AuPd/Fe₃O₄-based three-dimensional electrochemical system for efficiently catalytic degradation of 1-butyl-3-methylimidazolium hexafluorophosphate

Yinghua Qin^{a,b}, Meng Sun^{a,b}, Huijuan Liu^a, Jiuhui Qu^{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 100039, China

ARTICLE INFO

Article history:

Received 18 August 2015

Received in revised form 21 October 2015

Accepted 22 October 2015

Available online 28 October 2015

Keywords:

three-dimensional system

AuPd/Fe₃O₄

ionic liquids

kinetic study

degradation mechanism

ABSTRACT

Ionic liquids (ILs) have been reported to be toxic and harmful to aquatic and terrestrial organisms, thus it is imperative to remove the residual ILs in various effluents. In this work, a three-dimensional (3D) electrocatalytic system with synthesized AuPd/Fe₃O₄ nanoparticles (NPs) as particle electrodes (PEs) was established for the degradation of typical 1-butyl-3-methylimidazolium ([BMIM]) based ILs. The as-synthesized AuPd/Fe₃O₄ possessed preferable electrochemical properties for in situ supplement of H₂O₂ and renewable Fe species. This 3D electrocatalytic system exhibited excellent performance with 100% removal rate of BMIM in 90 min under 120 mA, pH 3, and 1 g/L dosage of AuPd/Fe₃O₄ NPs. Kinetics study revealed that the degradation rate of BMIM well followed the anodic Fenton treatment (AFT) model, in which the variation of the degradation rate was positively correlated with that of dissolved Fe²⁺, while significantly differed from the evolution of H₂O₂. Particularly, the appearance of the H₂O₂ inflection point suggested the optimal effectiveness of AuPd/Fe₃O₄-based 3D electrocatalysis. During this electrocatalytic process, the active HO[•] was produced over the AuPd/Fe₃O₄ PEs, thereby initiated the highly efficient degradation of BMIM into 1-butyl-3-methyl-2,4,5-trioxoimidazolidine, 1-butyl-3-methylurea and N-butyl-formamide as main intermediates. The electrocatalytic stability of the AuPd/Fe₃O₄ PEs over seven times further indicated the potential applicability for organic wastewater treatment.

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1. Introduction

Ionic liquids (ILs), which are well known as “green liquid” for the negligible vapour pressure, high ionic conductivity and chemical stability [1], have been widely used in biotechnologies [2], catalysis [3], synthetic chemistry [4]. These widespread applications inevitably lead to the improper release of ILs into environment via the effluents emission, resulting in serious threats to aquatic and terrestrial ecosystems [5]. As the most commonly used imidazolium based ILs, 1-butyl-3-methylimidazolium (BMIM) are widely confirmed to have critical inhibitory effects on acetylcholinesterase of organisms, especially leading to various heart diseases or myasthenia in humans [6]. Due to the hydrophobicity and high stability affected by its alkyl chains and complex macrocycles, the conventional treatment methods of

BMIM including physical adsorption [7] and chemical oxidation [8] are either inefficient or highly costly. Moreover, the toxicity of BMIM significantly impact the activity of microbial consortium in bioreactor [9], resulting in a devastating strike to the biological treatment. Therefore, it is imperative to exploit efficient and reliable treatment method for the degradation of BMIM.

Electrocatalysis is recognized as the most promising advanced electrochemical oxidation processes (AEOPs) by virtue of its superiorities such as the environmental compatibility, strong catalytic ability and easy to control. Therefore, it has been gradually applied to the pretreatment or mineralization of bio-refractory or toxic organic wastewater [10]. The electrocatalytic oxidation was first introduced by Stolte et al. to the oxidative degradation of BMIM based ILs [11]. Subsequently, two-dimensional electrocatalytic systems including boron-doped diamond (BDD) anode oxidation, zero-valence iron activated carbon micro-electrolysis and plasma electrolysis [12–15] were systemically investigated for the treatment of BMIM. Although these works almost achieved complete removal of these constituents, the requirement of long

* Corresponding author. Tel.: +86 10 62849151; fax: +86 10 6292355.
E-mail address: jhqu@rcees.ac.cn (J. Qu).

reaction time and large reagent usage could not be neglected. Additionally, the conventional two-dimensional heterogeneous electrocatalytic system with limited surface area of electrodes can't satisfy the needs of sufficient interactions between the electrodes and target contaminant [16,17]. To overcome these drawbacks, novel electrocatalytic system with low energy consumption, improved electrode surface areas, and large contact efficiency should be necessarily established.

Three-dimensional (3D) electrocatalytic system with mounts of particle electrodes (PEs) regularly or randomly dispersed in the reactor has been proven to prominently enlarge the contact efficiency between the electrode and electrolyte, greatly resolving the problems mentioned above. The added particles are polarized and functionalized as charged microelectrodes [18], around which electrochemical reactions take place with a shortened transfer distance and an enlarged specific reaction area, greatly improving the reaction rate. The 3D electrocatalytic system has been applied into the degradation of organic pollutants including dyes, oil refinery wastewater, phenolic compounds and derivatives [18–21]. In these cases, PEs with nanoscale, high specific surface area, good catalytic activity and stability are highly recommended, all of which play a vital role in determining the electrocatalytic efficiency. Hence, a range of PEs with different catalytic function [22,23] have been exploited to extend the application scope of 3D electrocatalysis. Some thorny problems still remain to be solved. For instance, it is inconvenient to recycle the highly efficient PEs, which markedly reduces their cyclic efficiency and causes huge wastes. Given this, developing new 3D electrocatalytic system with highly efficient and facilely recyclable PEs will make great sense.

Magnetic nanoparticles (MNPs), with the facility for reclaiming and reuse, have been increasingly utilized for water treatments in recent years [24]. The most typical and popular magnetite (Fe_3O_4) NPs not only can be easily recycled by magnetic method, but also hold great potential in in-situ providing Fe^{2+} in electrocatalysis [25]. In addition, bimetallic alloys (e.g., AuPd) were confirmed by our previous study [26] to be capable of in-situ generating H_2O_2 from H_2 and O_2 provided by water electrolysis, contributing to the electrocatalytic oxidation of organic pollutants. Considering the aforementioned characteristics, it is proposed that the electrocatalytic oxidation of BMIM can be effectively facilitated by a 3D electrocatalytic system with an integrated AuPd/ Fe_3O_4 PEs.

Herein, a 3D electrocatalytic system with AuPd/ Fe_3O_4 NPs as PEs and dimension stable electrodes (DSE) as cathode and anode was built for highly efficient removal of BMIM. For the purpose of establishing a highly efficient 3D system with practical applicability, several issues should be concerned in this work: 1) whether applicable and multifunctional AuPd/ Fe_3O_4 PEs were synthesized as expected; 2) the electrocatalytic performance of the assembled 3D system and the corresponding degradation kinetics rule of BMIM during the 3D electrocatalytic process; 3) the degradation mechanism of BMIM in the 3D system in detail.

2. Experimental

2.1. Chemicals

All chemicals were at least of analytical grade and were used without further purification. 1-butyl-3-methylimidazolium hexafluorophosphate ($\geq 97\%$), palladium dichloride (PdCl_2 , $>99.9\%$) and chloroauric acid hydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, $>99.9\%$) were obtained from Sigma-Aldrich. Other chemical reagents were purchased from Sino pharm Chemical Reagent (Shanghai, China). All solutions were prepared with ultrapure water produced by a Millipore Water Purification System (Advantage A10, Millipore).

2.2. Synthesis of AuPd/ Fe_3O_4 particle Electrodes

Fe_3O_4 substrates were synthesized through a polyol route as previously described [27]. Briefly, 1.5 mL hydrazine monohydrate (55 vol%), 2 mL FeSO_4 solution (0.5 M), 1 mL NaOH solution (5 M) and 20 mL ethylene glycol were intensive stirred and transferred into a 40 mL stainless steel Teflon autoclave and maintained at 200°C for 24 h. The resulting products were collected, washed and finally dried in a vacuum oven at 40°C for 6 h. AuPd/ Fe_3O_4 PEs were synthesized by a one-step chemical solution deposition method according to our previous work [26]. As illustrated in Fig. S1, a mixture containing pre-weighed PdCl_2 , HAuCl_4 (with the same weight of Pd and Au), Fe_3O_4 substrates and 200 mL water were ultrasonically to be dispersed. Then 10 mL 1 M NaBH_4 was added as the temperature dropped to about 5°C and the mixture was kept in an ice bath for 3 h. The sediments were centrifuged, washed with ultrapure water and ethanol, and then dried in a vacuum oven.

2.3. Electrocatalytic degradation of 1-butyl-3-methylimidazolium hexafluorophosphate

The experiments were carried out in a cylindrical glass reactor (150 mL) at $20 \pm 1^\circ\text{C}$, with the previously polarized dimension stable electrodes (DSE, $2.5\text{ cm} \times 5.0\text{ cm}$) as the working anode and cathode. Constant electric current was provided by an automatic electrode change-over frequently power adapter. The mixture containing a certain concentrations of BMIM, 2.13 g Na_2SO_4 powder and 0.15 g 5% AuPd/ Fe_3O_4 (wt%) was constantly stirred at 600 rpm after ultrasonic treatment for 10 min, and adjusted to a stated pH with 1 M H_2SO_4 . For the experiment of electrolysis alone, the mixture only contained a certain concentration of BMIM, 2.13 Na_2SO_4 , and were also ultrasonically treated for 10 min, adjusted to pH 3 with 1 M H_2SO_4 and finally stirred at 600 rpm during the reaction. Samples were collected periodically at intervals and filtered by $0.45\text{ }\mu\text{m}$ polytetrafluoroethylene (PTFE) membrane for chemical analysis. The performance of BMIM degradation was evaluated under various conditions: current from 0 to 300 mA, pH from 1 to 7, initial BMIM concentration from 1 to 10 mM. The AuPd/ Fe_3O_4 PEs were recycled for eight times by magnetic separation and reused for degradation with the same condition to test the recyclability of the electrocatalysts.

2.4. Characterization and analysis

Powder X-ray diffraction (XRD) analysis was recorded on a Bruker D8 Advance X-ray Diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54059\text{ \AA}$, step size and scan rate were set at 0.05 and $0.025^\circ\text{ s}^{-1}$). Scanning electron microscopy (SEM) images were obtained from an FEI Sirion 200 scanning electron microscope. The X-ray photoelectron spectroscopy (XPS) data were taken on an AXIS-Ultra instrument (Kratos Analytical, UK) using monochromatic $\text{Al K}\alpha$ radiation (225 W, 15 mA, 15 kV) and low-energy electron flooding for charge compensation. N_2 adsorption-desorption was conducted at 77 K using a Brunauer-Emmett-Teller (BET) surface area apparatus (Micromeritics ASAP2020). Electrochemical characterizations of linear scan voltammetry (LSV) and cyclic voltammetry (CV), differential pulse stripping voltammetry (DPASV) of bare glass carbon (GC) and AuPd/ Fe_3O_4 coated GC were all performed on an electrochemical station (CHI 760D, Chenhua Co, China). Electrochemical impedance spectroscopy (EIS) was conducted at an open-circuit potential (OCP) under an applied AC potential amplitude of 5 mV within the frequency range from 10^5 to 10^{-2} Hz. Saturated silver chloride electrode was used as the reference electrode.

The concentration of Fe^{2+} and the total iron ion was determined by O-Phenanthroline spectrophotometric method using a UV–vis

spectrophotometer (Hatachi Co, Japan), equipped with 10 mm quartz cuvettes. The H_2O_2 concentration during the degradation process was determined by Titanium potassium oxalate spectrophotometry at a wavelength of 400 nm. Electron spin resonance (ESR) spectra were assayed by the Bruker Electron Paramagnetic Resonance Spectrometer (ESP 300E). The measurement of $\text{HO}^\bullet$ was indirectly determined by using DMPO as the scavenger. The main operating parameters: center field, $3480.00 \times \text{G}$; microwave frequency, 9.79 GHz; microwave power, 5.00 mW; modulation frequency, 100 kHz. The concrete operating procedures are as follows: Firstly, 1 mL DMPO (0.25 vol%) solution was put into a 5 mL centrifuge tube, secondly, 1 mL solution were taken and injected into the centrifuge tube containing DMPO, and then the mixture was indrawn by a capillary and placed in the sample channel of the spectrometer.

BMIM was determined by reversed-phase high performance liquid chromatography [12] (HPLC, Agilent 1260, USA) consisting of a chromatographic interface, binary pump, UV/VIS variable wavelength detector, vacuum degasser and rheodyne injection valve. Symmetry C-18 column ($250 \times 4.6 \text{ mm}$, $5 \mu\text{m}$) was used to separate BMIM. The mobile phase consisted of methanol (35 vol%) with 25 mM phosphate buffer ($\text{KH}_2\text{PO}_4/\text{H}_3\text{PO}_4$) containing 0.5% triethylamine at pH 3. The analyses were performed with an injection of $5 \mu\text{L}$, a flow rate of 0.8 mL/min, a column temperature at 30°C , and a detection wavelength of 212 nm. The intermediates were analyzed by GC-MS (Agilent, USA) [13]. The samples were extracted with dichloromethane, and then analyzed with the following conditions: Agilent capillary column: DB-17MS fused silica capillary column ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$); carrier gas: He (1.0 mL/min); temperature program: column oven temperature: 40°C (2 min isotherm), heating rate: $10^\circ\text{C}/\text{min}$, final

temperature: 250°C (5 min isotherm), injection temperature: 250°C ; injection mode: splitless; MS detector: ionization mode: EI (70 eV); scan mode: full scan (10 m/z–350 m/z); interface temperature: 270°C , ion source temperature: 230°C ; injected sample volume: $2 \mu\text{L}$. The structure identification was based on the interpretation of fragmentation pathways and the NIST05 library for the mass spectra. All experiments were performed in duplicate, and the analysis of each parameter was done in triplicate for each run.

3. Result and Discussion

3.1. Characterization of AuPd/Fe₃O₄ particle electrodes

For the purpose of confirming the crystallographic information, the synthesized AuPd/Fe₃O₄ PEs were characterized by XRD. As shown in Fig. 1a, the main diffraction peaks of AuPd/Fe₃O₄ located at 35.7° , 59.0° , 63.0° well correspond to the (311), (511), (440) planes of standard Fe₃O₄ [JCPDS 19-0629], respectively [28]. The typical peaks of AuPd/Fe₃O₄ at 39.5° , 45.6° , 66.7° , and 80.4° , are well located between pure Au [JCPDS 04-0784] and Pd [JCPDS 46-1043], which are assigned to the (111), (200), (220), and (311) crystal faces of the AuPd alloy structure [29], indicating that the well-crystallized AuPd alloys were anchored on the synthesized Fe₃O₄ substrates as expected. In order to gain insights of the microstructure of AuPd/Fe₃O₄ PEs, the apparent morphology was observed through scanning electron microscopy (SEM). As shown in Fig. 1b, the Fe₃O₄ NPs own an octahedral structure with an average size of about 500 nm. The AuPd alloys dispersed on the surface of Fe₃O₄ substrates are much smaller with a mean size of ac. 100 nm. The inset of Fig. 1b illustrates the elemental composition of the selected area, which demonstrates an

Fig. 1. (a) XRD patterns of AuPd/Fe₃O₄ PEs. (b) SEM of the as-synthesized AuPd/Fe₃O₄ PEs. The inset shows the EDX of the red zone. (c) XPS spectra of the as-synthesized AuPd/Fe₃O₄ PEs. (d) High resolution XPS spectra of Au 4f, Pd 3d and Fe 2p of as-synthesized AuPd/Fe₃O₄ PEs.

approximate weight ratio of 2.5% Au and 2.5% Pd as designed. The Brunauer-Emmett-Teller (BET) analysis indicated that a calculated surface area of 1.72485 m^2 could be sufficiently applied in this 3D system, significantly higher than that of DSE under the same condition ($\sim 0.05 \text{ m}^2$, see Fig. S2 and Table S1). The elementary composition and metallic state of Au, Pd, Fe, and O of the AuPd/Fe₃O₄ PEs were further confirmed by X-ray photoelectron spectroscopy (XPS) in depth. As shown in Fig. 1c, Fe 2p, O 1s, Au 4f, Pd 3d can be found on AuPd/Fe₃O₄ without any impurity. High-resolution XPS spectra of Au 4f, Pd 3d, Fe 2p are shown in Fig. 1d. The Au 4f signals can be well divided into two peaks at round 87.56 and 83.89 eV, corresponding to the Au 4f_{5/2} and Au 4f_{7/2} hybridized orbital of metallic Au⁰ [29], respectively, indicating that elemental Au was obtained on AuPd/Fe₃O₄ PEs. Meanwhile, the two peaks at 334.8 and 340 eV are attributed to the Pd 3d_{3/2} and Pd 3d_{5/2} hybridized orbital of Pd⁰ [30]. The XPS signal of Fe 2p depicts two predominant band peaks at 724.3 and 710.6 eV, which can be assigned to Fe 2p_{1/2} and Fe 2p_{3/2}, respectively. The peak at 719 eV belongs to the satellite peak, which is particular for the Fe³⁺ signals, showing the presence of both Fe²⁺ and Fe³⁺. The high-resolution XPS spectrum of O 1s is presented in shown Fig. S3, with three peaks proving the existence of oxygen contained bonds in the crystal lattice (O²⁻, $\sim 529.8 \text{ eV}$), absorbed oxygen species (O₂ $\sim 530.85 \text{ eV}$), hydroxyl and carbonate species (H-O or C-O, $\sim 531.3 \text{ eV}$) [31].

3.2. Electrochemical properties of AuPd/Fe₃O₄ particle electrodes

The potential electrocatalytic properties over AuPd/Fe₃O₄ coated GC and bare GC in N₂- and O₂-saturated 1 mM BMIM were investigated by CVs measurement. As shown in Fig. 2a, a typical peak of oxygen reduction on GC is observed in O₂-saturated solution with the peak potential at -0.6 V compared to that of in N₂. Moreover, this oxygen reduction peak over AuPd/Fe₃O₄ in O₂ condition positively changed with a lower peak potential of -0.265 V and a higher current density of -9.48 mA/cm^2 , demonstrated the enhanced oxygen reduction ability of AuPd/Fe₃O₄. Additionally, a redox peak of Fe^{2+/3+} at $\sim 0.6 \text{ V}$ was perceived for AuPd/Fe₃O₄ both in the N₂- and O₂-saturated solution [32], indicating the AuPd/Fe₃O₄ enabled a renewable redox conversion of Fe species. However, the redox peak current density in N₂-saturated solution was much stronger than that in O₂, suggesting that the intensive oxygen reduction might affect the redox performance of Fe species. The conductivity of AuPd/Fe₃O₄ PEs was further evaluated by LSV and EIS measurement (Fig. 2b and Fig. S4), the higher LSV current density on AuPd/Fe₃O₄ indicated the enhanced electrochemical conductivity and the EIS results showed a low resistance of AuPd/Fe₃O₄, which was beneficial for the electron transfer. The enhanced electrochemical property of the AuPd/Fe₃O₄ was further validated by DPSV in O₂-saturated BMIM solution (Fig. 2c). The current density on the AuPd/Fe₃O₄ was nearly five times higher than that of bared GC, indicating its better electrocatalytic response for BMIM oxidation. Furthermore, a new peak located at approximate 0 V again revealed an outstanding electrochemical activity of the AuPd/Fe₃O₄.

3.3. Electrocatalytic performance of AuPd/Fe₃O₄-based three-dimensional system

To acquire the electrocatalytic performance of AuPd/Fe₃O₄-based 3D system, the concentration evolutions of BMIM in different electrocatalytic degradation processes were investigated. As shown in Fig. 3a, the degradation with a current of 0 mA resulted in less than 2% decrease in BMIM concentration, indicating that the adsorption of BMIM by AuPd/Fe₃O₄ PEs was negligible. Moreover, the degradation efficiency under 120 mA without the PEs (i.e. electrolysis alone) only contributed to a decline of about 5%. In

Fig. 2. Electrochemical measurements of CV (a), LSV (b), DPSV (c) on bare GC and AuPd/Fe₃O₄ coated GC. Measurement conditions of CV: solution = 1 mM BMIM, 0.1 M Na₂SO₄, pH 3, potential range = -1.2 to 1.4 V , scan rate = 50 mV/s ; LSV: solution = 1 mM BMIM, 0.1 M Na₂SO₄, pH 3, potential range = -1.5 to 2 V , scan rate = 50 mV/s ; DPSV: solution = 1 mM BMIM, 0.1 M Na₂SO₄, pH 3, potential range = -1.1 to 0.6 V , scan rate = 50 mV/s .

sharp contrast, the electrocatalytic degradation efficiency under 120 mA (i.e. 9.6 mA/cm^2) coupled with AuPd/Fe₃O₄ PEs achieved 100% within 90 min, demonstrating the great electrocatalytic performance of AuPd/Fe₃O₄-based 3D systems for BMIM degradation. The factors including currents, initial pH and concentrations of BMIM during AuPd/Fe₃O₄-based 3D electrocatalytic process were further studied (Fig. S5–7). The results showed that the optimal degradation of 1 mM BMIM by the AuPd/Fe₃O₄-based 3D electrocatalysis was obtained under 120 mA , pH 3 within 90 min. It

was worth noting that when the initial concentration of BMIM increased to a high level of 5 mM (which was rarely reached in other studies), an acceptable removal rate of 60% could still be attained, indicating the outstanding electrocatalytic ability of the assembled 3D system.

Along with the degradation of BMIM, the concentrations of H_2O_2 and Fe^{2+} were simultaneously examined. As shown in Fig. 3b, the amount of H_2O_2 ($>10\ \mu\text{M}$) yielded in the electrocatalytic process is markedly higher than that of the electrolysis alone ($<8\ \mu\text{M}$). Obviously, the generation of H_2O_2 mainly benefited from the AuPd/ Fe_3O_4 PEs. Furthermore, Fe^{2+} were also measured with a result that the Fe^{2+} rapidly increased to the maximum of 85 mg/L and then decreased to 3 mg/L during the electrocatalytic process (Fig. 3c), suggesting that the released Fe^{2+} from AuPd/ Fe_3O_4 PEs were effectively involved in certain catalytic reactions. As a result, it was shown that the AuPd/ Fe_3O_4 -based 3D system also exhibited desirable performance in providing H_2O_2 and Fe^{2+} simultaneously,

which were able to initiate the subsequent catalytic degradation of the target BMIM. In other words, the efficient degradation of BMIM was highly dependent on the in-situ synthesis of H_2O_2 and release of Fe^{2+} derived from AuPd/ Fe_3O_4 PEs.

3.4. Degradation kinetics of BMIM in AuPd/ Fe_3O_4 -based three-dimensional system

The electrocatalytic degradation kinetic characteristics of BMIM were systemically studied for the deep understanding of the relations among degradation rate, H_2O_2 and dissolved Fe^{2+} . For this purpose, normal first-and second-order kinetics were initially

Fig. 3. (a) Electrocatalytic degradation ability of BMIM, (b) H_2O_2 generation ability and (c) Fe^{2+} releasing ability with different currents and PEs. The experimental conditions were based on pH 3 and 1 mM initial concentration of BMIM.

Fig. 4. (a) Kinetics fitting results of first-order kinetics model under different currents. (b) Kinetics fitting results of second-order kinetics model under different currents. (c) Kinetics fitting results of AFT model under different currents.

Table 1

Regression results of BMIM degradation kinetics under different currents using the AFT Model.

Applied current (mA)	$K = k_1 k_2 \lambda \omega \pi v_0^2$ (min^{-2})	Correlation coefficients (R^2)	Regression results
300	0.0044	0.9944	$\ln(C_t/C_0) = -0.0044 \times t^2$
200	0.0021	0.9996	$\ln(C_t/C_0) = -0.0021 \times t^2$
120	6.21696×10^{-4}	0.9970	$\ln(C_t/C_0) = -6.21696 \times 10^{-4} \times t^2$
100	3.82072×10^{-4}	0.9856	$\ln(C_t/C_0) = -3.82072 \times 10^{-4} \times t^2$
80	2.52613×10^{-4}	0.9961	$\ln(C_t/C_0) = -2.52613 \times 10^{-4} \times t^2$
60	7.42523×10^{-5}	0.9771	$\ln(C_t/C_0) = -7.42523 \times 10^{-5} \times t^2$
40	3.32949×10^{-5}	0.8157	$\ln(C_t/C_0) = -3.32949 \times 10^{-5} \times t^2$
20	2.46445×10^{-5}	0.7092	–
0	5.88194×10^{-7}	–	–

Note: K is the substitution of $k_1 k_2 \lambda \omega \pi v_0^2$; $k_1 k_2 \lambda \omega \pi v_0^2$ is an integrated parameter in the AFT model [33], which signifies the overall degradation rate in the process.

utilized to match the data, while proven to be deficient in describing the patterns (Fig. 4a, b, Table S2–3). As shown in Fig. 4c, the degradation plots versus time appear to have an S shape, which is quite similar to that in the anodic Fenton treatment (AFT) model [33]. The concentration of BMIM suffered a subtle concentration decrease in the beginning and at the end, while a relatively sharp decrease in the middle stage of the degradation proceeding. Thus, the AFT model (Eq. (1)–(2)) was used and finally proven to fit well with the plots under different currents, initial pH and initial concentrations (Fig. S8–9). As shown in Fig. 4c and Table 1, the degradation curves with the currents from 80 to 300 mA better follow the AFT model with the calculated correlation coefficients (R^2) ranging from 0.9856 to 0.9996, than that less than 40 mA. Fig. 5a indicates that the calculated K value (Eq. (3)), which

signifies the overall degradation rate, is positively related with the currents, corresponding to the result that higher current contributed to faster degradation.

In a typical AFT system, the iron plate working as anode could continuously supply Fe^{2+} by anodizing and H_2O_2 was consistently externally added. In this 3D electrocatalytic system, the AuPd/ Fe_3O_4 PEs were polarized to form numbers of charged micro-electrodes with one surface of which was positively charged and can be considered as anode [21], thus Fe^{2+} can be in-situ released by polarized anodizing, which was similar to the AFT system. Meanwhile, the effective reducing capacity of AuPd alloys can't be ignored. The consensus was that Fe^{2+} could also be reproduced through the reduction of Fe(III) by chemically atomic H produced on the active crystal facets of AuPd alloys [34]. In the meantime,

Fig. 5. (a) Linear fitting of $\ln I$ and $\ln(k_1 k_2 \lambda \omega \pi v_0^2)$. The experimental conditions were based on pH 3 and 1 mM initial concentration of BMIM. (b) The relationship between the degradation rate and the concentrations of Fe^{2+} and H_2O_2 .

H₂O₂ was continuously and sufficiently generated from AuPd/Fe₃O₄ PEs in the applied electric field. In fact, based on the experimental observation, the AFT model was not restricted specifically to the electrochemical system with sacrificial iron anode, but also applied to this AuPd/Fe₃O₄-based 3D electrocatalytic system. Our finding provided a theoretical basis of kinetics study for the similar electrocatalytic degradation of complex organic compound, being accompanied with the in-situ supply of H₂O₂ and Fe²⁺.

Furthermore, the absolute value (*k*) of the first-order derivative of the degradation curve (Eq. (4)) informed the instantaneous degradation rate constant's change as a function of time. As shown in Fig. 5b, the overall changing trends of *k* and the concentration of Fe²⁺ resemble each other, while differ from the tendency of the accumulation of H₂O₂. When *k* reaches a peak value of 0.022 min^{−1} at 30 min, the detected concentrations of Fe²⁺ and H₂O₂ are both at their low levels, demonstrating that rapid degradation rate was profited from the large consumption of Fe²⁺ and H₂O₂. Soon after, a gradual decrease of *k* is related with the increasing concentration of Fe²⁺ and increased accumulation rate of H₂O₂. As *k* further decreases to about 75% of the peak value, the Fe²⁺ reaches its maximum value and then suffers a sharp decline for the oxidation and transformation into iron hydroxylation flocculation (e.g., Fe(OH)²⁺ and Fe(OH)₂⁺) as pH increased (Fig. S10). By striking contrast, the changes of H₂O₂ performs completely different, it keeps rising since the peak of the degradation rate appeared. It can be clearly noted that the variation of H₂O₂ is qualified as an indicator for the efficiency of AuPd/Fe₃O₄-based electrocatalysis. Specifically, the H₂O₂ inflection point (the sudden increase in H₂O₂) not only suggests the highest oxidation efficiency and the fastest degradation rate, but also indicates the optimum utilizing of Fe²⁺. Actually, the above results indicated how to control the electrocatalytic performance of this AuPd/Fe₃O₄-based 3D electrocatalytic process. It was believed that the indicating function of H₂O₂ holds great potential in guiding an efficient utilization for efficient electrocatalytic degradation of organic pollutants.

$$\ln \frac{C_t}{C_0} = -\frac{1}{2} k_1 k_2 \lambda \pi \omega v_0^2 t^2 \quad (1)$$

$$\frac{C_t}{C_0} = e^{-\frac{1}{2} k_1 k_2 \lambda \pi \omega v_0^2 t^2} = e^K \quad (2)$$

$$K = -\frac{1}{2} k_1 k_2 \lambda \pi \omega v_0^2 \quad (3)$$

$$|f'(t_0)| = \left| \frac{d(C_t/C_0)}{dt} \right|_{t=t_0} = \lim_{\Delta t} \frac{\Delta C/C_0}{\Delta t} = \frac{(C_{t+\Delta t} - C_t)/C_0}{\Delta t} \quad (4)$$

3.5. Proposed mechanisms of AuPd/Fe₃O₄-based three-dimensional system

For better elucidation of the mechanism of AuPd/Fe₃O₄-based 3D electrocatalytic degradation process, the involved free radicals and generated intermediates during the process were both investigated. The free active radicals generated from the 3D electrocatalytic process were carefully analyzed by ESR. As shown in Fig. 6a, HO• were effectively generated in the AuPd/Fe₃O₄-based 3D electrocatalytic process, validating that HO• was the predominant oxidants. The signal intensity variation of HO• resembled the evolution of dissolved Fe²⁺, optimizing earlier than Fe²⁺ (at 20 min), and gradually decreasing as the reaction went on. The maximum intensity of HO• instructed the highest electrocatalytic oxidation

efficiency, which was highly dependent on the dissolved Fe²⁺. In the AuPd/Fe₃O₄-based 3D electrocatalytic process, H₂O₂ was in-situ generated from cathodic oxygen reduction from water electrolysis (Eq. (5)) [35] and the hydrogenation of AuPd alloys (Eq. (6)) on which O₂ dissociation (the dissolved oxygen greatly decreased from 9 to 0 mg/L as shown in Fig. S11) was blocked and selectively reacted with atomic H [36]. In addition, Fe²⁺ was provided from the anodizing of the PEs and the reduction of dissolved Fe³⁺ by chemisorbed atomic H (Eq. (7)), thus Fenton reaction (Eq. (8)) was initiated and produced active HO•.

In the presence of HO•, BMIM was stepwise degraded. In the beginning of the electrocatalytic process, BMIM was the only target of HO• and was gradually degraded into three main kinds of intermediates (Fig. 6b and Table 2). The first intermediate was identified by the GC-MS method to be 1-butyl-3-methyl-2,4,5-trioximidazolidine (**a**) (Fig. S12), which was formed by the attacks of the 2,4,5 positioned H atoms of the imidazolium ring by HO• (see Fig. 7, right part). The **a** was not stable and apt to be further oxidized. Reports [37,38] have proven that N1-C2 and C2-N3 bonds in the ring of BMIM can be treated as 'one-and-a-half' N-C bond, the bond lengths of which is much shorter than that of N3-C4 and N1-C5 in the imidazolium ring of BMIM. Thus the N1-C2 and C2-N3 bonds were in less energy and better stability. Consequently, the N3-C4 and N1-C5 bonds of **a** were preferentially attacked, leading to the resulting urea, 1-butyl-3-methyl- (**b**) (Fig. S13). The **b**

Fig. 6. (a) Production of HO• measured by ESR. (b) High performance liquid chromatography analysis of BMIM during the 3D electrocatalytic process within 90 min, the inset indicates the peak area of the major intermediates (**a**, **b** and **c**) at different reaction time. The experimental conditions were based on pH 3, 120 mA and 1 mM initial concentration of BMIM.

Table 2
Degradation intermediates of BMIM detected by GC–MS.

Intermediates	Retention time/min	Main fragment (m/z)	Molecular structure	Name
BMIM				1-butyl-3-methylimidaz-olium
a	16.65	56		1-butyl-3-methyl-2,4,5-trioximidazolidine
b	15.956	58,30		Formamide, N-butyl-
c	10.456	58,30		Urea, 1-butyl-3-methyl-

was further oxidized by the attack on the C–N (CH₃) bond, and the products were formamide, N-butyl- (**c**) (Fig. S14). The **c** is commonly low-toxic organic species, and can be easily decomposed into small molecule organic acid, H₂O and CO₂. In general, the concentrations of the intermediates continuously accumulated accompanied when BMIM was degraded (the inset in Fig. 6b). However, since most of BMIM was oxidized at 45 min, the intermediates became the main attack targets and gradually decreased. Ultimately, both BMIM and the emerging intermediates were mostly decomposed into CO₂ and H₂O, as Fig. S15 shows that the Total Organic Content was 71% removed. Based on what was discussed above, the general mechanism of the AuPd/Fe₃O₄-based electrocatalytic degradation of BMIM is accordingly summarized in Fig. 7.

Fig. 7. The Proposed mechanism of AuPd/Fe₃O₄-based electrocatalytic degradation of BMIM.

3.6. Applicability of AuPd/Fe₃O₄ particle electrodes

The applicability of the AuPd/Fe₃O₄ PEs was investigated by repeated degradation of BMIM using the same batch of AuPd/Fe₃O₄. For each test, AuPd/Fe₃O₄ were reclaimed by a magnet and reused for the next degradation experiment under identical condition. As seen from Fig. S16 and Fig. S17a, the AuPd/Fe₃O₄ can be well adsorbed to the magnet at the bottom and achieve the solid-liquid separation, indicating the feasibility of the recycle method and the stability of the physical properties of the PEs (Fig. S18). Moreover, the removal rate of BMIM steadily remained at more than 90% after seven circles of electrocatalytic degradation (Fig. S17b), demonstrating a desired level of electrocatalytic durability of the AuPd/Fe₃O₄ PEs. Thus, it can be concluded that the AuPd/Fe₃O₄ PEs have the potential for sustainable use and great promise in applicability for the electrocatalytic degradation of organic pollutants.

4. Conclusions

A 3D electrocatalytic system with synthesized AuPd/Fe₃O₄ PEs was built and applied to the removal of toxic BMIM. The assembled 3D electrocatalytic system hold excellent performance on the degradation of BMIM and in-situ generation of Fe²⁺ and H₂O₂ under an optimal condition of 120 mA, pH 3, 1 g/L AuPd/Fe₃O₄ PEs. The kinetic rule during the process was best revealed by the AFT model, which not only extended the application of AFT model, but also held great guiding significance for the optimal control of the AuPd/Fe₃O₄-based 3D electrocatalysis. The involved active species and generated intermediates during the electrocatalytic degradation of BMIM were elucidated. The electrocatalytic durability of the AuPd/Fe₃O₄ PEs over seven times indicated an outstanding recycling capacity for long-term electrocatalytic degradation of BMIM.

Acknowledgement

This work was supported financially by the Major Program of National Natural Science Foundation of China (No. 51290282),

National Science Fund for Distinguished Young Scholars of China (Grant No. 51225805).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.electacta.2015.10.122>.

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