Facile preparation of a novel catalytic particle electrode from sewage sludge and its electrocatalytic performance in three-dimensional heterogeneous electro-Fenton

Baolin Hou, Renjian Deng, Bozhi Ren and Zhi Li

ABSTRACT

A novel type of catalytic particle electrode (SAC-Fe) was developed from sewage sludge and iron sludge via a facile method. The catalytic particle electrodes (CPEs) were also supposed to be heterogeneous catalyst for electro-Fenton (EF). The CPEs were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). SAC-Fe showed superior porous structure and higher adsorption capacity and catalytic activity than Fe3O4 magnetic nanoparticles. Catechol and total organic carbon (TOC) removal efficiency can reach 96.7% and 88.3% after three-dimensional (3D) EF with SAC-Fe as CPEs. A possible mechanism was deduced based on adsorption tests and radicals detection. Meanwhile, the stability and reusability of the CPEs were evaluated.

Key words | catalytic particle electrodes, sewage sludge and iron sludge, three-dimensional heterogeneous electro-Fenton

INTRODUCTION

Advanced oxidation processes (AOPs) have been attracting attentions for organic pollutants treatment by involving the formation of hydroxyl radicals (·OH). As one of AOPs, Electro-Fenton (EF) has drawn considerable attention as a promissory alternative technology by overcoming some drawbacks of traditional Fenton process (Zhao et al. 2016, 2017). EF employs electrochemical reactions to generate in situ Fenton reagents as presented in Equation (1) (Brillas et al. 2009).

\[ \text{O}_2(g) + 2H^+ + 2e^- \rightarrow H_2O_2 \] (1)

In essence, electrochemical processes involve the heterogeneous electron transfer between a solid electrode and the ionic species (Fockedey & Lierde 2002). A three-dimensional electrode was proposed in the 1960s as a means of enlarging the electrode surface area by involving particle electrodes. The complicated preparation process and expensive or unavailable raw materials restrict the development of such kind of particle electrodes. Therefore, it is of great importance to prepare efficient and stable catalytic particle electrodes (CPEs) with available and cost-effective raw materials, which is beneficial to full scale application. An increasing amount of sewage sludge generated from wastewater treatment plant has become an issue of particular concern. Recently, sludge derived carbon has been widely used as an adsorbent for organic pollutants (Li et al. 2011) or heavy metals (Phuengprasop et al. 2011). Iron sludge generated in traditional Fenton process, Fe/C micro-electrolysis process and other physico-chemical methods, which mainly consists of iron and organic compounds, would result in secondary pollution to environment without appropriate disposal. Many studies have been focus on the reusability of iron sludge as iron source for the electrochemical Fenton-type process and Fenton-based process in wastewater treatment (Kishimoto et al. 2013; Bolobajev et al. 2014).

In the current study, a novel mesoporous material developed from sewage sludge and iron sludge was facilely synthesized and it served as both CPEs and catalyst in three-dimensional (3D) EF system (Hou et al. 2015; Hou et al. 2016). Catechol is widely used in the synthetic aromatic compounds, and have already been reported to be toxic for bacteria and higher organisms, and catechol is even more toxic than phenol (Park et al. 2003; Wang et al. 2015). Thus, catechol was selected as model target pollutant in the electrochemical Fenton-type process and Fenton-based process in wastewater treatment (Kishimoto et al. 2013; Bolobajev et al. 2014).

In the current study, a novel mesoporous material developed from sewage sludge and iron sludge was facilely synthesized and it served as both CPEs and catalyst in three-dimensional (3D) EF system (Hou et al. 2015; Hou et al. 2016). Catechol is widely used in the synthetic aromatic compounds, and have already been reported to be toxic for bacteria and higher organisms, and catechol is even more toxic than phenol (Park et al. 2003; Wang et al. 2015). Thus, catechol was selected as model target pollutant in the 3D EF system. The CPEs exhibit high catalytic activity and good cyclic performance during degrading catechol in 3D EF. Importantly, the most probable mechanism of 3D EF with the prepared CPEs was proposed as well.


Baolin Hou (corresponding author)
Renjian Deng
Bozhi Ren
Zhi Li
Hunan Provincial Key Laboratory of Shale Gas Resource Utilization, School of Civil Engineering, Hunan University of Science and Technology, Xiangtan 411201, China
E-mail: h3i3t0@126.com
Furthermore, this research was committed to providing a useful base and reference for the practical application of 3D electrochemical reactors on wastewater treatment, meeting the concept 'using waste to treat waste'.

**MATERIALS AND METHODS**

**Preparation of CPEs**

The dewatered sewage sludge sample used in this study was collected from the Wenchang wastewater treatment plant in Harbin, China. Iron sludge was obtained from a pilot industrial wastewater treatment plant (Harbin, China) setup with the combined process of Fe/C micro-electrolysis and Fenton oxidation. The sewage sludge derived activated carbon-supported iron oxide catalyst (SAC-Fe) was prepared via a one-step method combining the carbonization and Fe-loading process. The facile synthesis process was as follows:

1. The dewatered sewage sludge and iron sludge were dried at 105 °C for 24 h, and then ground and sieved into a uniform size of less than 200 mesh.
2. 20.0 g mixture of sewage sludge and iron sludge samples according to a certain proportion was added into a 150 mL of 3.0 mol/L ZnCl2 solution as activation agent (sludge: ZnCl2 = 1:3, by mass). The suspension was stirred for 24 h slowly at ambient temperature, evaporated in a rotary evaporator at 60 °C and dried at 105 °C.
3. The dried solid was pyrolyzed under flowing nitrogen (100 mL/min) in a horizontal quartz furnace at 700 °C for 2 h at a rate of 20 °C/min.
4. The pyrolyzed samples were washed with 3.0 mol/L HCl to rinse inorganic impurities followed by thoroughly washed with deionized water several times until pH of rinsed water became constant to remove the loosely bonded metal irons.

Sewage sludge derived active carbon (SAC) was prepared without adding iron sludge. Finally, the samples were dried at 105 °C and stored in desiccators prior to use. Fe3O4 magnetic nanoparticles (MNPs) (as a comparison) were synthesized from chemical co-precipitation method (Hong et al. 2009).

**Experimental producer**

3D EF integrated EF and three-dimensional electrodes system. 3D EF system was established by adding the as-synthesized CPEs between the anode and cathode to form the third electrodes. 3D EF reaction was conducted in a one-compartment electrochemical cell (1.0 L). In a typical run, the as-synthesized CPEs were filled into catechol aqueous solution. Then the vessels were shaken for 48 h to ensure the adsorption equilibrium. After equilibrium, the adsorption saturated CPEs (5.0 g/L) were transferred to electrolysis cell. The degradation reaction was initiated by switching on the DC current. The current density was maintained at 10.0 mA/cm². Air was bubbled from the bottom of the reactor (4.0 L/min) to provide oxygen and generate stirring. Samples were withdrawn at pre-selected time intervals followed by being filtered with 0.45 μm filter paper. Then the samples were stored at 4 °C for further analysis.

**Analytical methods**

The specific surface area (SBET) was determined using Micromeritics ASAP 2020. Micropores volume was calculated by t-plot method and the macro(meso)pores volume, as well as the pore diameter, were calculated using the Barrett–Joyner–Halenda method. The point of zero charge (pHpzc) was determined using a zeta potential analyzer. The total dissolved iron was determined by inductively coupled plasma atomic absorption spectroscopy (ICP–AAS) (AA-6500, Shimadzu, Japan). Surface morphology was characterized on a field-emission scanning electron microscope (SEM, FEI Quanta 200F). Elemental analysis was carried out on a X-ray diffractometer (XRD, D/max-rb). Fourier transform infrared spectroscopy (FTIR) spectra were obtained on a KBr disk (Perkin Elmer Spectrum One B). The generation of hydroxyl radicals (·OH) was monitored by means of terephthalic acid fluorescent probe method on RF-6500 fluorescence spectrometer. Hydrogen peroxide generated in the solution was measured with the iodide method (Wang et al. 2005).

**RESULTS AND DISCUSSION**

**Characterization of CPEs**

The main physicochemical properties of CPEs are listed in Table 1. SAC and SAC-Fe show mesoporous character. In contrast, Fe3O4 MNPs exhibit lower specific surface area, micropores and meso(macro)pores volumes. C and O are the dominant elements in SAC and SAC-Fe, and Si and Al are the main inorganic elements. It was noteworthy that Fe content increased from 1.28% to 15.43% by adding iron...
sludge, suggesting that iron sludge was the main iron source for SAC-Fe.

The crystalline structures of the CPEs were characterized by XRD (Figure 1(a)). The peaks at 2θ = 26.2° in all patterns (SAC and SAC-Fe) can be attributed to the diffraction of the (002) plane of the graphite structure, which is due to the carbonization of sewage sludge, giving carbon structures with some degree of graphitic order (Ros et al. 2006). These diffraction peaks of SAC-Fe and Fe3O4 MNPs are respectively assigned to the diffraction patterns of the spinel structure, corresponding to the standard card Fe3O4 (JCPDS No. 19-0629). A typical SiO2 (quartz) crystallite structures was also found in SAC-Fe. Both FeII and FeIII existed in SAC-Fe CPEs (Figure 1(b)).

A more complete understanding of the surface chemistry can be acquired through determining functional groups and the chemical bonds on the CPE surfaces (Figure 1(c)). All of the spectra exhibit a prominent peak of C=O, C=O, Si-O-Si, Si-O-C and hydroxyl groups. A new group (Si-O-Fe) is found in SAC-Fe, indicating the chemical bonds between the inorganic compound in the sewage sludge and the loaded Fe compound were formed. The SEM images displayed porous structures of SAC and SAC-Fe, a few particles encapsulated inside the carbon can be observed in the image of SAC-Fe (Figure 1(d)). Homogeneous texture demonstrated the high decentrality of iron species. The embedded structure was rose from the premixture of sewage sludge and iron sludge.

The formation of chemical bands between Fe and carbon matrix, carbonaceous texture, high Fe content and large specific surface area of the as-synthesized SAC-Fe sample guarantees the potential to act as a stable and efficient CPEs and heterogeneous catalyst for the 3D EF system.

### Adsorption performance and catalytic activity

The adsorption isotherms of the CPEs for catechol adsorption were conducted and the Langmuir model (Equation (2)) was employed to simulate the adsorption isotherms and it fitted well with the adsorption isothermal data (r² > 0.99) (Figure 2). The maximum adsorption capacities of SAC, SAC-Fe were 30.3, and 27.1 mg/g respectively, indicating the high sorption affinity of the pollutants onto these carbonaceous CPEs. In contrast, the adsorption capacity (10.1 mg/g) of Fe3O4 MNPs was much poorer than those carbonaceous CPEs due to its lower specific surface area. The excellent adsorption performance of SAC-Fe was believed to be more favorable for afterward EF reactions.

\[
\frac{x}{m} = \frac{Q_0bq_e}{1 + bq_e} \quad (2)
\]

where \(x/m\) is the amount adsorbed at equilibrium (mg/g), \(Q_0\) is the maximum adsorption capacity (mg/g), \(q_e\) is the equilibrium concentration (mg/L) and \(b\) is the Langmuir constant (L/mg).

Figure 3(a) reveals the results of catechol degradation experiments. It was observed that the removal efficiency of catechol was scarcely observable without CPE addition (2D). The degradation efficiency was 96.7% when SAC-Fe was added as CPEs, much higher than the removal efficiencies of 64.6% and 23.2% when using Fe3O4 MNPs and SAC as CPEs. It was noteworthy that the reaction occurred near neutral pH, indicating a wide pH range of high activity.

As can be seen from Figure 3(b), a high total organic carbon (TOC) elimination degree was obtained in 3D EF with the addition of SAC-Fe (88.3%), far higher than the TOC removal efficiency (49.4% and 12.9%) obtained in the system with the addition of Fe3O4 MNPs and SAC. It was noteworthy that the Fe3O4 MNPs catalyzed EF oxidation achieved 49.4% TOC removal, being indicative of the catalytic ability of magnetite to the H2O2 activation. As an inverse spinel crystal structure, it exhibits unique electric properties based on the transfer of electrons between ferrous ions and ferric ions in the octahedral sites under external electric field (Equation (3)).

\[
\equiv Fe^{III} + e^- \rightarrow \equiv Fe^{II} \quad (3)
\]

---

### Table 1 | Properties of the as-synthesized CPEs

<table>
<thead>
<tr>
<th>Parameters</th>
<th>SAC</th>
<th>SAC-Fe</th>
<th>Fe3O4 MNPs</th>
</tr>
</thead>
<tbody>
<tr>
<td>(S_{BET}) (m²/g)</td>
<td>388.9</td>
<td>351.6</td>
<td>71.3</td>
</tr>
<tr>
<td>(V_{meso(macro)}) (cm³/g)</td>
<td>0.282</td>
<td>0.258</td>
<td>0.026</td>
</tr>
<tr>
<td>(V_{micro}) (cm³/g)</td>
<td>0.133</td>
<td>0.122</td>
<td>0.007</td>
</tr>
<tr>
<td>Pore size (nm)</td>
<td>3.711</td>
<td>3.614</td>
<td>2.112</td>
</tr>
<tr>
<td>Ash (wt%)</td>
<td>16.94</td>
<td>19.32</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>1.28</td>
<td>15.43</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>6.89</td>
<td>5.99</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>3.29</td>
<td>2.86</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>1.31</td>
<td>1.26</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>60.84</td>
<td>59.49</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>20.17</td>
<td>19.25</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>2.11</td>
<td>1.89</td>
<td></td>
</tr>
<tr>
<td>pH_{pzc}</td>
<td>6.2</td>
<td>7.8</td>
<td>7.3</td>
</tr>
</tbody>
</table>

---

Downloaded from http://iwaponline.com/wst/article-pdf/76/9/2350/209068/wst076092350.pdf by guest
The sharp decline of the degradation efficiency using SAC was probably associated with lack of iron species. The lower degradation efficiency with Fe3O4 MNPs as CPEs than SAC-Fe was mainly due to the weak 3D effect. In addition, some inorganic components (SiO2 and Al2O3) in the catalyst support of sewage sludge-derived activated carbon exhibited co-catalytic effect for Fenton or photo-Fenton reaction (Tu et al. 2012; Tu et al. 2014). The obvious enhanced degradation efficiency with SAC-Fe might be critical to the formation of radicals, probably due to the appreciable quantities of magnetite Fe oxide and the requisite surface functionalities of porous carbon.

**Reaction mechanism**

In order to understand the promotion effect of the prepared CPEs in 3D EF, amounts of electro-generated H2O2 were measured. Fluor photometer was employed to detect the generation of ·OH to further investigate the possible role of ·OH. It was observed that with the addition of CPEs,
the amount of H$_2$O$_2$ generated from electrochemical reaction increased significantly. It was determined that the corresponding amount of H$_2$O$_2$ was 442.7 $\mu$mol/L with SAC as CPEs, much higher than that (259.9 $\mu$mol/L) in a 2D system, which demonstrated that the high efficient pollutants removal in 3D EF was mainly related to the greater amount of H$_2$O$_2$ generation. As shown in Figure 4, the 3D reaction system with SAC-Fe generated more ·OH than with SAC and Fe$_3$O$_4$ MNPs, which was consistent with the observed degradation. It can be regarded that SAC-Fe has stronger ability to generate H$_2$O$_2$ and ·OH and was a much more appropriate CPEs in 3D EF for enhancing the efficiency of pollutants degradation.

Since the catalytic site of Fenton reaction was immobilized on the solid CPEs, decomposition of H$_2$O$_2$ was
almost completely surface-catalyzed process (Hou et al. 2017). Based on the above study, the possible reaction mechanism involved in 3D EF with the prepared CPEs was proposed (Figure 5).

The reaction was possibility initiated by the carbon adsorption. Firstly an abundance of active O2 and catechol were rapidly diffused toward the CPE surface and enriched in diverse size pores and kept a high local concentration. Then, active O2 was reduced to H2O2 in situ via two-electron reduction (Equation (1)). Meanwhile, once H2O2 molecules were generated on the CPEs, it would be catalytically decomposed to strong oxidizer ·OH by embedded iron oxide on the surface and internal of the CPEs promptly (Equations (4) and (5)). The formed ·OH then reacted with catechol and degraded those compounds into intermediates or complete mineralization (Equation (6)). Since catechol was enriched and maintained at a high concentration on the CPEs, these pollutants in situ captured ·OH and improved ·OH utilization.

\[ \text{Fe}^{III} + \text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{II} \cdot \text{H}_2\text{O}_2 \]  

(4)

\[ \text{Fe}^{III} \cdot \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{II} + \text{OH} + \text{OH}^- \]  

(5)

\[ \text{Pollutants}_{\text{ads}} + \cdot\text{OH} \rightarrow \text{degraded products or CO}_2 + \text{H}_2\text{O} \]  

(6)

Abundant iron species embedded in porous CPEs with high exposure endowed more catalytic active sites. When the H2O2 was electro-generated on the CPEs, it was in situ decomposed promptly at the numerous catalytic sites, which resulted in the ·OH yield increasing remarkably.

**Stability and reusability**

The stability and reusability of the prepared CPEs were key properties for its application. Successive batch experiments and leaching tests were conducted to evaluate the stability and reusability of the prepared CPEs. Catechol abatement efficiency still reached 89.9% after eight cycles' utilization, decreasing 6.8% compared to the fresh CPEs in 3D EF (Figure 3(c)), suggesting that the reused CPEs remained with high catalytic activity. In spite of this, it was found that Fe leaching from SAC-Fe was 1.88 mg/L in the first run and declined in the subsequent cycles, exhibiting much higher attrition resistance, which is guaranteeing its reusability. In addition, as presented in the XRD patterns of reused CPEs (Figure 1(a)), there was no obvious change of characteristic peaks before and after the EF reactions, indicating superior stability of the CPEs.

**CONCLUSIONS**

In summary, we have developed a novel type of CPE from sewage sludge and iron sludge via a facile method, which could be catalyst of EF oxidation as well. The SAC-Fe exhibited excellent adsorption capacity and catalytic activity in 3D EF oxidation of catechol. A possible mechanism was deduced based on adsorption tests and radicals detection. The results offered new insights for environmentally friendly reuse of sewage sludge and iron sludge and provided a facile method for synthesizing CPEs from sludge. We believe this novel type of CPEs would have exciting potential in wastewater treatment.
ACKNOWLEDGEMENTS

This work was supported by the open foundation of Hunan Provincial Key Laboratory of Shale Gas Resource Utilization, Hunan University of Science and Technology (No. E21721), the National Natural Science Foundation of China (No. 2014JQ6041) and the Hunan Provincial Natural Science Foundation of China (No. 2016J6041).

REFERENCES


First received 4 April 2017; accepted in revised form 21 June 2017. Available online 7 July 2017.