Removal of tetracycline by coupling of flow-through electro-Fenton and in-situ regenerative active carbon felt adsorption

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ABSTRACT

Tetracycline (TC) was cost-effectively removed by coupling of flow-through electro-Fenton (EF) and in-situ regenerative active carbon felt (ACF) adsorption system, which used a modified graphite felt as the cathode. It proved the coupling process achieved a higher removal efficiency (5–44%) than single flow-through EF system and kept stable performance in 600 min treatment, contributed to the dynamic regeneration of ACF by utilizing the remaining oxidants from EF. Some important parameters such as current, initial pH, flow rate and initial TC concentration were optimized. For the TC of initial concentration of 50 mg/L, the TC removal efficiency reached above 90% with a low energy consumption of 48.6 kWh/(kgTOC) at the current of 80 mA and flow rate of 7 mL/min. This coupling process was not only more cost-effective than single flow-through EF, but also advantaged over wider adaption of pH range till 7, providing a more promising approach for organic pollutants removal.

1. Introduction

In recent years, pharmaceuticals and personal care products (PPCPs) have been widely used in all aspects of life and their presence in the environment has aroused dramatic attention [1–4], since a lot of effluents from urban wastewater treatment plants are contaminated with PPCPs residues [5,6]. As a general consensus, the existence of PPCPs can not only affect drinking water quality, but also exist a potential risk for ecosystem and human health in a long term [7–9]. In particular, tetracycline (TC), the second highest antibiotics in production and use, which belongs to one kind of PPCPs, is universally used as human and veterinary medicines to treat diseases and promote growth [10–13]. However, it is non-biodegradable and has toxicity [14–16], and in some cases the TC concentrations in surface soil and surface water were detected to be as high as 86–199 $\mu g/kg$ and 0.07–1.34 $\mu g/L$, respectively [17]. Obviously, it is imperative to develop efficient methods to remove TC.

In the past two decades, electro-Fenton (EF) has attracted great interests because it can continuously generate H_2O_2 in-situ on suitable cathode via a two-electron reduction of oxygen, and H_2O_2 can be further converted into powerful hydroxyl radicals, as shown in reactions 1 and 2 [18,19]. EF can avoid some problems existed in the traditional Fenton process such as transportation and storage risk of H_2O_2 and have been widely studied for the removal of different kinds of PPCPs [20,21].

$$O_2(g) + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{1}$$

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + \cdot OH + OH^- \tag{2}$$
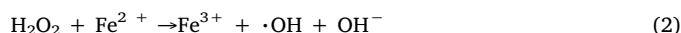
In addition to the selection and modification of cathode [22,23], it was also verified that efficient EF reactor played an important role in improving the treatment performance [21]. Many novel reactors such as three-dimensional reactor, rotating disk reactor and electrochemical jet-cell, were attempted to minimize oxygen mass transport limitation and reduce energy consumption [20,24–26]. For example, the rotating disk reactor could achieve the efficient production of H_2O_2 without oxygen aeration and the complete removal of 25 mg/L MO within 15 min, offering a potentially cost-effective EF method for organic pollutants degradation [26]. Compared with regular flow-by EF, flow-

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through EF was found to be more efficient, requiring lower energy consumption for organic pollutants degradation [22]. For example, in our previous flow-through EF work, the removal of methylene blue could reach above 90% with a low energy consumption of 23.0 kWh/(kgTOC) [22].

On the other hand, adsorption is commonly used as an advanced treatment process for organic pollutant removal. Due to its high surface area and porousness, active carbon felt (ACF) is widely used as the adsorption material [27,28]. However, its adsorption capacity is finite, so the regeneration of ACF is very important to reduce the treatment cost. Many regeneration methods such as thermal regeneration and electrochemical regeneration have been attempted [29]. Account for the facts that after flow-through EF treatment, some of the oxidants (e.g. hydrogen peroxide) could still be detected due to a short retention time [22], it would be reasonable that some pollutants adsorbed on ACF would be further attacked and degraded, in which partial recovery of the saturated ACF would be expected.

Based on above considerations, to improve the utilization efficiency of the electro-generated oxidant and realize the in-situ ACF regeneration, a coupling process of flow-through EF and ACF adsorption was proposed, using TC as the target contaminant. This coupling process would be advantageous over individual EF or ACF adsorption process, providing a new integrated and efficient alternative for organic pollutants removal. The objectives of this work were: 1) to demonstrate the advantage of the coupling process; 2) to investigate important parameters of the coupling process; and 3) to disclose possible mechanism of ACF regeneration and its efficiency.

2. Experimental

2.1. Chemicals and materials

All chemical reagents were of analytical grade and used without further purification. The graphite felts (Shanghai Qijie Carbon Material Co., Ltd), polytetrafluoroethylene (PTFE) and carbon black (Shanghai Hesen Electric Co., Ltd) were used for cathode preparation, while ACF (Shanghai Lianbing Environmental Protection Tech. Co., Ltd) was used as adsorption material. The hydroxyl radical quencher, isopropyl alcohol, was purchased form Tianjin Labrich-tech Co., Ltd. In all experiments, the supporting electrolyte was 0.05 M Na_2SO_4, and the Fenton catalyst was 0.3 mM $FeSO_4 \cdot 7H_2O$. The solution pH was adjusted by 1 M H_2SO_4 or 3 M NaOH. All experiments were operated at room temperature.

2.2. Experimental apparatus and procedure

Fig. 1 shows the schematic diagram of the coupling process of flow-through EF and ACF adsorption, operating in a continuous flow mode. The TC synthetic wastewater was pumped into the EF system and adsorption system with a peristaltic pump (TL-BT-600T, Baoding), simultaneously air aerator and DC power supply were turned on. The flow-through EF system with a reactor volume of about 5.65 mL was similar with that of our previous work [22], using a round perforated DSA anode ($\varphi = 3$ cm) and the modified graphite felt with an inter-electrode distance of 8 mm. The DSA was bought from Baoji Changli Co. Ltd with the active composition of IrO_2 and RuO_2, while the cathode was the graphite felt modified with carbon black and PTFE, which was prepared as our previous study [30].

After treatment with flow-through EF, the effluent was further pumped into the flow-through ACF ($\varphi = 3$ cm) adsorption system. The flow rate was adjusted by the rotation speed of peristaltic pump, and the applied current was changed by the output voltage of DC power supply. At given intervals, the samples at site of point a and point b were collected for analysis. Obviously, the TC removal efficiency at point a could show the contribution of flow-through EF oxidation in the coupling process, while the difference on TC removal efficiency
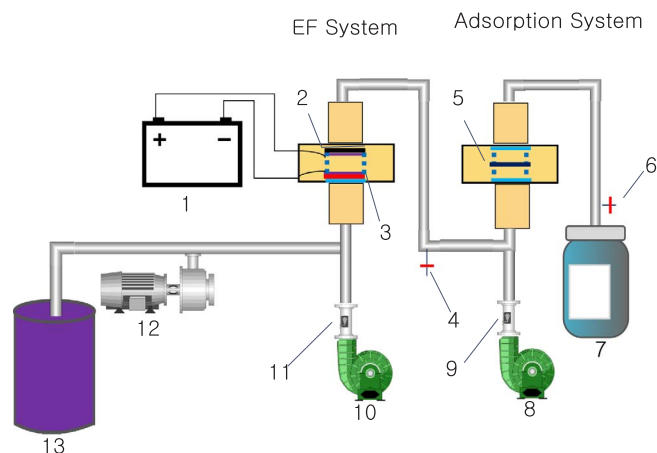

Fig. 1. The schematic diagram of experimental apparatus. 1. DC Power Supply; 2. DSA Anode; 3. Graphite Felt Cathode; 4. Point a; 5. ACF; 6. Point b; 7. Effluent; 8, 10. Aerator; 9, 11. Flow meter; 12. Peristaltic pump; 13. Influent.

between point b and a indicated the role of ACF adsorption.

2.3. Analytical methods

The concentration of H_2O_2 was determined by the method of potassium titanium (IV) oxalate by UV–vis spectrophotometer (UV835, Shanghai Lab-Spectrum Instrument Co., Ltd.) at wavelength of 400 nm [31]. The current efficiency (CE) for H_2O_2 production was determined according to the following formula (3) [32]:

$$CE(\%) = \frac{2FCV}{\int_0^t I dt} \times 100\%$$

(3)

where 2 is the number of electrons transferred from oxygen reduction for H_2O_2, F is the Faraday constant (96,485 C/mol), C is the concentration of H_2O_2 (mol/L), V is the bulk volume (L), I is the applied current (A) and t is the electrolysis time (s).

The total organic carbon (TOC) was determined by TOC analyzer (Analytikjena multi N/C 3100, Germany). The electric energy consumption (EEC, in unit of kWh/kg) for TOC or H_2O_2 was calculated by the following formula (4) [33]:

$$EEC(kWh/kg) = \frac{1000UIt}{CVs}$$

(4)

where U is the applied voltage (V), I is the current (A), t is the electrolysis time (h), C is the concentration of the removed TOC (mg/L) or the concentration of the produced H_2O_2 (mg/L) and Vs is the solution volume (L).

The concentration of TC was monitored by high performance liquid chromatography (HPLC, FL2200-2) on a Beckman ODS C18 column (5 μm, φ4.6 × 250 mm) at a flow rate of 1.0 mL/min using the mobile phase of 0.01 M oxalic acid, acetonitrile and methanol at 60:30:10, and the UV detector was set at 357 nm. The TC removal efficiency (η) was calculated by the following formula (5):

$$\eta(\%) = (1 - \frac{C_i}{C_0}) \times 100\%$$

(5)

where C_0 is the initial concentration of TC, C_i is the TC concentration at given time t.

The adsorption capacity (q) and regeneration efficiency (RE) of ACF was calculated by the following formula (6) and (7), respectively.

$$q(mg/g) = \frac{(C_0 - C_i) \times V}{m_{ACF}} \times 100\%$$

(6)

$$RE(\%) = \frac{q_i}{q_0} \times 100\%$$

(7)