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Degradation of sulfadiazine in drinking water by a cathodic electrochemical membrane filtration process

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ABSTRACT

In this study, a novel electrochemical membrane filtration (EMF) process was proposed to degrade sulfadiazine (SDZ) in drinking water, and the oxidation mechanisms, kinetics, byproducts and primary impact factors were investigated. In the EMF process, a novel membrane was used as the cathode and two graphite plates were used as anodes. Five oxidation byproducts including 4-OH-sulfadiazine or 5-OH-sulfadiazine, 2-aminopyrimidine, 4-amino-*N*-carbamimidoyl benzene sulfonamide and 2,5-dihydroxypyrimidine were identified. Possible degradation pathways for SDZ were proposed, and •OH and $O_2^{\bullet-}$ were recognized to be the major reactive oxygen species contributed for SDZ degradation. The degradation of SDZ by EMF followed pseudo-first-order kinetics in batch experiment and the rate constant increased as the applied voltages increased. Compared with the batch experiment, the flow-through mode of EMF slowed SDZ degradation, and the degradation rate also decreased as the flux increased. However, on the base of mass balance calculations more SDZ was degraded in flow-through mode as compared with that in batch experiment. Finally, the degradation of SDZ in natural waters from a municipal drinking water treatment plant was investigated with flow-through mode, and the result shows that the degradation rate (79%) was slightly lower than that obtained for deionized water due to the low conductivity of real-world water systems.

1. Introduction

The existence of antibiotics in aquatic environments has become an increasingly severe problem due to its potential adverse effects on human health and aquatic ecology. The conventional drinking water treatment methods can't remove antibiotics in raw water in an effective manner, and it's inevitable that traces of antibiotics remain in the tap water and increase human exposure [1]. A variety of antibiotics have been detected in the aquatic environments such as drinking water [2], surface water [3] and groundwater [4] around the world. Therefore, research efforts have been made to degrade and remove antibiotics from aquatic environments.

It is proven that electrochemical advanced oxidation processes (EAOPs) are effective to remove refractory emerging contaminants [5–7]. In EAOPs, the generation of highly reactive oxygen species (ROS), primarily hydroxyl radicals (•OH), are essential to the oxidation of pollutants. •OH is very powerful oxidizing agent and can break down complicated organic molecules into small molecules, even down to CO_2 and H_2O [8]. •OH could be generated by 1) direct electrolysis of water at the anode or 2) the electro-Fenton (EF) reaction in bulk solution [9]. Both the anodic oxidation process [10,11] and the EF process [8,12] have been successfully used in the removal of micropollutants which shows a promising future of EAOPs. However, for practical application, the primary drawback of EAOPs is their relatively high costs and energy consumption, as well as the potential risk of byproducts. Therefore, the novel process by combining EAOPs with other technology appears to be a promising alternative for the cost-effective removal of refractory emerging contaminants.

Recently, investigations on the combination of electrochemical oxidation with membrane filtration have been raised. Zhao et al. [13] modified a polyester filter cloth membrane with graphene (Gr) and polypyrene (PPy) and used it as a cathode to investigate the degradation of Methylene Blue (MB) by E-Fenton process. It was reported that 90% of MB was degraded under optimal conditions and the Gr/PPy membrane also showed excellent stability during long term tests. Our research group has developed a novel

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conductive microfiltration (MF) membrane, which can be used as cathode and separation membrane in a MBR system. Our previous study found that the conductive MF membrane had a better anti-fouling ability under a 2 V/cm electric field due to the *in-situ* cleaning of H_2O_2 generated by membrane cathode [14]. Furthermore, we have investigated the mechanisms of cathodic electrochemical membrane filtration (EMF) and found that •OH generated heterogeneously by the Fenton process in the system was mainly responsible for the degradation of sulphanilic acid [15]. These results manifested that EMF could be an effective water purification technology. Currently, the development of EMF process was just launched and the investigation on its application for removal of refractory micropollutants was still very limited. Therefore, further understanding of these processes, such as the impact factors and energy consumption, is required to promote the practical application of this novel process.

In this study, we systemically investigated the mechanisms and impact factors of the degradation of sulfadiazine (SDZ) in drinking water by EMF and assessed the energy consumption of EMF process. SDZ is one of the most commonly used sulfonamides, and has high stability and strong hydrophilicity. SDZ has been detected at high concentrations in aquatic environments around the world, such as 157 ng/L in the Beiyun River in Beijing [16], 147 ng/L in the Soeste River in Germany [17] and 94.2 ng/L in the Langat River basin in Malaysia [18]. Therefore, SDZ was selected as target contaminant in this study. Quenching experiments were carried out to determine the responsible reactive oxidants during EMF. The byproducts of SDZ oxidation were identified by high performance liquid chromatography (HPLC) and liquid chromatography-mass spectrometry (LC-MS). The possible degradation pathways of SDZ by EMF process were proposed. The main impact factors such as applied voltage, initial concentration, operational mode and membrane flux on the degradation of SDZ by EMF process were studied. Furthermore, the degradation of SDZ in natural water from a municipal drinking water treatment plant (DWTP) was investigated in flow-through mode. Finally, the energy consumptions of EMF were evaluated. The results obtained in this study are expected to provide a first evaluation of the new technology and contribute to the determination of its applicability in the future.

2. Experimental

2.1. Materials

Sulfadiazine (SDZ, $C_{10}H_{10}N_4O_2S$, >99.0%) was purchased from TCI Development Co., Ltd. (Shanghai, China) and used as received. Other materials (2′,7′-dichlorodihydrofluorescein diacetate (H_2DCF-DA), *tert*-butyl alcohol (TBA), 4-Hydroxy-2,2,6,6-tetramethylpiperidinyloxy (TEMPOL), furfuryl alcohol (FFA) -ferrozine) and sodium alginate (SA) were analytical reagent grade and purchased from Aladdin Biological Technology Co., Ltd. (Shanghai, China). All organic solvents used for the HPLC analysis including acetonitrile and acetic acid were HPLC grade and obtained from Aladdin Biological Technology Co., Ltd (Shanghai, China). All solutions were prepared with Milli-Q water (MQ, Millipore) with resistivity of 18 MΩ cm^{-1} unless otherwise stated. The membrane used in present study was a polyvinylidene fluoride (PVDF) microfiltration membrane prepared via the phase inversion method as described previously [14]. The average pore size of the membrane was 0.062 ± 0.024 μm with a stainless steel mesh embedded in the active layer.

2.2. Electrolytic system

To characterize the electrochemical properties of the graphite plate, linear sweep voltammetry (LSV) was carried out in a typical three-electrode system driven by electrochemical workstation (CS 350, Wuhan Coretest Instrument Co., Ltd., China). A graphite plate electrode with a surface area of 2 cm^2 was used as the working electrode. An Ag/AgCl/0.1 M KCl electrode was the reference electrode and a Pt electrode was the counter electrode. Na_2SO_4 (50 mM) was used as the supporting electrolyte with different SDZ concentrations of 0, 0.4, 4.0, and 40.0 μM. LSV measurements were performed at ambient temperature (25 ± 2 °C) with a scan rate of 50 mV/s.

All experiments were conducted in an EMF reactor and details are shown in Fig. 1. The reactor was made of plexiglass with an effctive volume of 480 mL (dimension = 6 × 6 cm, height = 15 cm). The membranes (dimension = 6 × 8 cm, effective area = 48 cm^2) were adhered to the module by acrylonitrile butadiene styrene glue and used as the cathode in the electrochemical system. Two graphite plates were used as anodes on either side of the membrane module with a 1.0 cm gap between the anode and cathode. A direct current (DC) power supply (YH-605D, GuangZhou YiHua Electronic Equipment Co., Ltd. China) was used to provide constant voltages. An aeration pipe (flow rate of 400 mL min^{-1}) was set below the membrane module to provide O_2 (or N_2 in some tests) and mitigate membrane fouling and the dissolved oxygen (DO) in the bulk solution was maintained as 8.16 ± 0.07 mg/L.

2.3. Operating condition

The influence of operation parameters including applied voltages and initial concentration of SDZ on the degradation of SDZ were investigated in batch experiments. To investigate the influence of membrane filtration on the performance of EMF process, experiments with circulation flow mode and flow-through mode were carried out. In the circulation flow mode, solutions passed through the membrane and the effluent was drawn back into the reactor to form a cycle by a peristaltic pump (BT 300-2 J, Longer Percision Pump Co., Ltd. China). The membrane flux was 25 L m^{-2} h^{-1} (LMH) and the hydraulic retention time (HRT) was equivalent to the eletrolysis time of 240 min in batch experiments. Flow-through mode experiments were conducted to investigate the influence of membrane flux. Briefly, SDZ solutions passed through the membrane with different membrane flux (25, 50, and 75 LMH) which corresponded to HRT of 1, 2 and 4 h, respectively. The SDZ solutions were prepared with deionized water containing 50 mM Na_2SO_4 and the initial pH was adjusted to 7.0 with H_2SO_4 and/or NaOH.

SDZ degradation experiments by the EMF process in natural water were also conducted in flow-through mode. The concentration of SDZ in natural aquatic systems is quite low, thus 0.4 μM SDZ was added to the natural water samples. The influence of electrolyte (50 mM Na_2SO_4) were also studied. All experiments were repeated at least twice to obtain duplicate results.

2.4. Analytical methods

2.4.1. Analysis of SDZ and degradation byproducts

The concentration of SDZ was measured by reversed-phase HPLC (Agilent 1200). The mobile phase used in the HPLC was a mixture of 0.1% acetate and acetonitrile with a ratio of 20:80 (v/v). The column used during the analyses was an Agilent Zorbax Eclipse Plus C18 (150 mm × 4.6 mm, 5 μm). The flow rate was 1.0 mL min^{-1} with a detection wavelength of 270 nm and an injection volume of 20 μL. To analyze the degradation byproducts of SDZ, LC–MS (Thermo Scientific™ TSQ Quantum Ultra™) equipped with a Waters XB C18 column (150 mm × 2.1 mm, 3 μm) was used. A 10 μL solution was injected into the column; the mobile phase was a 20:80% methanol-water mixture (flow rate of 0.3 mL min^{-1}). The