Decomposition of ibuprofen in water via an electrochemical process with nano-sized carbon black-coated carbon cloth as oxygen-permeable cathode integrated with ultrasound

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HIGHLIGHTS

- A new integration of electrochemical process with ultrasound for degradation of ibuprofen.
- Synthesis of a novel oxygen-permeable cathode for electro-synthesis of hydrogen peroxide.
- Synergistic degradation of ibuprofen by the integrated process.

ARTICLE INFO

ABSTRACT

The main aim of the present investigation was the treatment of ibuprofen (IBP)-polluted aquatic phase using a novel oxygen-permeable cathode (OPC)-equipped electrochemical process (ECP) integrated with ultrasound (US). According to kinetic modeling, the decomposition rate of IBP by the integrated process was 3.2×10^{-2} min^{-1} which was significant in comparison with the OPC-equipped ECP (1.4×10^{-2} min^{-1}) and US alone (2.4×10^{-3} min^{-1}). Increasing the current resulted in the enhanced generation of H_2O_2 and consequently, improved the degradation of IBP in the solution. Excessive concentrations of Na_2SO_4 as supporting electrolyte led to no significant enhancement in the reactor efficiency. At initial IBP concentration of 1 mg L^{-1}, complete removal of IBP with reaction rate of 1.7×10^{-1} min^{-1} was happened within a short reaction time of 30 min. The pulse mode of US led to more than 10% increase in the removal efficiency compared with the normal mode. The presence of scavenging compound of methanol caused the highest drop in the efficiency of the integrated treatment process, indicating the substantial role of free hydroxyl radicals in the degradation of IBP. Intermediate byproducts generated in the solution during the decomposition were also identified and interpreted.

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1. Introduction

Pharmaceutically active compounds (PhACs) have been detected in aquatic environments such as surface water and groundwater (Klavarioti et al., 2009). Most of PhACs are toxic to aquatic life (Rakic et al., 2015). The presence of PhACs causes long-term effects to human health, especially to vulnerable groups such as children, elders, and pregnant women (Xiang et al., 2016; Thokchom et al., 2017). Among PhACs, ibuprofen (IBP) is classified as non-steroidal anti-inflammatory drug, which can causes long-term harmful health effects. It has been widely consumed for the treatment of migraine, toothache, arthritis, inflammatory rheumatic and musculature-bone pains (Wang et al., 2016; Xiang et al., 2016; Gong et al., 2017). IBP is the most widely used anti-inflammatory drug discovered in water samples. It is one of the high priority PhACs in water resources management (Chang et al., 2017). This anti-pain drug is the third most consumed PhAC which is listed by the World Health Organization (WHO) as one of the "Essential Drugs" (Estevez et al., 2014). IBP can be discharged into aquatic environments via various human activities (human excreta and excess non-prescription drugs), hospital effluents, septic tanks, wastewater treatment plants and industrial effluents (Estevez et al., 2014; Gong et al., 2017). Hence, it is very important and vital to establish efficient treatment technologies for the elimination of IBP from water resources. IBP like most PhACs are categorized as refractory organic

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compounds which is resistant to biological treatment processes (Tran et al., 2015; Xiang et al., 2016). In addition, the application of adsorption process, as a conventional physicochemical treatment process, on the basis of granular activated carbon is not efficient enough to remove IBP from the aquatic phase due to its low hydrophobicity (Xiang et al., 2016). Some physical treatment methods such as membrane filtration do not degrade IBP and just transfer it to another phase, leading to another contamination problem (Taheran et al., 2016; Wang et al., 2016). Compared with existing physicochemical treatment processes, advanced oxidation processes (AOPs) are efficient for the removal and effective degradation of refractory organic compounds such as IBP (Klavarioti et al., 2009; Hou et al., 2013; Wang et al., 2016; Chang et al., 2017). The main advantage of AOPs is the generation of strong free radical species, especially hydroxyl radical (HO•), which attack and then decompose the target organic pollutants in the aqueous phase (Darvishi Cheshmeh Soltani et al., 2013b; Chang et al., 2017; Thokchom et al., 2017). Among various AOPs, the implementation of electrochemical AOPs (EAOPs) has attracted much more attentions for the degradation of emerging organic compounds (García-Rodríguez et al., 2016). The main classification of EAOPs is anodic oxidation (AO) via the direct anodic oxidation (electron transfer from the target compound to the anode surface) and the degradation by the produced physisorbed HO• (generated through the dissociation of water molecules) (Akbarpour et al., 2016); while, in the present study, an oxygen permeable cathode (OPC)-equipped electrochemical process (ECP) was used instead of conventional ECP for in situ generation of hydrogen peroxide through the reduction of oxygen at a porous cathode as represented in below reaction (Darvishi Cheshmeh Soltani et al., 2013b; Khataee et al., 2014a; Bocos et al., 2015; Petrucci et al., 2016):

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (1)$$

In situ generation of hydrogen peroxide in an ECP, along with anodic oxidation, leads to the oxidation of the target organic pollutant without the need to add chemicals and adjust the solution at optimum pH value (Darvishi Cheshmeh Soltani et al., 2013b; Soltani et al., 2013; Bocos et al., 2015; Thokchom et al., 2015). In our previous research, carbon paper (CP) was coated by nano-sized carbon black (CB) powder and used as OPC for in situ generation of hydrogen peroxide (Soltani et al., 2013). As a novel and different work, in the present study, a flexible carbonaceous matter named carbon cloth (CC) was utilized for the synthesis of OPC instead of CP. Many researchers have examined and developed the integration of ECP with ultrasound (US) as one of the most efficient treatment processes for the degradation of PhACs such as IBP (Bringas et al., 2011; Thokchom et al., 2015, 2017; Tran et al., 2015). The US waves bring about the generation of HO• in water via the formation, growth, and collapse of the "cavitation bubbles" as a result of the high pressure and temperature (Al-Hamadani et al., 2016; Rayaroth et al., 2016). However, as an individual treatment process, the decomposition rate of US for the removal of organic compounds is time consuming and requires a lot of energy for an acceptable efficiency (Darvishi Cheshmeh Soltani et al., 2015; Darvishi Cheshmeh Soltani et al., 2016b; Hassani et al., 2016; Jorfi et al., 2017). The integration of US with ECP results in the enhanced efficiency of the ECP (Thokchom et al., 2015; Rayaroth et al., 2016; Yang et al., 2016). Apart from the potential oxidative properties, US irradiation prevents the formation of by-products on the anode surface and enhances mass transfer and current efficiency of the ECP (Tran et al., 2015). According to our literature review, the integration of OPC-equipped ECP with US has not been implemented until now. Therefore, in the present study, OPC-equipped ECP was integrated with US for the decomposition of

IBP in the aqueous phase. Considering economic considerations, the CC was covered by CB powder and the ECP was operated at low current intensities and oxygen flow rate. The effect of some operational parameters, including current intensity, electrolyte concentration, IBP concentration, and irradiation pattern was also assessed in order to achieve the best operational conditions of the integrated process. The efficiency of the integrated process was also evaluated in the presence of other organic and inorganic compounds. The intermediate byproducts of IBP generated during the treatment process were identified using gas chromatography-mass spectroscopy (GC-MS).

2. Materials and methods

2.1. Preparations and reactor set-up

IBP (purity $\geq$ 98%, molecular structure: $C_{13}H_{18}O_2$, molecular weight: 206.29 g mol^{-1}) was obtained from Sigma-Aldrich Co, USA. CB (VULCAN® XC72R) used in the present study was purchased from Cabot Co, USA and used as received. Teflon-treated CC with specific surface area of 3.53 m^2 g^{-1} (taken by BEL SORP mini II, Japan) and thickness of 0.11 mm was prepared from ElectroChem, Inc (USA). Teflon treatment makes the CC hydrophobic. PTFE binder (Teflon Emulsion, 5 wt%) was also purchased from ElectroChem. PTFE inhibits the CC from being saturated by water and lets oxygen gas pass through the pores without restriction. All other chemicals were purchased from Merck, Germany and used without purification. OPC was synthesized using abovementioned materials according to our previous studies (Darvishi Cheshmeh Soltani et al., 2013b; Soltani et al., 2013), but flexible CC was used as precursor of OPC instead of CP. The hydrophobic structure of as-prepared OPC was put into the electrochemical cell equipped with a DC power supply, Pt anode and Na$_2$SO$_4$ (purity $\geq$ 99%) as supporting electrolyte. As-synthesized OPC was located at the bottom of a cylindrical holder made by polypropylene. The electrochemical cell was an undivided cylindrical glass reactor with working capacity of 200 mL. The OPC-equipped ECP cell was placed inside an ultrasonic bath (Elma, P30H, Germany) with the applied power of 320 W and fed with oxygen gas supplied by an oxygen concentrator (flow rate of 0.1 L min^{-1}). A schematic flow-diagram of as-fabricated experimental set-up is illustrated in Fig. SM-1.

2.2. Analysis

For each analysis, a 10-mL sample was collected from the set-up and centrifuged for 5 min at 10000 rpm to separate particles from the solution. The resulting sample was analyzed using a high performance liquid chromatography (KNAUER HPLC, Model: AZURA, Germany) to measure the residual concentration of IBP after the treatment process. The analyzer was operated by a RP Amide column and a UV detector (230 nm) adapted to laboratory temperature. A mixture of phosphate buffer (pH: 3.5) and acetonitrile (volumetric ratio of 45:55) was prepared as mobile phase and fed at flow rate of 1 mL min^{-1}. The surface components of the samples were analyzed by the Fourier transform infrared spectroscopy (FTIR, Thermo scientific, Nicolet Avatar, USA) equipped with attenuated total reflection accessory (ATR). Electro-generated hydrogen peroxide was spectrophotometrically measured using a UV−Vis spectrophotometer, (Hach Co, USA). For this, 4-mL sample was picked up from the reactor and 3 mL buffer solution (0.1 M potassium biphthalate), accompanying 3 mL of iodide reagent (10^{-4} M ammonium molybdate, 0.4 M potassium iodide and 0.06 M NaOH) were immediately added to the withdrawn sample. Finally, the spectrophotometer adjusted at wavelength of 351 nm was operated for the measurement of the light absorbance and