), the reduction from Co³⁺ to Co²⁺ can be achieved by receiving an electron which accelerated the PMS activation process and increased the generation of the active radicals. Meantime, the cobalt leaching was also inhibited by the high applied bias in PEC system via the cathodic reduction process. In this PEC system, generated active radicals of SO₄⁻ and HO[•] were responsible for the efficient degradation of phenol.

3.6. Stability of the prepared Co₃O₄/CFP electrode

The stability of the Co₃O₄/CFP cathode was investigated by using a same electrode in three successive experiments under the same condition. As shown in Fig. 9(a) and (b), the loaded Co₃O₄ particles become a little bigger than those fresh one. Yu et al. reported that the activation mechanism of Co₃O₄ was that Co²⁺ ions leached from the crystal lattice and participated in the homogeneous reaction in the aqueous solution and then Co³⁺ ions returned back to the Co₃O₄ crystal lattice [40]. Therefore, the generation of bigger particles may be due to this process and the regenerated particles precipitated onto the CFP again. The XRD patterns of the used Co₃O₄/CFP electrodes were recorded in Fig. 10(a). Five peaks at 2θ = 19.08°, 31.35°, 36.91°, 59.45° and 65.30° could be also assigned to Co₃O₄, indicating that the main crystalline remained stable after successive runs. The surface composition of the used Co₃O₄/CFP was determined by XPS. As shown in Fig. 10 (b), the main elements of the Co₃O₄/CFP electrode remain unchanged. As the high resolution spectrum of the Co 2 p peak

for the electrode shown, two peaks centered at 781.2 and 780.1 eV are assigned to Co_3O_4 before the reaction, which is in agreement with the previous studies. After the reaction, peak centered at 779.6 eV is assigned to Co_3O_4 and peak centered at 780.8 eV is assigned to Co^{3+} . The presence of Co^{3+} may be due to the absorption effect of aqueous Co^{3+} during the reaction. Coupled with Raman spectroscopic analysis in Fig. 10(d), above characterization results indicated that the prepared cathode remained relative stable after successive cycles. The phenol degradation reactions were also conducted by three successive runs. As shown in Fig. 11, the phenol degradation efficiency remains relative stable after three cycles. Thus, the stability of this system was exhibited.

4. Conclusions

In this work, Co_3O_4 was loaded onto the carbon fiber paper via a facile hydrothermal method and used as a cathode in the PEC system. It was demonstrated that phenol can be efficiently degraded with the addition of PMS to this PEC system. With addition of 2 mM PMS at 1.5 V applied bias, the degradation efficiency was enhanced to be 100% at 90 min. The degradation rate constant of phenol was increased to be 0.0496 min^{-1} with PMS addition. In the presence of PMS, Co_3O_4 loaded on CFP can active PMS into $\text{SO}_4^{\cdot-}$ radicals, which were responsible for the phenol degradation. Moreover, cobalt leaching was largely inhibited in the PEC system with the applied bias. Simultaneous generation of active radicals of $\text{SO}_4^{\cdot-}$ and $\text{HO}^{\cdot}$ was achieved in this combined system. Construction of this system may expand the further development of the different advanced oxidation techniques for the catalytic removal of organic pollutants.

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