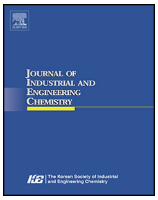
Journal of Industrial and Engineering Chemistry xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec



Heterogeneous Fenton-like catalytic oxidation of tetracycline by AC@Fe_3O_4 as a heterogeneous persulfate activator: Adsorption and degradation studies

Babak Kakavandi[a,b,*]

[a] Department of Environmental Health Engineering, School of Health, Jundishapur University of Medical Sciences, Ahvaz, Iran
[b] Environmental Technologies Research Center, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran

A R T I C L E I N F O

Article history:
Received 7 April 2015
Received in revised form 20 March 2016
Accepted 29 September 2016
Available online xxx

Keywords:
Fe_3O_4 nanoparticles
Heterogeneous catalyst
Fenton-like degradation
Tetracycline
Activator persulfate

A B S T R A C T

Fenton-like catalytic degradation of tetracycline (TC) was studied by using ferro–ferric oxide (Fe_3O_4) nanoparticles coated on activated carbon (AC@Fe_3O_4) which acts as a peroxidase mimetic and persulfate (PS) as a green oxidant. Adsorption and degradation experiments were carried out in a batch system as functions of pH, PS, catalyst and TC concentrations. Kinetic and pathway of TC degradation by AC@Fe_3O_4/PS system was also investigated. Under the optimum conditions, the removal efficiency of TC and total organic carbon (TOC) were 99.8 and 50.6%, respectively. AC@Fe_3O_4 retained its activity and degradation efficiency remained even after five concessive cycles of use.

Introduction

Recently, advanced oxidation processes (AOPs) especially Fenton and Fenton-like oxidation have successfully been utilized as promising pathways for degradation and mineralization of organic pollutants [1,2]. Fenton reaction can be performed through activation of hydrogen peroxide (H_2O_2), as an oxidant, and the couple of Fe^{2+}/Fe^{3+}, as a catalyst, according to Eqs. (1) and (2) [3]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + OH^{-} \quad (1)$$

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe^{2+} + HOO^{\bullet} + H^{+} \quad (2)$$

However, the reagent (H_2O_2/Fe^{2+}) has certain limitations such as formation of sludge residues, requiring low pH ($pH < 3.0$), ineffective utilization of quickly generated hydroxyl radicals ($^{\bullet}OH$) and limited removal of organic carbon [4].

Over the last decade, sulfate radical ($SO_4^{\bullet-}$) has attracted great interest among researchers as an alternative to $^{\bullet}OH$ for degradation of organic substrates. Compared to $^{\bullet}OH$ (v 1.8–2.7 v), $SO_4^{\bullet-}$ is of higher redox potential (2.5–3.1 v) at natural pH and more selective for destruction of pollutants. Moreover, $SO_4^{\bullet-}$ is longer-lived than $^{\bullet}OH$ due to its preference for electron transfer reactions [5,6]. $SO_4^{\bullet-}$ can also be produced mainly from oxidants, namely persulfate (PS, $S_2O_8^{2}$) and peroxymonosulfate (PM, HSO_5^{-}) by thermal, UV, electrochemistry method and with transition metal ions (e.g., Co^{2+}, Fe^{2+}, Mn^{2+}, Ag^{2+}, V^{2+}, Ni^{2+}, Ce^{3+} and Ru^{3+}) [5,7]. Both above-mentioned oxidants have just been introduced and successfully employed by researchers in contaminated-water treatment applications [8–10]. Generally, application of metal ions has been limited due to the disadvantages including secondary pollution, economical infeasibility and environmental toxicity. Nevertheless, among these transition metals, ferrous ions are the most preferable and widely applied as activator of PS since the others are toxic. The mechanism of activation of PS by Fe^{2+} can be illustrated as follows (Eqs. (3) and (4)):

$$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{\bullet-} + Fe^{3+} + SO_4^{2-} \qquad k_1 = 27\ M^{-1}\ s^{-1} \quad (3)$$

$$SO_4^{\bullet-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} \qquad k_2 = 3 \times 10^{8}\ M^{-1}\ s^{-1} \quad (4)$$

Meanwhile, the application of homogeneous Fenton catalysis has been limited since most dissolved metal ions are harmful to the environment as well as being the main source of metal hydroxide sludge. It is also noted that requirement to neutralization of treated

---

* Correspondence address: Department of Environmental Health Engineering, School of Health, Jundishapur University of Medical Sciences, Ahvaz, Iran. Fax: +98 611 3738282.
E-mail address: kakavandi.b@ajums.ac.ir (B. Kakavandi).

http://dx.doi.org/10.1016/j.jiec.2016.09.044
1226-086X/© 2016 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.

sludge is uneconomical [3,9,11]. To overcome these problems, the heterogeneous Fenton system (HFS) using iron-containing solids (Fe_2O_3, Fe_3O_4, Fe^o, FeOOH, etc.) have been developed. Recently, Fe_3O_4 nanoparticles have been used as heterogeneous catalysts in PS activation for oxidation of organic pollutants [2,12–15]. Fe_3O_4 MNPs can decompose PS anions to produce $SO_4^{\bullet -}$ through Fenton reaction, Eqs. (3) and (4).

However, Fe_3O_4 nanoparticles have a strong tendency to agglomerate into larger ones due to intra-particle interactions such as the Van der Waals and intrinsic magnetic interaction. This can reduce Fe_3O_4 nanoparticles characteristics such as surface/volume ratio, dispersion stability and catalytic activity [3].

A useful and effective approach to overcome these problems is to incorporate Fe_3O_4 nanoparticles into porous supporting materials such as graphene, activated carbon, zeolite, clay, multi-walled carbon nanotubes and polymer. Activated carbon (AC) as a supporting material for Fenton catalysts has proved to be promising and economical due to wide availability, low cost, high specific surface area and porosity [3,16]. This can increase the performance of the Fenton catalytic process through adsorption of pollutants and facilitates the separation of catalyst from aquatic media with great flexibility. Recently, this technique widely attracted the attention of scientific researches because that the iron immobilization onto a support provides a physical retention of the catalyst avoiding the iron release in the treated water [15,17].

For these reasons, the present study was centered on the decoration of AC with Fe_3O_4 nanoparticles by a facile method. The method was implemented to fabricate AC@Fe_3O_4 magnetic composite for catalytic activation of PS and degrade tetracycline (TC) in contaminated-water samples. Techniques such as SEM, TEM, BET, XRD and VSM were applied to characterize the catalyst structure. Herein, we selected TC as a model pollutant because it is a well-known antibiotic with second highest in production and use and being widely employed as veterinary medicine in human and animal treatment infectious disease against gram-positive and gram-negative bacteria [3]. Conventional wastewater treatment methods have been less effective to remove TC due to its biological resistance and stability. Therefore, we focused on the integration of adsorption and degradation using AC@Fe_3O_4 as a heterogeneous catalyst in the presence of PS. To the best of our knowledge, so far this has been the first report on the application of AC@Fe_3O_4 for the activation of PS and degradation of TC. The optimum experimental conditions were used to evaluate reusability, stability and degree of mineralization. The mineralization of TC was assessed by total organic carbon (TOC) and chemical oxygen demand (COD) abatement under the optimum conditions. Besides, a reasonable pathway of activation and degradation was proposed.

Materials and methods

Fe_3O_4 nanoparticles fabrication

All chemicals used were of analytical grade and provided by Merck Co. (Merck, Darmstadt, Germany). Fe_3O_4 nanoparticles were prepared by an in situ chemical co-precipitation of ferrous and ferric under alkaline conditions, as described in Eq. (5). Firstly, DI-water was purged with N_2 gas for 30 min. The aqueous solutions of ferrous chloride (0.04 M) and ferric chloride (0.06 M) were prepared, mixed and stirred for 45 min at 70 ± 1 °C. Afterwards, 30 mL of 28% (w/w) ammonia solution (NH_3^-. H_2O) was added drop wise into the above mixture for 30 min to raise the pH of supernatant to around 10–11. The suspension was mixed on a magnetic stirrer and heated to 80 °C for 1 h followed by cooling. The resulting black solid was then collected by an external magnet and washed several times with DI-water and ethanol until the pH became neutral. Finally, the black solid was dried overnight at 105 °C in a hot air oven for 2 h and stored in an air tight container for subsequent experiments.

$$Fe^{2+} + 2Fe^{3+} + 8NH_3{}^{-}\ H_2O \rightarrow Fe_3O_4 + 8NH^{+}{}_4 + 4H_2O \qquad (5)$$

AC@Fe_3O_4 catalyst fabrication

AC@Fe_3O_4 catalyst was prepared using the same method as described above with little modification (i.e., a known amount of AC was added into the mix of ferro/ferric prior to the addition of ammonia). In the end, the black solid (AC@Fe_3O_4) was separated from the suspension by a magnet placed on the edge of the flask. As a result, all AC@Fe_3O_4 nanoparticles were excluded from the sample during the washing cycle. The obtained AC@Fe_3O_4 composite was then washed several times with DI-water until the pH became neutral and dried in an oven at 70 °C for 12 h.

Catalyst properties

In order to characterize physico-chemical, textural, morphological and magnetic features of AC@Fe_3O_4 as well as the size of the synthesized Fe_3O_4 nanoparticles, various techniques (i.e., XRD, SEM, TEM, BET, EDX and VSM) were applied are illustrated in Table 1.

Batch experiment set-up and method

Experiments regarding the degradation process of TC by heterogeneous Fenton-like system (AC@Fe_3O_4/PS) were conducted in a batch reactor and a 500-mL Pyrex vessel containing 200 mL of sample. Firstly, a known amount of catalyst was added into TC solution and placed on a shaker to achieve an adsorption/desorption equilibrium with an agitation speed of 200 rpm for 180 min. At selected time intervals, the catalyst was separated from the solution by a magnet, and residual TC concentration was measured. Prior to analysis by high-performance liquid chromatography (HPLC), the samples were filtered using 0.22 μm syringe filters. Following that, the adsorption isotherms and kinetics were studied over different catalyst concentrations (0.1–0.5 g/L) during 180 min reaction to model the adsorption process.

After equilibrium time and adjustment of pH, PS was added to the sample to start the Fenton-like reaction. The samples were mixed again using a shaker for a certain period of time with an agitation speed of 200 rpm to ensure an ideal agitation of the

Table 1
Details of experimental equipment used to characterization of AC@Fe_3O_4 properties.

Q10

Method	Equipment type	Application
XRD	Quantachrome, NOVA 2000, USA	To X-ray powder of AC, Fe_3O_4 and AC@Fe_3O_4 diffraction pattern
SEM	PHILIPS, XL-30, Netherlands	To morphological properties study of AC and AC@Fe_3O_4
TEM	PHILIPS, EM, Netherlands	To determine the size and shape of Fe_3O_4
EDX	PHILIPS, XL-30, Netherlands	For elemental analysis of AC@Fe_3O_4
BET	Quantachrome, NOVA 2000, USA	To determine the specific surface area of AC, Fe_3O_4 and AC@Fe_3O_4
VSM	7400, Lakeshare, USA	To determine the magnetic properties of Fe_3O_4 and AC@Fe_3O_4

Please cite this article in press as: B. Kakavandi, Heterogeneous Fenton-like catalytic oxidation of tetracycline by AC@Fe_3O_4 as a heterogeneous persulfate activator: Adsorption and degradation studies, J. Ind. Eng. Chem. (2016), http://dx.doi.org/10.1016/j.jiec.2016.09.044