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# Heterogeneous electro-Fenton using modified iron–carbon as catalyst for 2,4-dichlorophenol degradation: Influence factors, mechanism and degradation pathway

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## ARTICLE INFO

### Article history:

Received 10 June 2014

Received in revised form

18 September 2014

Accepted 14 December 2014

Available online 20 December 2014

### Keywords:

Heterogeneous electro-Fenton

Modified iron–carbon

2,4-Dichlorophenol

Air diffusion electrode

Degradation mechanism

## ABSTRACT

Modified iron–carbon with polytetrafluoroethylene (PTFE) was firstly investigated as heterogeneous electro-Fenton (EF) catalyst for 2,4-dichlorophenol (2,4-DCP) degradation in near neutral pH condition. The catalyst was characterized by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD), and the effects of some important operating parameters such as current intensity and pH on the 2,4-DCP degradation were investigated. After the catalyst modification with 20% PTFE, the degradation performance maintained well with much lower iron leaching, and at current intensity 100 mA, initial pH 6.7, catalyst loading 6 g/L, the degradation efficiency of 2,4-DCP could exceed 95% within 120 min treatment. Two-stage pseudo first-order kinetics of 2,4-DCP degradation was observed, including a slow anodic oxidation stage (first-stage) and much faster heterogeneous EF oxidation (second-stage), in which the automatic drop of pH in the first-stage initiated the Fe<sup>2+</sup> release from micro-electrolysis and thus benefited to the subsequent EF reaction. Aromatic intermediates such as 3,5-dichlorocatechol, 4,6-dichlororesorcinol and 2-chlorohydroquinone were detected by GC–MS. Oxalic acid, acetic acid, formic acid and Cl<sup>−</sup> were quantified by ion chromatograph. Based on these analysis as well as the detection of H<sub>2</sub>O<sub>2</sub> and •OH, a possible mechanism and degradation pathway for 2,4-DCP were proposed. This work demonstrated that such a heterogeneous EF using cheap modified Fe–C catalyst was promising for organic wastewater treatment in initial neutral pH condition.

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<http://dx.doi.org/10.1016/j.watres.2014.12.022>

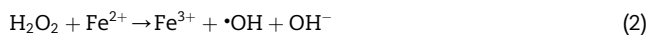
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## 1. Introduction

2,4-dichlorophenol (2,4-DCP) is extensively used in many industries such as herbicides, pharmaceuticals, preservatives, paper making and coloring textiles (Contreras et al., 2003; Chu et al., 2010). Due to its relative stability, 2,4-DCP removal by conventional biological treatment does not always achieve a satisfactory performance. In recent years, electrochemical advanced oxidation processes (EAOPs) have drawn great attention, because they can degrade persistent organic pollutants (POPs) effectively until mineralization to final products of CO<sub>2</sub>, H<sub>2</sub>O and inorganic ions (Martinez-Huitle and Ferro, 2006; Isarain-Chávez et al., 2010; Dirany et al., 2012).

Electrochemical oxidation process can be generally divided into two categories: direct oxidation and indirect oxidation (Chen, 2004; Martinez-Huitle and Ferro, 2006). Direct oxidation means the organic pollutants can be oxidized by direct charge transfer, due to the generated adsorbed hydroxyl radicals (M(·OH)) and oxygen in the oxide lattice (MO<sub>x+1</sub>) on anode surface (Martinez-Huitle and Ferro, 2006). Thus anode material plays an important role in direct oxidation, determining the catalytic activity, selectivity and current efficiency of the process (Zhang et al., 2013). Compared with other anode materials, e.g., boron-doped diamond (BDD) and Pt, dimensionally stable anode (DSA) (e.g., RuO<sub>2</sub>/Ti, IrO<sub>2</sub>/Ti) is more suitable for industrial utilization account for its inexpensive price, long lifetime and relatively high catalytic activity (Wang et al., 2007; Radjenovic et al., 2011).

In addition, electro-oxidation of organics can be also achieved by indirect oxidation through in-situ production of some active species, including hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), hypochlorite (ClO<sup>-</sup>) and ozone (Martinez-Huitle and Ferro, 2006). Electro-Fenton (EF) is one of the most important processes in indirect oxidation, in which H<sub>2</sub>O<sub>2</sub> can be electro-generated by the reduction of oxygen (Eq. (1)), and then it can be converted to a highly powerful ·OH in the presence of Fe<sup>2+</sup> (Eq. (2)) (Brillas et al., 2009). So in EF process it is essential to choose an appropriate cathode material for effective production of H<sub>2</sub>O<sub>2</sub>. Carbonaceous materials are the most familiar materials used as cathode, such as activated carbon fiber (Xu et al., 2008), graphite (Scialdone et al., 2013), carbon sponge (Özcan et al., 2009), carbon or graphite felt (Zhou et al., 2012; Oturan et al., 2013) and carbon–polytetrafluoroethylene (PTFE) air diffusion electrode (ADE) (Brillas et al., 2000). Among these cathodes, ADE is regarded as the most effective one to produce H<sub>2</sub>O<sub>2</sub> (Brillas et al., 2000; Borràs et al., 2013).



Generally adding homogeneous iron sources into the solution directly is the most simple and effective way for Fenton reaction (Eq. (2)). But some disadvantages limit its practical application, such as narrow working pH range (optimal value 3), iron ions deactivation, high iron sludge production and inconvenient process due to adding iron ions every runs (Duarte et al., 2011; Zhang et al., 2012). Utilizing heterogeneous catalysts is a good idea to overcome these disadvantages. Stoichiometric amounts of iron ions can be dissolved out from

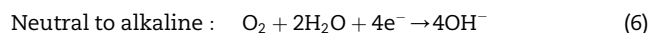
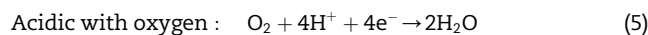
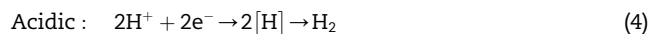
heterogeneous Fenton catalysts, which can reduce the concentration of iron ions and promote life span of catalysts effectively, also may expand the working pH range. Most of the Fenton catalysts studied are iron series, including zero-valent iron (Fe<sup>0</sup>) (Wang et al., 2010; Xu and Wang, 2011; Segura et al., 2013), iron oxides (Xu and Wang, 2012; Zhao et al., 2012) and iron oxyhydroxide (FeOOH) (Ortiz de la Plata et al., 2010; Zhang et al., 2012). Although, the Fenton catalysts mentioned above may exhibit good catalytic property, they are still limited in industrial utilization due to short service life and low cost effectiveness.

In the past few years, iron–carbon (Fe–C) micro-electrolysis has been widely used in wastewater treatment, including dyes (Ruan et al., 2010; Qin et al., 2012), ionic liquids (Zhou et al., 2013a), landfill leachate (Ying et al., 2012), petroleum wastewaters (Li et al., 2010), and coking wastewater (Liu et al., 2012). Recently, in order to improve the degradation efficiency of organic contaminants and reduce adverse effect of refractory pollutants on traditional wastewater treatment, much attention has been paid to the combination of Fe–C micro-electrolysis with other technologies, such as anaerobic treatment (Huang et al., 2013), membrane bioreactor (Qin et al., 2012), biological aerobic filter (Fan et al., 2009), pulsed high voltage discharge (Yin et al., 2009) and ultrasound (Zhou et al., 2013a). When iron and carbon particles are in contact with electrolyte solution, numerous microscopic galvanic cells are formed (Fan et al., 2009; Lai et al., 2013), in which iron acts as anode, losing two electrons to form ferrous ion. And the carbon as cathode can accelerate the reduction by accepting electrons and transferring the electrons to the pollutants or oxygen. The reactions can be represented as follows (Fan et al., 2009; Ruan et al., 2010; Liu et al., 2012; Lai et al., 2013):

Anodic oxidation:



Cathodic reduction:



The formed Fe<sup>2+</sup> by anodic oxidation of Fe–C micro-electrolysis can be iron source for Fenton reaction. Fe–C particle can be good alternative as catalyst for Fenton reaction due to its inexpensive price, high catalytic property, long life span and easy practical utilization.

Since Fenton reaction is usually favorable in acidic condition but some kinds of wastewaters are neutral, it is crucial to develop a catalyst which is suitable for electro-Fenton in neutral pH condition. In the present work, industrial Fe–C particles were modified and then used as heterogeneous electro-Fenton catalysts, using 2,4-DCP as the target contaminant to test degradation and mineralization efficiency. In order to reduce the leaching of iron ions, for the first time, PTFE was used to modify the surface characteristics of Fe–C particles. It was proved that these modified Fe–C particles could achieve a good treatment performance in initially

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