The improvement of boron-doped diamond anode system in electrochemical degradation of p-nitrophenol by zero-valent iron

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Boron-doped diamond (BDD) electrodes are promising anode materials in electrochemical treatment of wastewaters containing bio-refractory organic compounds due to their strong oxidation capability and remarkable corrosion stability. In order to further improve the performance of BDD anode system, electrochemical degradation of p-nitrophenol were initially investigated at the BDD anode in the presence of zero-valent iron (ZVI). The results showed that under acidic condition, the performance of BDD anode system containing zero-valent iron (BDD-ZVI system) could be improved with the joint actions of electrochemical oxidation at the BDD anode (39.1%), Fenton’s reaction (28.5%), oxidation–reduction at zero-valent iron (17.8%), and coagulation of iron hydroxides (14.6%). Moreover, it was found that under alkaline condition the performance of BDD-ZVI system was significantly enhanced, mainly due to the accelerated release of Fe(II) ions from ZVI and the enhanced oxidation of Fe(II) ions. The dissolved oxygen concentration was significantly reduced by reduction at the cathode, and consequently zero-valent iron corroded to Fe(II) ions in anaerobic highly alkaline environments. Furthermore, the oxidation of released Fe(II) ions to Fe(III) ions and high-valent iron species (e.g., FeO42−, FeO43−) was enhanced by direct electrochemical oxidation at BDD anode.

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1. Introduction

Electrochemical treatment of wastewaters containing bio-refractory organic compounds is promising because electrochemical techniques are friendly to the environment, efficient in oxidation and easy to control [1,2]. Hitherto, many electrodes have been examined to improve the effectiveness and efficiency of electrochemical processes, including Pt, IrO2, RuO2, SnO2, PbO2, and boron-doped diamond (BDD) electrodes [2–6]. Recently, BDD electrodes have attracted much attention due to several unique technologically properties such as: an extremely wide potential window, corrosion stability in very aggressive media, an inert surface with low adsorption properties, a strong tendency to resist deactivation and strong oxidation power [2,6,7]. Studies have demonstrated that BDD electrodes are very effective in removing various bio-refractory organic pollutants, e.g., phenols [8], surfactants [9], herbicides [10], dyes [11] and endocrine disrupting chemicals [12]. The strong oxidation capability of BDD electrodes was revealed to be attributed to the existence of free hydroxyl radicals [6,13,14]. In order to further improve the performance of electrochemical systems using BDD anodes, zero-valent iron (ZVI, wasted scrap iron) was added to the BDD anode system (i.e., BDD-ZVI system) considering the expected free hydroxyl radicals generated according to the classic Fenton’s reaction (Eq. (1)) [15,16].

Fe2+ + H2O2 → Fe3+ + *OH + OH−

where Fe2+ is released from zero-valent iron and H2O2 is formed by the reduction of dissolved oxygen (Eq. (2)) at certain cathodic materials, including mercury, gold, reticulated vitreous carbon [17], carbon-felt [18], activated carbon fiber [19] and carbon-polytetrafluoroethylene (PTFE) O2-diffusion cathodes [20].

O2(g) + 2H+ + 2e− → H2O2

Fenton’s reagent (Fe2+ and H2O2) was proved very effective in degradation of organics under acid condition (usually pH 3) [21–23]. The influences of Fe2+ ion on electrochemical degradation of organic compounds at BDD anodes under acidic condition were investigated [15,16], but the influences of zero-valent iron on BDD anodes systems have rarely been studied, especially under alkaline condition. In the presence of zero-valent iron, complex reactions would occur, such as oxidation–reduction at zero-valent iron, coagulation of iron hydroxides and catalytic behavior of Fe2+ ion.

In this study, the influences of zero-valent iron on the electrochemical degradation of p-nitrophenol (a common, toxic and
non-biodegradable organic pollutant) in the BDD anode system was investigated under both acidic and alkaline conditions and the reactions in the integrated BDD-ZVI system are systematically discussed.

2. Experimental

2.1. Bulk electrolysis

Electrochemical degradation of p-nitrophenol (PNP) was conducted in an undivided cylindrical glass tank under galvanostatic condition. A Nb/BDD mesh with a diameter of 8 cm (bought from CONDIAS GmbH, Germany) was used as the anode. The BDD electrode was prepared by Hot Filament Chemical Vapor Deposition (HFCVD) and was used as received. The specification of the mesh is 12.5 mm × 7.5 mm × 1.7 mm × 1.5 mm. A Ti mesh with the same size was used as the cathode in alkaline condition, while a Ti mesh with carbon felt (Ti/CF, diameter 8 cm) was used as the cathode in acidic condition, because H2O2 was expected to be generated at the Ti/CF cathode. The electrodes were set to be parallel to the tank bottom, the cathode was set above the anode and the electrode gap was kept to be 10 mm. The solution of 450 ml volume was stirred by bubbling with air from the tank bottom. The scrap iron was cleaned with NaOH (4.5 M) and HCl (5 M) both for 30 min and then washed three times with deionized water to remove residual Fe2+ and HCl [24]. When electrolysis was performed in the presence of zero-valent iron, 20 g pretreated scrap iron was immediately added to the tank bottom, which was very close to the anode but not contact with either electrode. During electrolysis, samples were collected from the cell at various intervals for chemical analysis.

2.2. Analytical methods

In order to distinguish the roles of coagulation from other reactions during electrochemical degradation of p-nitrophenol in the presence of zero-valent iron, two samples were collected from the cell at the same time. One sample was centrifuged at 3000 r/min for 1 h to remove the flocs (iron hydroxides), while concentrated H2SO4 was added into the other sample to dissolve the flocs before chemical analysis.

The concentration of p-nitrophenol was measured by using Agilent HP1100 HPLC with a ZORBAX SB-C18 column and a DAD detector. The mobile phase was methanol/water (50/50) and the flow rate was 1.0 ml min⁻¹. The UV detector was set at 314 nm. Total organic carbon (TOC) concentration was determined by Multi-TOC/TN Analyzer (Analytik Jena AG Corporation, Germany). Fe concentration was measured by using AAS vario 6 atomic absorption spectrometer (Analytik Jena AG Corporation, Germany).

The electrochemical measurements were conducted with a CHI 760B electrochemical workstation in a conventional three-electrode cell at room temperature. The working volume of the cell was 60 ml. A BDD electrode with an exposed geometric area of 4 cm² was used as the working electrode. A platinum plate was used as the counter electrode, and saturated calomel electrode (SCE) as the reference electrode in a separate compartment with a Luggin capillary.

3. Results and discussion

3.1. Acidic condition

Three systems with the BDD anodes and Ti/CF cathodes were investigated in acidic solution (1 mM PNP + 0.1 M Na2SO4, pH 3) at current 0 mA with zero-valent iron (System I), current 400 mA without zero-valent iron (System II) and current 400 mA with zero-valent iron (System III). Fig. 1 shows the evolution of PNP removal percentage (panel a), TOC removal percentage (panel b) and Fe concentration (panel c) as a function of electrolysis time in these three systems.

When no current was applied in the cell with zero-valent iron (System I), p-nitrophenol was removed by 100% (solid squares in Fig. 1a) and the removal percentage of TOC was 15.4% (solid squares in Fig. 1b) after 5 h, which was attributed to the oxidation–reduction reaction at zero-valent iron. After the flocs were removed by centrifugation, the removal percentages of p-nitrophenol (open squares in Fig. 1a) and TOC (open squares in Fig. 1b) further increased, which demonstrated that coagulation played a role in the presence of zero-valent iron. The decrease of
Fe concentration after centrifugation (open squares in Fig. 1c) confirmed that iron hydroxides were generated and played a role of coagulation.

When 400 mA current was applied in the BDD anode cell without zero-valent iron (System II), the removal percentage of p-nitrophenol quickly reached 100% after 40 min (solid circles in Fig. 1a) and TOC was removed by 82.1% after 5 h (solid circles in Fig. 1b). Previous researches [6,13] indicated that p-nitrophenol and TOC were removed by direct electrochemical oxidation at the BDD anode and indirect electrochemical oxidation by electrogenerated oxidants (*OH, S2O82−, H2O2, etc.).

When 400 mA current was applied in the BDD anode cell with zero-valent iron (BDD-ZVI, System III), the removal percentages of both p-nitrophenol (open pentacles in Fig. 1a) and TOC (open pentacles in Fig. 1b) were moderately greater than those in Systems I and II. The performance improvement of BDD-ZVI system could be attributed to the simultaneous occurrence of more complex reactions, which included oxidation–reduction at zero-valent iron (Reaction 1 in Fig. 2), coagulation of iron hydroxides (Reaction 2 in Fig. 2), direct electrochemical oxidation at the BDD anode (Reaction 3 in Fig. 2), indirect electrochemical oxidation by electrogenerated oxidants (Reactions 4–7 in Fig. 2) and Fenton’s reaction (Reactions 8–11 in Fig. 2).

It should be noted that the BDD-ZVI system was not a simple combination of Systems I and II since a different reaction (Fenton’s reaction) was expected in this new system. At the Ti/CF cathode, H2O2 was generated by reduction of dissolved oxygen (Reaction 8 in Fig. 2), which reacted with Fe2+ (dissolved from zero-valent iron, Reaction 9 in Fig. 2) to produce free hydroxyl radicals (Reaction 10 in Fig. 2). Organics could react with these free hydroxyl radicals to be degraded (Reaction 11 in Fig. 2). On the other hand, Fe2+ would have negative effects on electrochemical oxidation processes at BDD anodes by direct oxidation at the BDD anode surface (Reaction 12 in Fig. 2), reaction with hydroxyl radicals (Reaction 13 as shown in Fig. 2 and Eq. (3)) and electrogenerated oxidants (e.g., S2O82−) at BDD anode (Reaction 14 as shown in Fig. 2 and Eq. (4)).

\[
\begin{align*}
\text{Fe}^{2+} + \cdot\text{OH} & \rightarrow \text{Fe}^{3+} + \text{OH}^- \\
\text{2Fe}^{2+} + \text{S}_2\text{O}_8^{2-} & \rightarrow \text{2Fe}^{3+} + 2\text{SO}_4^{2-}
\end{align*}
\]

(3)

(4)

To identify the contributions of coagulation, Fenton’s reaction, oxidation–reduction at zero-valent iron, and electrochemical oxidation at the BDD anode in BDD-ZVI system, following steps were carried out and the corresponding results are shown in Fig. 3.

Firstly, the role of coagulation should be identified. The coagulation contribution in BDD-ZVI system is directly related to the removal capability of flocs. Therefore, experiments were made to compare the TOC removal percentages before and after elimination of flocs. As results, TOC removal percentages were 73.9% (TOC1, solid pentacles in Fig. 1b) and 86.5% (TOC′1, open pentacles in Fig. 1b) before and after eliminating flocs, respectively, which implies that the TOC removal percentage by coagulation in BDD-ZVI system was 12.6% (TOCcoagulation = TOC1 − TOC′1).

Secondly, the role of Fenton’s reaction could be identified through electrolysis with the same BDD anode but a Ti cathode as a substitute of the original Ti/CF cathode in the presence of zero-valent iron (Fig. 4). TOC2 (49.3%) and TOC′2 (78.2%) were the TOC removal percentages before and after eliminating flocs. The primary purpose for this substitution of the cathode was to eliminate Fenton’s reaction in the system. Therefore, the TOC removal percentage by Fenton’s reaction in BDD-ZVI system was 24.6% (TOCfenton’s = TOC1 − TOC′2).

Thirdly, the role of oxidation–reduction at zero-valent iron could be examined by deducting the coagulation contribution when no current was applied in the cell with zero-valent iron (squares in Fig. 1b). TOC3 (15.4%) and TOC′3 (33.6%) were the TOC removal percentages before and after eliminating flocs. Then, the TOC removal percentage by oxidation–reduction at zero-valent iron was 15.4%.
Fig. 4. Evolution of TOC removal percentage as a function of electrolysis time in acidic solution (1 mM PNP + 0.1 M Na2SO4, pH3) with the BDD anode and Ti cathode. Symbols: (●) at current 400 mA with zero-valent iron (flocs dissolved) and (○) at current 400 mA with zero-valent iron (flocs removed).

(\text{TOC}_{\text{ox/red}} = \text{TOC}_3). \text{ It should be noted that the oxidation–reduction at zero-valent iron would be slightly different in the presence of current. This approximate value is just for reference.}

Fourthly, the role of electrochemical oxidation could be directly isolated. Note that the total TOC removal percentage was 86.5\% (\text{TOC}_3), the TOC removal percentage by electrochemical oxidation was determined as 33.8\% upon the contributions by coagulation (12.6\%), Fenton’s reaction (24.7\%) and oxidation–reduction at zero-valent iron (15.4\%) being deducted (\text{TOC}_{\text{electrochem}} = \text{TOC}_1 - \text{TOC}_{\text{coagulation}} - \text{TOC}_{\text{Fenton’s}} - \text{TOC}_{\text{ox/red}}).

In summary, the role of the aforementioned actions could be identified and quantified in the order of electrochemical oxidation, Fenton’s reaction, oxidation–reduction at zero-valent iron and coagulation in terms of their contributions over the total TOC removal percentage in the BDD-ZVI system, i.e., 39.1\%, 28.5\%, 17.8\% and 14.6\%, respectively (Fig. 3). Although the role of electrochemical oxidation at the BDD anode decreased in the presence of zero-valent iron due to the negative effects of Fe^{2+} (Reactions 12–14 in Fig. 2), it was still the main action due to the strong oxidation ability of BDD anode. The performance of BDD-ZVI system was improved with the joint actions of electrochemical oxidation at the BDD anode, Fenton’s reaction, oxidation–reduction at zero-valent iron and coagulation of iron hydroxides.

3.2. Alkaline condition

Three cases with BDD anodes and Ti cathodes were examined in alkaline solution (1 mM PNP + 0.1 M Na2SO4 + 5 M NaOH) at current 0 mA with zero-valent iron (case I), current 100 mA without zero-valent iron (case II) and current 100 mA with zero-valent iron (case III). As results, the evolutions of PNP removal percentage (panel a), TOC removal percentage (panel b) and Fe concentration (panel c) as a function of electrolysis time in these three cases are shown in Fig. 5.

When no current was applied in the cell with zero-valent iron (case I), the removal percentages of p-nitrophenol (squares in Fig. 5a) and TOC (squares in Fig. 5b) were almost zero, which implied that oxidation–reduction reaction at zero-valent iron was negligible in alkaline solution.

When 100 mA current was applied in the BDD anode cell without zero-valent iron (case II), the removal percentages of p-nitrophenol (solid circles in Fig. 5a) and TOC (solid circles in Fig. 5b) reached 20\% and 5\% after 1 h of electrolysis, respectively. Nevertheless, in the following 4 h of electrolysis, the degradation of p-nitrophenol and TOC became very slow, which might be due to the electrode fouling.

At low current, direct electrochemical oxidation of p-nitrophenol at the BDD anode would occur. The p-nitrophenolate, which was the main species of p-nitrophenol in alkaline solution, was oxidized to p-nitrophenoxy radical and further to p-nitrophenoxy cation at electrode surface (Eq. (5)). These two electrochemically formed compounds (p-nitrophenoxy radical and p-nitrophenoxy cation) are very reactive and can couple to form polymers, which resulted electrode fouling [13,25–27]. The cyclic voltammograms of p-nitrophenol at BDD electrode (Fig. 6) confirmed the electrode fouling resulted from the direct electrochemical oxidation of p-nitrophenol. It can be observed that the oxidation peak current of
p-nitrophenol decreased as the increasing scan cycles due to the electrode fouling.

\[
\begin{align*}
\text{O}^- & \rightarrow \text{O}^+ \\
\text{O}^+ & \rightarrow \text{O}^- 
\end{align*}
\]  

Interestingly, when 100 mA current was applied in the BDD anode cell with zero-valent iron (BDD-ZVI, case III), the removal rate of p-nitrophenol increased significantly compared to that in the BDD anode cell without zero-valent iron. After 4 h of electrolysis, the removal percentage of p-nitrophenol in BDD-ZVI reached 100% (solid uptriangles in Fig. 5a), which was over three times of that (31.6%) in the BDD anode cell without zero-valent iron (solid cycles in Fig. 5a).

Considering that (1) the contribution of coagulation was proved very small to removal of p-nitrophenol according to the comparison of the removal percentages before (solid uptriangles in Fig. 5a) and after (open downtriangles in Fig. 5a) the removal of flocs; (2) oxidation-reduction at zero-valent iron was negligible according to the experimental results from case I (squares in Fig. 5a); (3) Fenton’s reaction could not occur under alkaline condition according to previous studies [14,15,21]. It was deduced that the great improvement of BDD-ZVI system under alkaline condition would be attributed to the enhanced release of Fe(II) ions from ZVI by electrochemical oxidation. The dissolved oxygen concentration could be significantly reduced by reduction of Fe(II) ions in anaerobic highly alkaline environments. This was confirmed by the higher Fe concentration in the BDD-ZVI system (uptriangles in Fig. 5c).

To distinguish the role of Fe(II) ions (including HFeO\textsuperscript{2+}, FeO\textsubscript{2}\textsuperscript{2−}, FeOH\textsuperscript{2+}, Fe(OH)\textsubscript{3}, etc. in alkaline solution) on the removal of p-nitrophenol, degradation of p-nitrophenol in Fe(II) ions, EC and Fe(II) ions + EC systems was performed, respectively, and the intermediates in each system were analyzed. For Fe(II) ions and Fe(II) ions + EC systems, 0.5 g l\textsuperscript{-1} Fe\textsubscript{3+}SO\textsubscript{4} \textsubscript{7H}_2O was added instead of zero-valent iron. For EC and Fe(II) ions + EC systems, 100 mA current was applied. Fig. 7 showed the evolution of p-nitrophenol concentration as a function of the applied electrical charge in Fe(II) ions, EC and Fe(II) ions + EC systems.

In Fe(II) ions system, p-nitrophenol was quickly degraded by 22% in 0.2 Ah l\textsuperscript{-1} of electrolysis time and thereafter no further p-nitrophenol was removed. This system, electrons might be directly transferred from Fe(II) ions to p-nitrophenol, which resulted in the reduction of p-nitrophenol to p-aminophenol [27,28]. In addition, the oxidation of Fe(II) ions to Fe(III) ions (including FeO\textsubscript{2}\textsuperscript{2−}, Fe(OH)\textsubscript{2}\textsuperscript{2+}, Fe\textsubscript{2}OH\textsubscript{4}\textsuperscript{4+}, Fe(OH)\textsubscript{3}, etc. in alkaline solution) would initiate the reduction of oxygen to H\textsubscript{2}O\textsubscript{2} (Eqs. 6 and 7), and further Fe(II) ions/Fe(III) ions react with H\textsubscript{2}O\textsubscript{2} to form high-valent iron species (e.g., FeO\textsubscript{2}\textsuperscript{2−}, FeO\textsubscript{2}\textsuperscript{2−}) to oxidize p-nitrophenol (Eq. 8) [29–31]. The standard electrode potentials (E vs. SHE) for iron in alkaline solution (pH 14) are given in Eq. (9) [32]. It can be seen that they are much lower than the standard electrode potential (0.878 V vs. SHE) of H\textsubscript{2}O\textsubscript{2}/H\textsubscript{2}O at pH 14 [33]. Therefore, the reactions shown in Eq. (8) should occur. As a matter of fact, FeO\textsubscript{2}\textsuperscript{2−} has been detected in Fe\textsuperscript{2+}+H\textsubscript{2}O\textsubscript{2} systems in previous studies [34,35]. The intermediates analysis indicated that p-aminophenol and benzoquinone were both produced in this system (Fig. 8a), which further confirmed that reduction and oxidation of p-nitrophenol occurred simultaneously in Fe(II) ions system.

Fe(II) ions + O\textsubscript{2} → *O\textsubscript{2}− + Fe(III) ions
(6)
Fe(II) ions + *O\textsubscript{2}− + 2H\textsuperscript{+} → Fe(III) ions + H\textsubscript{2}O\textsubscript{2}
(7)
Fe(II) ions + H\textsubscript{2}O\textsubscript{2} → high-valent iron species
(8)
Fe\textsubscript{2}O\textsubscript{3} + 0.55 VFeO\textsubscript{2} + 0.69 VFeO\textsubscript{2} − ca. 0.8 VFe
(9)

In EC system, p-nitrophenol was degraded slowly and was only removed by 34% at the end of treatment, which was due to the small applied current density. Small quantity of p-aminophenol and benzoquinone were formed (Fig. 8b), which might be attributed to the reduction of p-nitrophenol at the cathode and the oxidation at the anode, respectively.

In Fe(II) ions + EC system, the removal rate of p-nitrophenol was greatly improved. At the end of treatment, the removal percentage of p-nitrophenol reached 83%, which was much higher than those in Fe(II) ions (22%) and EC (34%) systems. Furthermore, the intermediates analysis (Fig. 8c) demonstrated that the amount of benzoquinone in Fe(II) ions + EC system (Peak area 1037 mA\textsubscript{s}U\textsubscript{s}) was much higher than the sum in Fe(II) ions (Peak area 218 mA\textsubscript{s}U\textsubscript{s}) and EC (Peak area 65 mA\textsubscript{s}U\textsubscript{s}) systems, while the quantity of p-aminophenol in Fe(II) ions + EC system (Peak area 167 mA\textsubscript{s}U\textsubscript{s}) was almost the sum in Fe(II) ions (Peak area 105 mA\textsubscript{s}U\textsubscript{s}) and EC (Peak area 82 mA\textsubscript{s}U\textsubscript{s}).
area 61 mAU s) systems. These results indicated that the oxidation of p-nitrophenol was significantly enhanced electrochemically in Fe(II) ions + EC system. In this system, the oxidation of Fe(II) ions to Fe(III) ions and high-valent iron species (e.g., FeO2+, FeO42−) would occur directly at BDD electrode. During electrolysis, oxygen evolution was observed at BDD anode, which implied that the anode potential was larger than the oxygen evolution potential (ca. 1.04 V vs. SHE) at BDD electrode in alkaline solution (Fig. 9). Since the standard electrode potentials of iron at pH 14 (Eq. (9)) are much lower than 1.04 V vs. SHE, the oxidation of Fe(II) ions to Fe(III) ions and high-valent iron species should occur directly at BDD anode. In fact, FeO42− has been produced by oxidation of Fe(II) ions/Fe(III) ions at the BDD anode in previous studies [36,37]. Therefore, it can be concluded that the oxidation of p-nitrophenol in BDD-ZVI system under alkaline condition was significantly improved mainly attributed to the accelerated release of Fe(II) ions from ZVI and the enhanced oxidation of Fe(II) ions.

4. Conclusions

The performance of BDD anode system on electrochemical oxidation of p-nitrophenol was improved by adding zero-valent iron under both acidic and alkaline conditions. The improvement under acidic condition was due to the joint actions of electrochemical oxidation at the BDD anode (39.1%), Fenton’s reaction (28.5%), oxidation–reduction at zero-valent iron (17.8%) and coagulation of iron hydroxides (14.6%). The significant enhancement under alkaline condition was attributed to the accelerated release of Fe(II) ions from ZVI and the enhanced oxidation of Fe(II) ions. The dissolved oxygen concentration was significantly reduced by reduction at the cathode, and thus iron corroded to Fe(II) ions in anaerobic highly alkaline environments. Moreover, the oxidation of released Fe(II) ions to Fe(III) ions and high-valent iron species (e.g., FeO2+, FeO42−) was enhanced by direct electrochemical oxidation at BDD anode.

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Fig. 8. Intermediates analysis of p-nitrophenol degradation in Fe(II) ions (a), EC (b) and Fe(II) ions + EC (c) systems at the end of treatment under alkaline condition. Analysis of initial p-nitrophenol solution (d) shown for comparison.

Fig. 9. Cyclic voltammograms of BDD electrode in 5 M NaOH solution. Scan rate: 100 mVs−1. Auxiliary electrode: Pt. Reference electrode: SCE.