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Effective ultrasound electrochemical degradation of biological toxicity and refractory cephalosporin pharmaceutical wastewater

Bo Yang, Jiane Zuo *, Peng Li, Kaijun Wang, Xin Yu, Mengyu Zhang

State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing 100084, China

HIGHLIGHTS

- Sonolysis can liberate ·OH from the surface of the 'active' anode.
- Synergy of the nanocoated electrode and the ultrasonic waves was discussed.
- The combination of the ultrasonic and nanocoated electrode was efficient.

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ABSTRACT

Biologically treated cephalosporin pharmaceutical wastewater is a complex industrial wastewater that is toxic and refractory for further biological treatment. For this purpose, a novel sonoelectrochemical catalytic oxidation-driven process using a nanocoated electrode has been developed to treat such wastewater. In the process, the synergy and mechanism of the sonoelectrochemistry using ultrasound enhancement of the nanocoated electrode activity to treat the wastewater was studied. The nanocoated electrode generated more radicals than the traditional coated electrode did; in the presence of ultrasonic waves, the mass-transfer effects on the nanocoated electrode surface were enhanced, resulting in rapid diffusion of the generated hydroxyl radicals into the solution, and quickly reacted with organic pollutants. Compared with the traditional coated electrode, the effect of the nanocoated electrode used on the wastewater treatment process was more enhanced by ultrasound under the same conditions. The biotoxicity of the wastewater in the sonoelectrochemical catalytic oxidation process was monitored and shown as having first increased and then decreased. The optimum operating conditions resulted in a 94% removal efficiency for COD and consisted of a current of density 8 mA/cm^2 and an ultrasound frequency of 45 kHz. All of the results showed that the sonoelectrochemical catalytic oxidation-driven process was found to be a very efficient method for the treatment of non-biodegradable cephalosporin pharmaceutical wastewater.

1. Introduction

Biologically treated cephalosporin pharmaceutical wastewater is a complex industrial wastewater generated by cephalosporin manufacturing factories [1–4]. Conventional biological wastewater treatment is the main technology used to treat cephalosporin pharmaceutical wastewater [5–7]. However, biologically treated cephalosporin pharmaceutical wastewater usually cannot meet China's current effluent discharge standards (GB 21903-2008), which specify the maximum limits for pharmaceutical wastewater discharge: TOC – 40 mg/l, COD_{cr} – 120 mg/l, BOD_5 – 40 mg/l, NH_3-N – 35 mg/l, TN – 70 mg/l, Color 60 – Abs_{475nm}/cm, acute toxicity ($HgCl_2$ TEQ) – 0.07 mg/l, and the wastewater is both toxic and refractory for further biological treatment, thus requiring further advanced treatment [8].

Recently, concerns have been raised over the removal of pollutants, especially the degradation of recalcitrant compounds, from industrial wastewater by various advanced oxidation processes (AOPs), which indicates that ·OH is the most dominant species in the oxidation processes [9–11], hydroxyl radicals play an important role in the AOPs process, and the quantity of hydroxyl radicals (·OH) that enter the solution is the primary determinant of the effectiveness of the oxidation in degrading organic pollutants in wastewater [12,13]. Among all AOPs, the combination of ultrasonic and electrochemical technology has been studied by an increasing number of scholars. In comparison to the other AOPs, the combination of ultrasound and the electrochemical process has many

* Corresponding author. Tel.: +86 135 01202663; fax: +86 10 62772455.
E-mail addresses: younbo@gmail.com, jiane.zuo@tsinghua.edu.cn (J. Zuo).

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advantages, such as using no external chemical reagents, avoiding secondary pollution, and requiring simple operation; furthermore, the procedures can be performed at room temperature and atmospheric pressure, thorough decomposition of the pollutants, etc. [14]. Sonoelectrochemical technology applications in wastewater treatment include degradation of textile dyes, degradation of chlorinated pollutants, degradation of nitro compounds, degradation of aromatic and phenolic derivatives, and treatment of wastewater with high organic content [14,15]. Thus, the technology can be used as an advanced treatment method for some refractory industrial wastewater.

The mechanism of sonoelectrochemistry, which is a combination of the ultrasound and electrochemical processes, has been widely studied [16,17]. In a separate electrochemical oxidation process, the pollutants in wastewater can be destroyed by either direct or indirect electrochemical oxidation [18,19]. The quantity of hydroxyl free radicals and other radicals produced in the electrode surface is important in indirect electrochemical oxidation, and the ability of radicals to quickly enter a solution to react with organic pollutants is equally important [20,21]. Meanwhile, in a separate ultrasound wastewater process, cavitation is the basis of wastewater treatment application. The hydroxyl radicals and heat generated during the cavitation process can be used to remove the organic pollutants in wastewater. Cavitation is a physical phenomenon resulting from the ultrasonic field that is set in the solution [22]. Cavitation is generated in liquid when the intense ultrasound exceeds the thresholds for cavitation of the liquid, at which point the cavitation bubbles undergo asymmetrical implosion; the collapsing microbubbles just before fragmentation reach high temperatures (4200–5000 K) and pressures (200–500 atm); finally, a strong micro-jet of the liquid and a violent shock wave, accompanied by free radical production, occurs [13]. In the combined process of ultrasound and electrochemistry, when intense ultrasound irradiation or strong physical phenomena, including acoustic streaming and cavitation/microstreaming, occur, these physical impacts have much ultrasonic and chemical benefit in the positive synergistic mechanism [23]. The attractive features of ultrasonic irradiation in sonoelectrochemistry are as follows: it cleans the electrode surfaces and provides in situ activation of the electrode surface; it decreases the diffusion-layer thickness and improves the mass transport of ions across the double layer; it reduces the adsorption of species involved in the electrode surface and accelerates the reaction process via the action of highly reactive radicals [14,22].

In our study, there are two distinctions from other sonoelectrochemistry process: the first is real cephalosporin pharmaceutical wastewater containing various non-degraded pollutants, including chlorinated pollutants, nitro, aromatic derivatives, and residual traces of cephalosporin antibiotic drugs; the second is that nanocoated electrodes are used during the sonoelectrochemistry process. Using nanocoated electrodes in the electrochemical oxidation process has advantages and disadvantages; on the one hand, the advantage is that electrodes coated with nanoscale rare-earth oxides can produce more hydroxyl radicals because the nanocoated anodes contain more active sites than traditional coated anodes (i.e., non-nanocoated electrodes) [24–26]; on the another hand, the disadvantage is that a large portion of the hydroxyl radicals produced by the nanocoated electrodes can be adsorbed by the nanocoating due to the large surface areas of the nanomaterials, as well as because hydroxyl radicals do not enter a solution quickly to react with the organic pollutants [27]. Meanwhile, nanocoated electrodes in the sonoelectrochemistry can give full play to the advantages of nanomaterials with high catalytic activity. Ultrasonic waves could enhance the chemical catalytic activity of the nanocoated electrode surface and promote the diffusion of hydroxyl radicals produced by the nanocoated electrode into the solution without being adsorbed [28]. Moreover, chlorine and chlorinated compounds are present in cephalosporin pharmaceutical wastewater, and the chlorine/hypochlorite species produced during the sonoelectrochemistry process are critical during the degradation of some intractable organic compounds in cephalosporin pharmaceutical wastewater and can accelerate the degradation process under ultrasound [29]. Sonication was seen to amplify the effect of active chlorine and the combination is significant [30].

The purposes of this work were to study the degradation of biologically treated cephalosporin pharmaceutical wastewater via sonoelectrochemistry using a nanocoated electrode. To improve the catalytic activity of electrodes and produce more hydroxyl radicals, nanocoated electrodes were manufactured; then, the mechanism of effective ultrasound plus electrochemical degradation of the wastewater using a nanocoated electrode was discussed. The change of COD and the effects of some parameters, such as current, frequency, and power, of ultrasonic radicals in the sonoelectrochemical catalytic oxidation process were assessed. Finally, the biotoxicity of wastewater was monitored during wastewater treatment.

2. Materials and methods

2.1. Analytical methods

Chemical oxygen demand (COD) analysis of the wastewater was carried out according to the APHA standard method. pH of the wastewater was determined using inoLab, the pH detector (WTW, Weilheim, 7110pH, Germany). The total organic carbon (TOC) of the wastewater was measured using a TOC analyzer (Shimadzu, model TOC-VCPH, Japan). Organic pollutants of the cephalosporin pharmaceutical wastewater were analyzed with GC–MS using a gas chromatograph (Agilent Technologies, 7890A GC, USA) coupled with a mass spectrometer (Agilent Technologies, 5973C MSD, USA). The $^{\cdot}OH$ radicals concentration was analyzed by using the terephthalic acid (TA) trapping protocol for the reaction between non-fluorescent TA and $^{\cdot}OH$, which produces highly fluorescent 2-hydroxyterephthalate ion (2-HTA) that is readily measured using a spectrofluorometer and can be correlated with the concentration of $^{\cdot}OH$ radicals [31,32]. According to the standard of ISO 11348-2007, the biotoxicity of the reaction solution was tested using a biotoxicity tester (Hach Company, LUMIStox 300, USA). The morphologies of the surface of the nanocoated electrode were examined using SEM (Jeol, JSM-5900 LV, Japan).

2.2. Wastewater characteristics

The pharmaceutical wastewater used in our research was biologically treated cephalosporin pharmaceutical wastewater, which is refractory for further biological treatment and cannot meet the current effluent discharge standards of China, thus requiring further advanced treatment. The wastewater was collected from the discharge of a wastewater treatment setup with a conventional biological treatment (anaerobic–anoxic–oxic) process of a pharmaceutical wastewater treatment workshop. The average qualities of the raw wastewater before biological treatment were as follows: COD, 17,630 mg/l; TOC, 7340 mg/l; TN, 7130 mg/l; pH, 5.3–8.2. The characteristics of the biologically treated pharmaceutical wastewater are shown in Table 1, and the wastewater composition analysis by GC–MS is shown in Fig. 1. Hazardous and refractory organic pollutants in the wastewater include esters, alcohols, alkanes, olefins, cycloalkanes, aromatic hydrocarbons, aldehyde, ketones, and others (Fig. 1).