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Electrochemical treatment of anticancer drugs wastewater containing 5-Fluoro-2-Methoxypyrimidine using a tubular porous electrode electrocatalytic reactor

Yonghao Zhang, Tingting Yu, Weiqing Han*, Xiuyun Sun, Jiansheng Li, Jinyou Shen, Lianjun Wang**

Jiangsu Key Laboratory of Chemical Pollution Control and Resources Reuse, School of Environmental and Biological Engineering, Nanjing University of Science and Technology, Nanjing 210094, Jiangsu Province, China

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ABSTRACT

A novel tubular porous electrode electrocatalytic reactor was employed to undertake electrochemical treatment of actual anticancer drugs wastewater containing 5-Fluoro-2-Methoxypyrimidine. Effects of operating parameters on the performance of the reactor were studied with the discussion of energy consumption. The results indicated that the optimal condition was flow rate of 0.31 L min^{-1}, pH value of 5.0, current density of 5 mA cm^{-2} and without supporting electrolyte. In addition, the degradation intermediates and final products of 5-Fluoro-2-Methoxypyrimidine were analyzed by GC-MS and IC system. A pathway for the electrochemical degradation was proposed as well by quantum chemical calculation using DFT method. After treatment in the reactor, COD and 5-Fluoro-2-Methoxypyrimidine of the wastewater were removed by 84.1% and 100%. Particularly, the BOD_5/COD value and $EC_{50,48h}$ value of wastewater were increased from 0.14 and 16.4% to 0.53 and 51.2% respectively, indicating a great biodegradability enhancement. Besides, the electric energy consumption and operating cost of the reactor were only 1.5 kWh kg^{-1} COD and $ 0.78 per ton, lower than the other conventional electrochemical reactors. The excellent performance as well as the low energy consumption of the electrocatalytic reactor confirmed that electrochemical oxidation is highly applicable for the treatment of anticancer drugs wastewater.

1. Introduction

Anticancer drugs represent the substances that are specially produced to inhibit cell growth or directly kill cells [1,2]. Because of the nonselective mode of action, affecting both cancerous and healthy cells, these compounds are proved to have potentially carcinogenic, genotoxic, mutagenic and teratogenic properties [2]. Reportedly, anticancer drugs have been detected in the aquatic environment at concentrations ranging from ng L^{-1} up to μg L^{-1} [3,4]. Some authors believe that the toxicological properties of anticancer drugs might do harm to organism, even at very low concentrations [1,5]. 5-Fluoro-2-Methoxypyrimidine (5FMP), as a typical pharmaceutical intermediate of commercial anticancer drugs, often contains the foregoing properties. What's worse is that these compounds belong to nitrogenous heterocyclic compounds (NHCs) have complete resistance to biodegradation [6]. Therefore, it is unlikely to remove them by conventional biological treatment. Generally, some physical-chemical methods such as chemical coagulation, activated carbon adsorption and membrane separation may be effective ways to remove these refractory organics. However, the most critical problem is that these methods cannot degrade organics, the organics will remain in the sludge or membrane for which they are still threatening the microorganisms, animals and humans. Since the removal of these pharmaceuticals by conventional wastewater treatment is often incomplete and inefficient [7,8], effective methods to remove them thoroughly are in immediate need.

In the last two decades, the so called advanced oxidation processes (AOPs) have received considerable attention because of their high oxidation efficiency, fast reaction rate, easy operation, amenability to automation, and environmental compatibility [9–12]. Advanced oxidation processes (AOPs) including wet

* Corresponding author. Tel./fax: +86 25 8435785.
** Corresponding author. Tel/fax: +86 25 84315941.
E-mail addresses: hwqnjust@aliyun.com (W. Han), wanglj@mail.njust.edu.cn (L. Wang).

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oxidation [13], electro-Fenton [14], electrochemical oxidation [15] and photo-catalytic oxidation [16] have been proved to be the powerful method to remove and even mineralize organic pollutants from wastewater. These methods based on the in situ generation of hydroxyl radical (•OH) which is a strong oxidant because it has so high standard reduction potential (E° (•OH/H_2O) = 2.80 V/SHE) that can non-selectively react with most organics [17]. Practically, complete mineralization of organic pollutants to carbon dioxide by AOPs might not be economical due to high-energy consumption [18]. Thus, AOPs are often employed in association with cheap biological treatments for wastewater treatment. In this case, AOPs function as pre-treatment to increase the biodegradability of wastewater [11]. Among these AOPs, electrochemical oxidation is a promising method to deal with actual wastewater for the reason that it can neither introduce any secondary pollution nor need harsh reaction conditions. Up to now, electrochemical oxidation has been successfully applied in the treatment of actual wastewaters, such as citric acid wastewater [19], textile wastewater [20], coking wastewater [21], industrial park wastewater [22] and paint manufacturing wastewater [23].

In our previous work, we fabricated a novel tubular porous electrode and designed a corresponding reactor. The electrode has larger electrochemical surface area than plate electrode with the same geometrical area due to its porous structure [24]. Furthermore, the micro-sized pores of electrode would achieve a vertical-flow between the anode and cathode with the help of pump (Fig. 1). Therefore, the reactor can not only increase the mean mass-transfer coefficient but also produce a more homogeneous velocity distribution and higher turbulent mixing around the electrode [25,26]. For these reasons, the reactor has shown remarkable efficiency on removal of refractory organics from wastewater [24]. Moreover, the reactor was operated with relatively low current density. Therefore, the reactor is more energy-efficient and cost-saving than the conventional electrochemical reactors. In addition, electrochemical degradation of NHCs often generates intermediates with unknown properties. These involved intermediates might be more toxic than the initial reactant [27,28]. Therefore, degradation mechanism of the organic pollution as well as identification of intermediates should be investigated. It is well known that the mechanisms of ·OH-mediated degradation for NHCs are generally complicated and multi-stepped. Meanwhile, some of intermediates are difficult to identify because they are very reactive or instable in electrochemical system. It has been reported that quantum chemical calculation was a useful tool to speculate intermediates, and meanwhile obtain reaction mechanisms and kinetics of refractory organics degradation, as well as offer a very valuable complement to experimental studies [29,30].

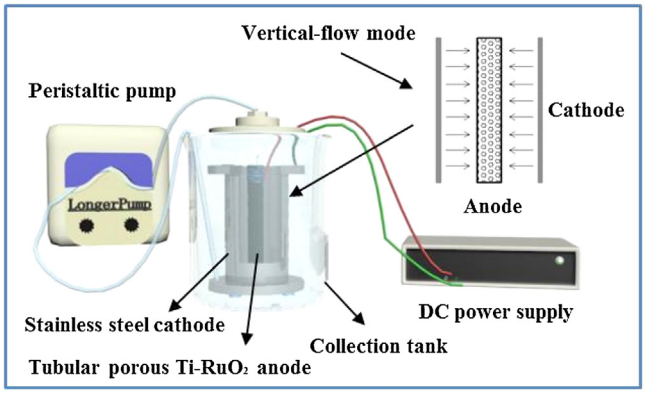

Fig. 1. Schematic diagram of the tubular porous electrode electrocatalytic reactor system.

Thus, the aim of the present study is to evaluate the electrochemical treatment of actual anticancer drugs wastewater containing 5FMP by tubular porous electrode electrocatalytic reactor. Operating parameters including flow rate, pH, supporting electrolyte and current density were studied with the special discussion of energy consumption. In addition, the electrochemical degradation pathway of 5FMP was also studied. To further have a better understanding of degradation mechanisms, the experiments were undertaken not only experimentally but also in combination with quantum chemical calculation. To the best of our knowledge, this work is the first time to give the electrochemical degradation pathway of 5FMP. The reactor performance under optimal conditions was evaluated. Furthermore, the economic evaluation of the reactor was carried out as well.

2. Materials and Methods

2.1. Characterization of actual anticancer drugs wastewater

Anticancer drugs wastewater was obtained from Jiangsu Zhongyuan Chemical Co., Ltd, Nantong, China. 5-Fluoro-2-Methoxypyrimidine (Purity ≥ 99%) was purchased from Aladdin. Physical and chemical characteristics of the anticancer drugs wastewater are presented in Table 1.

2.2. Electrolysis process

Electrochemical experiments were conducted by the tubular porous electrode electrocatalytic reactor. The reactor was formed by tubular porous Ti-RuO_2 electrode, stainless steel, pump and DC power supply. Tubular porous electrode (94.2 cm^2) was fabricated by loading a RuO_2 layer on porous Ti tube, detail fabrication process was described in our previous literature [24]. A stainless steel tube with the inner diameter of 5 cm, thickness of 0.3 cm and length of 10 cm was used as the cathode. Schematic diagram of reactor is shown in Fig. 1. In brief, the reactor was fully submerged in the wastewater during the experiments so as to avoid the entrance of air. The flow rate was controlled by a peristaltic pump so that the mass transfer of reactant can be significantly enhanced. During the experiment, the wastewater with volume of 1 L was circulated between the reactor and collection tank repeatedly. Aqueous H_2SO_4 and NaOH were added to adjust the pH value. Na_2SO_4 was used as electrolyte and the constant current was controlled by DC power supply.

2.3. Analytical method

Degradation intermediates of 5FMP were identified by gas chromatography −mass spectrometry (GC-MS). The GC-MS system consisted of a GC system (Agilent 7890A) and a MS instrument (Agilent 5975C). The solid-phase extraction was carried out with ethanol for 3 times in 250 mL separating funnel. Using nitrogen to extract further enrichment and analyzed using 30 m Agilent HP–

Table 1
Physical and chemical characteristics of the anticancer drugs wastewater.

Parameter	Value
pH	7.2
Conductivity ($\mu s\,cm^{-1}$)	3390
COD ($mg\,L^{-1}$)	4340
BOD_5 ($mg\,L^{-1}$)	260
BOD_5/COD	0.06
5FMP ($mg\,L^{-1}$)	61.2
Cl^- ($mg\,L^{-1}$)	226