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Performance and degradation mechanism of a sequencing batch biofilm reactor combined with an electrochemical process for the removal of low concentrations of cefuroxime

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HIGHLIGHTS

- The removal efficiency of specific contaminants could be significantly improved by bio-electrochemistry system.
- The degradation of antibiotics in SBBR, BES and ES conformed to the first-order kinetics.
- High electric current would destroy microbes.
- Active microbes promoted synergy effects on both antibiotics and COD removal.
- Strong redox reactions occurred in bio-electrochemistry system.

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ABSTRACT

A combination of biochemistry and electrochemistry was used as a strategy to remove antibiotics present in low concentrations at the laboratory scale. Experiments showed that the removal of antibiotics could be improved to 98% in the bio-electrochemical system (BES). The optimal operating conditions were a pH of 7, initial cefuroxime (CXM) concentration of 0.5 $mg \cdot L^{-1}$, reaction period of 12 h, aeration intensity of 15.8 $m^3 \cdot m^{-2} \cdot h^{-1}$, and influent COD concentration of 1000 $mg \cdot L^{-1}$. The chemical oxygen demand (COD) and ammonia-nitrogen (NH_3-N) removals were also improved to above 90% and 80%, respectively. A conventional sequencing batch biofilm reactor (SBBR) process was simultaneously operated for comparison. Simulation results indicated that the degradation followed first-order kinetics in the SBBR, BES, and electrochemical system (ES). Through further studies and SEM observation, we found that a high current electric field would destroy microbes. Conversely, the degradation of CXM was promoted by a low current electric field. In addition, cyclic voltammetry (CV) analysis was performed and we found that the degradation contained two oxidation reactions and one reduction reaction. According to the intermediates identified by LC–MS, we inferred that the degradation pathway included breakage of β-lactam rings and organic oxidations. In conclusion, the integrated process considerably enhanced the synergistic effects of biochemistry and electrochemistry for the removal of specific contaminants.

1. Introduction

From the time penicillin was first used to treat bacterial infections in 1928 [1], researchers have developed hundreds of antibiotics to control human, livestock, and fish diseases, and as feed additives to promote animal growth. Antibiotics play an important role in preventing bacterial infection, promoting digestion in animals, and replacing nutrients [2]. Cephalosporins are a series of broad-spectrum semisynthetic antibiotics [3]. They originate from 7-aminocephalosporanic acid (7ACA), which is formed from cephalosporin A [4]. The cephalosporins have strong antibacterial activity, high resistance to penicillinase, excellent clinical curative effects and cause less anaphylaxis than that caused by penicillin. The advantages of cephalosporin antibiotics have led to their widespread use in clinics [5,6]. Cefuroxime (CXM) is a second-generation semisynthetic cephalosporin [7]. It is effective against

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a wide range of gram-positive and gram-negative bacteria, and is less susceptible to most β-lactamases.

Owing to antibiotics abuse and imperfect sewage treatment technology, substantial quantities of antibiotics, that have not been completely absorbed or degraded, eventually enter the water table through various channels. These antibiotics directly or indirectly cause considerable environmental pollution, and long-term exposure can cause bacterial resistance to antibiotics [8,9]. Bacteria with antibiotics resistance genes can spread easily, potentially threatening human health [10]. At present, many countries have already detected antibiotics in rivers, lakes, and groundwater, including fluoroquinolone, sulfa, penicillin, large-ring lactones, and tetracycline [11,12]. Meanwhile, low concentrations of antibiotics have been detected in the effluent of urban wastewater treatment plants [13]. The refractory characteristics and inhibition of microbial activity insulate antibiotics from the treatment process, leading to concentrations in the range of $ng{\cdot}L^{-1}$–$\mu g{\cdot}L^{-1}$ in terminal water bodies [14]. Because of the negative effects of the presence of these drug residues in the aquatic environment, their treatment has become a popular research topic.

Furthermore, studies have shown that the half-life for the biodegradation of antibiotics in aquatic environments might be longer than that for abiotic degradation [15]. Even though antibiotics occur in trace amounts, they are difficult to fully degrade in natural environments [16]. Antibiotic resistance, which develops as a result of overuse is also a crucial issue [17–19].

Many methods have been tested for removing antibiotics from aqueous solutions. For example, Ncibi and Sillanpää used carbon nanotubes to remove antibiotics from aqueous solutions, and Chen et al. verified that the adsorption process was applicable to fluoroquinolone [20,21]. Putra et al. suggested that the use of activated carbon and bentonite was an efficient process for adsorbing amoxicillin, and the possible removal mechanisms were studied and described [22]. Even though adsorption processes are easy to operate, they are not capable of degrading pollutants, since they involve only a phase transfer. Oxidation methods, including ozonation [23], Fenton oxidation [24], and electrolysis [25], are clean technologies, that can thoroughly degrade pollutants. For example, Lin et al. examined the degradation of sulfonamide and macrolide by ozonation, and concluded that the addition of H_2O_2 in a suitable ratio was beneficial for the contaminant removal [26].These methods were suitable for antibiotics removal, but the high operating costs and limited treatment capacity are disadvantages that must be considered. Some conventional treatment methods, such as chlorination [27] and biological treatment [28], had notable effects on common pollutants, but could not effectively remove trace antibiotics. Overall, the different methods for antibiotic removal described in the literature all have certain advantages and disadvantages.

Recently, the combination of different processes, especially the integrated application of electrochemistry and biology, has attracted widespread attention [29]. Sakakibara et al. investigated the charge transfer mechanism in electrolytic and biological water treatment, and pointed out that the biofilm-electrode reactor showed superior performance in denitrification [30]. Some studies have revealed that low-level DC current electric fields could stimulate aerobic microbial activity and optimize the rate of electron transfer [31]. For recalcitrant organic compounds, application of an electric field enhanced the electrochemical redox process, and negatively charged microbes affected the transport pathway. Zhang et al. studied the degradation of 2,4-dichlorophenoxyacetic acid in an electro-biological system that included a biological system and an electro-catalytic system. They found that the kinetic constant of the electro-biological system was much higher than the sum of the constants of the biological system and the electro-catalytic system [32]. Most studies have emphasized the application of this strategy for the treatment of industrial wastewater having a high concentration of pollutants [33,34]. Some researchers have carried out electrochemical pretreatment to improve subsequent biological processes [35]. In our previous research, we integrated biochemical and electrochemical processes in a single reactor and examined the effects of this combination on the microbial community, but the degradation mechanism was not explored [36].

In this study, we investigated the factors affecting the removal of low concentrations of CXM in a sequencing batch biofilm reactor (SBBR) system and a bio-electrochemical system (BES). This novel system combined biochemical treatment with an electrochemical process to improve the removal performance of CXM, organic matter, and nitrates in sewage. The relevant factors, including pH, initial CXM concentration, reaction period, aeration intensity, and influent COD concentration were considered. Using optimal conditions, the degradation processes in the BES, SBBR, and electrochemical system (ES) were compared, and the kinetics of the processes in the different systems were analyzed. Cyclic voltammetry (CV) was used to explore characteristic features of the redox reactions. Intermediates were identified and the degradation pathway was inferred.

2. Materials and methods

2.1. Experimental agents

CXM (92.1% purity, CAS:55268-75-2) was purchased from the National Institutes for Food and Drug Control (Shanghai, China), and stored at 4 °C. Methanol and acetonitrile (HPLC grade) were purchased from J.T. Baker (California, USA). Ultrapure water used in the experiments was obtained from a deionized water machine (Molecular Water System Co. Ltd., Chongqing, China).

2.2. Reactor configuration

The cylindrical SBBR reactors were made of glass, with dimensions of Φ 125 × 150 mm (Diameter × Height), and a working volume of 0.8 L. About 130 pieces of white suspended packing rings (purchased from Dalian Yudu Environmental Engineering Technology Co., Ltd.) were chosen as biofilm carriers with a filling rate of 30%. The polypropylene packing rings were cylindrical in shape and had a decussation for structural support at the center. The shape of packing rings was regular, and they had a specific surface area of $0.1362\ m^2{\cdot}g^{-1}$, a density of $154\ g{\cdot}mL^{-1}$, a true density of $0.9577\ g{\cdot}mL^{-1}$, and dimensions of Φ10 × 10 mm (diameter × height). The packing rings shifted during aeration.

The BES reactor (as seen in SI Fig. S1) was similar to the SBBR reactors except for the presence of two graphite plate electrodes. The total effective area of the electrodes was $9300\ mm^2$ (actual length 40 mm × width 50 mm × thickness 5 mm) and the distance between the plates was 30 mm. We took the mass of the graphite electrode plate before and after each batch experiment, and ensured that the graphite plate did not decompose during the experiments. A constant DC current was supplied.

Both configurations were run simultaneously and continuously. Aeration was enforced with an air compressor pump at a stable airflow rate of $100\ L{\cdot}h^{-1}$and oxygen was distributed through fine-bubble diffuser stones. In addition, an electrolysis reactor was run for comparison. The electrolysis conditions were the same as those used in the BES.

2.3. Artificial solution

For reactor start-up, an experimental influent was prepared according to the typical nutritional needs for the acclimation of