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Photoperoxi-coagulation using activated carbon fiber cathode as an efficient method for benzotriazole removal from aqueous solutions: Modeling, optimization and mechanism

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ABSTRACT

In this research, benzotriazole (BTA) was removed from aqueous solution using photoperoxi-coagulation (PPC) in which activated carbon fiber (ACF) was used as a cathode. Box-Behnken design was used to optimize and analyze four parameters i.e. time, applied current, initial BTA concentration and UV light power. According to the results, the R-squared and adjusted R-squared were 0.982 and 0.964, respectively, implying that the model was statistically suitable. It was shown that under the optimal condition for BTA removal i.e. 60 mg/L initial BTA concentration, 50 min time, 200 mA applied current and UV light power of 12W, the efficiency of the PPC process was maximum (97.8%). The removal mechanisms were determined and their results showed that the oxidation mechanism of photoperoxi-coagulation process had a more contribution in BTA removal in comparison with coagulation mechanism. The results of scavenging experiments also confirmed the determined removal mechanisms. Synergistic effect was observed in PPC while first order rate constant of PPC was 2.7 fold more than that of sum of each mechanism. The removals of TOC and COD were 64.5% and 76.3% respectively. Average oxidation state and carbon oxidation state of BTA solution were increased after PPC process indicating biodegradability improvement indirectly.

1. Introduction

The entering of emerging pollutants into water resources is of important concern for the scientific and political communities. These pollutants are defined as compounds that have been recently recognized by advanced analysis instruments. Hence regulatory and monitoring plans are not accomplished yet [1,2]. These compounds are often non-biodegradable with high toxicity for microorganisms and human. Benzotriazole (BTA) is an emerging pollutant that is extremely used in different industries and products as a versatile compound [3]. BTA is applied in dishwasher detergents, pharmaceuticals and dyes as well as UV stabilizer on plastic products [4,5]. BTA is also exerted as flame retardant in aircraft de-icers and anticorrosive additive [6]. Moreover, the toxicity and mutagenic potential of BTA have been reported for some organisms which may influence human health considerably [7]. It is classified in high production volume chemicals (HPVC) and it has also high solubility in water (28 g/L) [6,8]. This property makes the presence of BTA in water resources as several monitoring studies have reported high concentrations of BTA in aquatic environment [4,5,9,10].

The non-biodegradability and toxicity of BTA are the reasons why various studies are focused on removal of emerging pollutants by advanced oxidation processes (AOPs). The AOPs are the methods that generates powerful hydroxyl radicals ($HO^{\bullet}$) with $E^{\circ} = 2.8$ V and have been proposed for degradation of persistent organics [11,12]. Several techniques can produce hydroxyl radical ($HO^{\bullet}$) as main agent for destruction of organic compounds. Fenton oxidation is likely the most common process for generating the $HO^{\bullet}$. Fenton oxidation is mixture of ferrous ion with H_2O_2 in acidic condition (Eq. (1)) [13–15].

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow HO^{\bullet} + Fe^{3+} + H_2O \quad (1)$$

The storage and shipment of concentrated H_2O_2 are the limitations of Fenton oxidation [16]. Electrochemical processes have proven that are very effective, environmentally compatible and green processes since their main reagent is electron [17,18]. Hydrogen peroxide can be electrochemically produced with

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reduction of oxygen molecule at carbon-based cathode at acidic electrolyte according to Eq. (2) [19,20].

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

On the other hand, ferrous ion is produced at anode when iron is used as anode. Indeed, both Fenton reagents are in-situ produced in electrochemical cell. In other words, H_2O_2 and ferrous ion are generated at cathode and anode respectively [21,22].

$$Fe \rightarrow Fe^{2+} + 2e^- \quad (3)$$

Moreover, ferric ion produced in Eq. (1), is reduced at cathode and ferrous ion is regenerated consequently. This phenomenon propagates chain reactions of Fenton oxidation [23].

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (4)$$

Ferrous and ferric ions produced can make hydroxide forms (flocs) which can effectively adsorb organic pollutants through coagulation mechanism based on Eq. (5). Coagulation and oxidation mechanisms are simultaneously fulfilled in electrochemical cell that is so-called peroxi-coagulation [21,23].

$$Fe^{3+} \text{or } Fe^{2+} + nOH^- \rightarrow Fe(OH)_{n(s)} \quad (5)$$

In order to enhance the efficiency of Fenton-based process, UV irradiation is usually used. In case of peroxi-coagulation, UV irradiation not only can directly decompose hydrogen peroxide to hydroxyl radical but also regenerates ferrous ion by photo-reduction of ferric ion producing more hydroxyl radicals [24,25].

$$H_2O_2 + UV \rightarrow HO^\bullet + HO^\bullet \quad (6)$$

$$Fe(OH)^{2+} + UV \rightarrow Fe^{2+} + HO^\bullet \quad (7)$$

Photoperoxi-coagulation (PPC) is actually a hybrid process consisting of UV irradiation and peroxi-coagulation which has been rarely considered for removal of organic compounds. PPC has been used only for degradation of some pesticides with carbon-PTFE or reticulated vitreous carbon cathode [25]. Activated carbon fiber (ACF) is a porous material which has high ability in electrogeneration of H_2O_2 that has not been considered for PPC. Although several AOPs have been studied to remove BTA from aqueous solution such as photocatalysis [26], UV/H_2O_2 [27], ozonation [28], electro-photocatalysis [7], no study has been conducted for degradation of BTA by PPC yet. In the current work, the performance of PPC was investigated for BTA removal with ACF cathode. In order to optimize PPC, Box-Behnken design (BBD) was used as a response surface method. Synergistic effect was also studied for PPC process. Chemical oxygen demand (COD) and total organic carbon (TOC) indices were used for mineralization degree of BTA and biodegradability improvement. Finally, the mechanism of the process was studied for determining the contribution of coagulation and oxidation mechanisms.

2. Materials and methods

2.1. Chemicals and reagents

Benzotriazole ($C_6H_5N_3$) was purchased from Merck Millipore Company with purity >98%. All the main reagents used for COD analysis were provided from Sigma-Aldrich that include sulfuric acid (98%), silver sulfate, mercury sulfate, potassium dichromate and ferrous ammonium sulfate. Sodium sulfate was purchased from BDH Chemicals Inc. Activated carbon fiber was provided from Sazeh Morakkab (Iran) with a specific surface area of 850 m^2/g and surface density of 150 g/m^2. Methanol and water with HPLC grade were provided by Samchun Chemical Co.

2.2. Photoperoxi-coagulation

Experiments were conducted in a 0.45 L cylindrical batch reactor made of quartz. The diameter and height of quartz reactor were 6 cm and 16 cm respectively. The cathode was activated

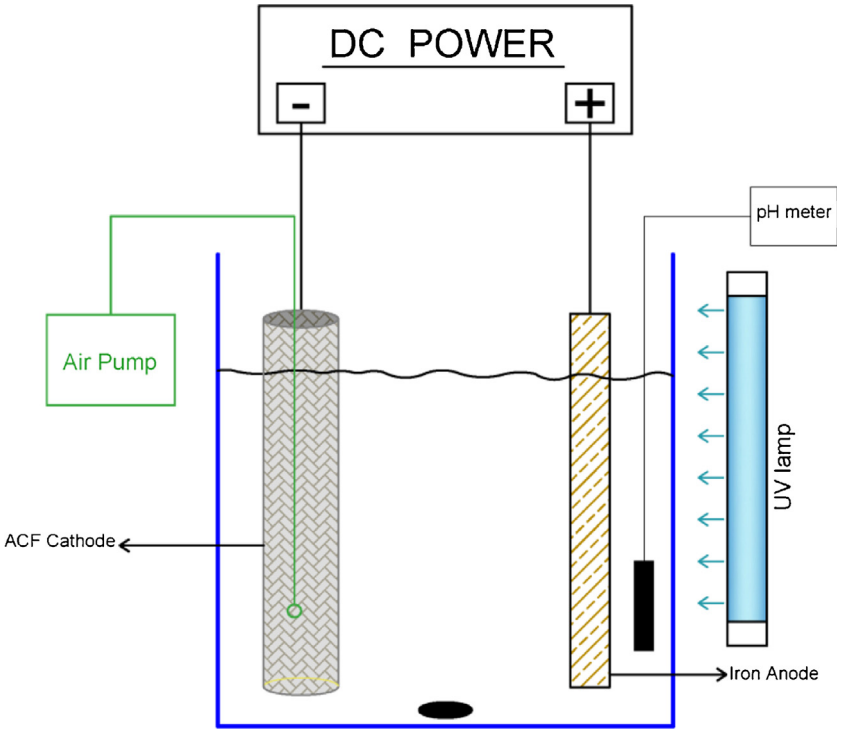

Fig. 1. Experimental set-up for photoperoxi-coagulation with ACF cathode.