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Degradation of nitrobenzene in aqueous solution by dual-pulse ultrasound enhanced electrochemical process ☆

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ABSTRACT

The present work reports a novel dual-pulse ultrasound enhanced electrochemical degradation (US-ECD) process that synchronizes alternatively ultrasound pulses and potential pulses to degrade nitrobenzene in aqueous solution with a high percentage degradation and low energy consumption. In comparison to the test results generated from the conventional US-ECD and original electrochemical degradation (ECD) process, the dual-pulse US-ECD process increased degradation percentages to nitrobenzene by 2% and 17%, respectively, while energy used in the pulse process was only about 46.5% of that was used in the conventional US-ECD process. Test results demonstrated a superior performance of the dual-pulse US-ECD process over those of other conventional ones. Impacts of pulse mode, initial pH value, cell voltage, supporting electrolyte concentration and ultrasonic power on the process performances were investigated. With operation conditions optimized in the study at pH = 3.0, cell voltage = 10 V, ultrasonic power = 48.84 W, electrolyte concentration = 0.1 M and an experiment running time of 30 min, the percentage degradation of nitrobenzene could reach 80% (US pulse time = 50 ms and ECD pulse time = 50 ms). This process provided a reliable and effective technical approach to degrade nitrobenzene in aqueous solution and significantly reduced energy consumption in comparison to the conventional US-ECD or original ECD treatment.

1. Introduction

Refractory organics produced in many industrial processes could pollute water and exert negative impacts to ecosystems integrity and human health. Most of the current treatment technologies, which include adsorption [1,2], ozonation [3], extraction [4,5], coagulation [6] and biochemical treatment [7,8], have issues such as high operation cost and complex and inefficient processes that hamper their treatment performances and limit further application.

Electrochemical degradation (ECD) has been demonstrated as an environmentally friendly technology in treating refractory organics because of minimum secondary pollution in its degradation ability [9]. However, it may also result in electrochemical polarization and concentration polarization that leads to high energy consumption and low efficiency. Another disadvantage is the fact that an electrode surface in an ECD is often passivated by reaction by-products [10]. In an effort to utilize inherent characteristics of ultrasound (US) that could increase diffusion mass transfer rates and activate the electrode surface [11] and enhance thermal fluctuations and formation of radicals from cavitations [12], researchers recently have tested an ultrasound enhanced electrochemical degradation (US-ECD) process for the treatment of different types of wastewater [13–15]. However, acoustic streaming and micro jetting produced by ultrasound [16,17] could also disrupt the directional movement of charged ions to the electrodes, resulting in a weak electrode reaction. At the same time ultrasound cavitations created a large number of bubbles that reduce conductivity of electrolytes [18]. In addition, simultaneously using US and Electrochemical (EC) reactions could greatly increase energy consumption of the treatment. As a result, even with its treatment process benefits to ECD, ultrasound enhanced electrochemical treatment were restrained in industrial applications as well.

Research has demonstrated that with the same amount of energy consumption, pulsed ultrasound could reduce energy consumption by 20% over continuous ultrasound [19]. Meanwhile, the pulsed ultrasound used in an electrochemical reaction could reduce ultrasonic cavitation erosion on electrodes, resulting in a longer service life of the electrodes. Otherwise, application of the pulsed electrochemical degradation not only could conserve energy [20], but also promote production of free radicals and improve

☆ Patent-pending technique.

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degradation efficiency [21]. In this work, we created a dual-pulse US-ECD technology that synchronized alternatively pulsed US and pulsed ECD so that the best of both could be utilized to degrade refractory organics.

Normally with an EC reaction, especially with a diffusion-controlled reaction, it often needs the pulse interval to be far longer than the pulse width to diminish the concentration polarization created by consecutive pulses. However, a total reaction time of a pulsed ECD is about the sum of all the pulse widths; a process with a long pulse interval and short width will need a longer time to accomplish an electrolytic reaction resulting in a slower reaction with a lower reaction efficiency. Ultrasonic pulses could enhance mixing as so does a mass transfer [22] due to an ultrasound generated cavitation, it helps to accelerate the reduction of the concentration polarization [23–25]. Even with a relatively short ECD pulse interval, an ultrasound pulse enhanced ECD could have big pulse currents that generate a high reaction rate and high efficiency. With an electrochemical reaction controlled process, by alternating pulsed ECD and pulsed US, energy consumption is reduced significantly and reaction efficiency increases through actions of the pulsed US that properly activate the electrode and reactant [26].

The objective of this study was to set up a dual-pulse US-ECD process and compare its performance to ones from the conventional US-ECD and original ECD. Nitrobenzene was chosen as a test sample constituent, a widely recognized refractory organic, which was commonly used for the production of pesticides, drugs, explosives, polymers, dyes and rubber chemicals etcetera [27]. The nitrobenzene percentage degradation and energy consumption were selected as major criteria for the comparison in this study. The impacts of process parameters such as initial pH, cell voltage, ultrasonic power and electrolyte concentrations have also been studied.

2. Materials and methods

2.1. Reagents used in the tests

All reagents used in this study were an analytical grade and applied without further purification. All solutions were prepared from distilled water. H_2SO_4 and NaOH were used for initial pH adjustment of nitrobenzene solution whenever required, and Na_2SO_4 was employed as a supporting electrolyte in the electrochemical reaction.

2.2. Experimental setup

In Fig. 1, we present a schematic of the experimental setup for the experiments carried out here. It included an electrochemical cell with 150 ml beaker, a magnetic stirrer, an ultrasonic generator (Guangzhou KEPU Ultrasonic Electric Technological Ltd., China), a DC power (Shenzhen Atten Instruments Co., China) and a programmable logic controller (PLC) (Mitsubishi Electric., Japan). The cell was installed with Ti/Sb–SnO_2 dimensionally stable anode (DSA) and titanium electrodes (Baoji De Chen industry & trade Ltd., China). Effective area of the electrode and electrode gap was set as 18 cm^2 and 2.5 cm, respectively. Solution inside the beaker was maintained at 30 °C by a thermostat. A titanium ultrasound horn was immersed 2.0 cm into the liquid phase with a frequency at 22 kHz. A programmed PLC was used to synchronize electrical power and ultrasonic generation so that a variation of durations of electric pluses and ultrasonic pluses were produced. The ultrasonic generator produced an ultrasonic pulse that was triggered immediately after an electric pulse. During the T_{ECD} time period, the ECD took place without ultrasound, avoiding the interference of ultrasound on the electrochemical reaction and for saving

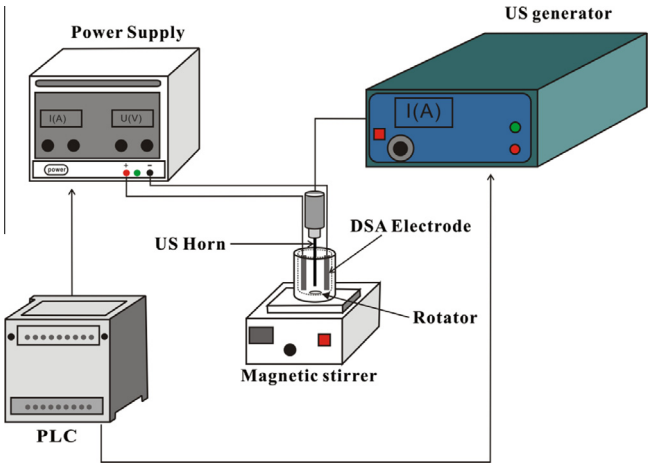

Fig. 1. Experimental setup for dual-pulse US-ECD, US-ECD and ECD processes.

energy. While during the T_{US} time period, the EC as well as ECD power was shut off, the ultrasound was kicked off and it not only activated the electrodes but also effectively eliminated the concentration polarization and electrochemical polarization occurring in the ECD prior to the T_{EC} time period. The conventional US-ECD and original ECD processes were also performed by this experiment apparatus.

2.3. Analysis

The ultrasonic power dissipated in the reactor, P_{US}, was measured by calorimetry [28].

Apparent electrical power of ultrasonic device was adjusted at 48, 80 and 108 W during the study. Calorimetric transfer efficiency (the ratio of calorimetric power and actual electrical power consumption) was 0.52, 0.44 and 0.45, respectively.

The concentration of nitrobenzene in tested solutions was determined by using UV–Visible spectrophotometer (U3010, Hitachi, Japan).

3. Results and discussion

3.1. Comparisons of ECD and US-ECD to the dual-pulse US-ECD process

The performance of the dual-pulse US-ECD process on removal of nitrobenzene in solution was assessed and its results were compared to ones using the conventional US-ECD and original ECD processes, respectively. Table 1 presents the performances of nitrobenzene degradation through different tested processes. It indicates that 63% of nitrobenzene degradation was obtained with an original ECD process in a 30 min test, and US-ECD achieved 78%, whereas 80% of nitrobenzene could be degraded in a dual-pulse US-ECD coupling process [with T_{ECD} = 50 ms, T_{US} = 50 ms expressed as (50, 50) hereafter]. The results reveal that both the US-ECD and dual-pulse US-ECD coupling processes performed much better on nitrobenzene removal than the method using ECD alone. Apparently, ultrasound significantly enhanced the ECD process in the tested solution on nitrobenzene degradation through both physical and chemical mechanisms. Furthermore, it is shown that there was an obvious synergetic impact between US and ECD processes [9]. As to the method with synchronizing US and EC pulses alternatively, their impacts were slightly better (3% increase) than the US-ECD method in which US and EC run continuously. The reason for this, as prior mentioned, is that the pulse mode diminished the interference of the ultrasound on the ECD process which then