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Modeling and kinetics study of electrochemical peroxidation process for mineralization of bisphenol A; a new paradigm for groundwater treatment

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ABSTRACT

To remove the bisphenol A (BPA) effectively from groundwater great attempts made in the current work to optimize the operating parameters of electrochemical peroxidation (ECP) process using response surface methodology (RSM) based on central composite design (CCD). The obtained data from ANOVA analysis revealed the significance of experimental variables. The obtained removal efficiency of BPA demonstrated that the predicted quadratic model is highly adequate and applicable. According to the experimental data, it found that the best removal efficiency of 100% achieved at initial concentrations BPA of 5.0 $mg \cdot L^{-1}$, hydrogen peroxide amount of 55.0 μL, pH 3.0, reaction time 12.0 min, and current density 6.0 $mA \cdot cm^{-2}$. The rate of the oxidation process of BPA reduced by increasing the amount of H_2O_2 and Fe^{2+} ions, which might be due to the reducing the amount of hydroxyl free radicals involved in the scavenging reaction. The kinetics of the process follows the pseudo first-order model with rate constants of 0.596 min^{-1} ($R^2 = 0.9908$). Since, most of the reported studies are based on one factor at the time method, in the current study, RSM was used to evaluate the main effects of parameters, their simultaneous interactions and quadratic effect to achieve the optimum condition for EC process. The kinetics studies of ECP process provide valuable information on the mechanism of the degradation process that attributes to the presence of free hydroxyl radicals.

1. Introduction

According to the official reports, overall water on the Earth with the volume of about 1400 million km^3 contains 97% salt water which is filled with salt and other minerals, and humans cannot drink this water, 2% glacier ice at the North and South Poles which is too far away from where people live to be usable and <1% is fresh water which is available for human uses such as drinking, transportation, heating and cooling, industry, and many other purposes [1]. Literature surveys revealed that aquatic environments are daily threatened by releasing large amounts of synthetic pollutants such as industrial chemicals [2], pesticides [3], dyes [4, 5] and pharmaceuticals and personal care products (PPCPs) [6, 7].

Among the mention synthetic organic pollutants, bisphenol A (BPA) as a known and widely used monomer with two phenol moieties with desirable properties of low vapor pressure, volatility and moderate water solubility extensively used for the production of polycarbonate plastics and epoxy resins. It also used as stabilizer or antioxidant for many types of plastics such as polyvinyl chloride [8]. The maximum amount of BPA reported in hazardous waste landfill leachates, stream water, and drinking water were 17.2 $mg \cdot L^{-1}$, 12 $\mu g \cdot L^{-1}$ and 0.1 $\mu g \cdot L^{-1}$, respectively [9].

Moreover, BPA observed in the dental sealant, preserved foods and beverages, dish and laundry detergents, cosmetics and personal care products such as conditioners, shampoos, body and face wash/lotions [10]. BPA as an endocrine-disrupting chemical involved in disrupting the hormonal system of living systems, thereby its presence in the aquatic environments may result in increasing the risk of disease occurrence related with metabolic syndrome including diabetes mellitus, insulin resistance, and obesity. Moreover, some other diseases such as breast cancer, infertility, genital tract abnormalities, and cardiovascular diseases reported (Fig. 1) [11].

Due to the harmful effect of BPA on living beings, several methods are developed for its effective removal including adsorption [11, 12], nano-filtration membrane [13], and biological treatment [14]. Furthermore, recently advanced oxidation processes (AOPs) as an environmentally friendly method received extraordinary attention because of their high efficiency for removal of non-biodegradable organic pollutants from aquatic environments such as wastewater, ground and surface

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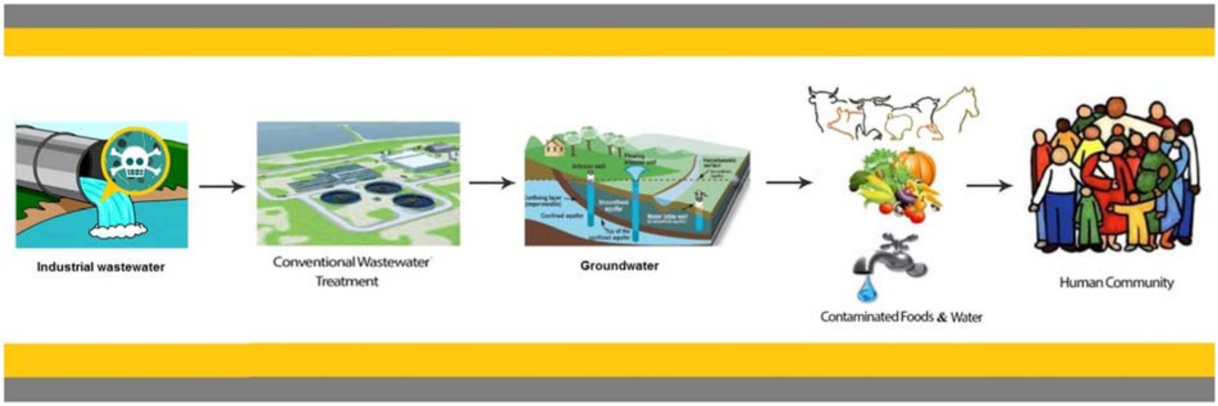

Fig. 1. Major pathway for bisphenol A releasing into the environment.

water by in-situ generation of the hydroxyl radical (•OH) as the oxidizing agent [15].

Electrochemical peroxidation process (ECP) as an effective combination of the advanced oxidation process and Fenton reaction applied in the current work to improve the degradation process of BPA as the pollutant. Hydrogen peroxide supplied externally and the ferrous ion generated by a sacrificial iron anode [16]. As seen from the following equations, the hydroxyl radicals (•OH) produced by the interaction between H_2O_2 and Fe^{2+} known as Fenton's reagents. The prepared hydroxyl radicals play an important role as a strong oxidant to react non-selectively with all exist organic molecules leading to their oxidation until reaching a high mineralization degree [16].

$$\text{Anode}: Fe \rightarrow Fe^{2+} + 2e^- \quad (1)$$

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

$$\text{Introduced}: H_2O_2 + Fe^{2+} + H^+ \rightarrow Fe^{3+} + H_2O + {}^{\cdot}OH \quad (3)$$

Treatment procedure deals with mineralization of BPA in groundwater by investigating the effect of the significant experimental parameters including, pH, reaction time, initial BPA concentration, current density and H_2O_2 dosage. Moreover, the kinetics of BPA degradation investigated to recognize the exact mechanism of ECP process. Besides the current studies using electrochemistry, on the other hand, using electrochemical sensors as a device which provides a certain type of response that is directly related to the quantity of a chemical species such as contaminants, showed a rapid growing scientific studies in environmental monitoring field and practiced by the current research group recently [17–24]. To the best of our knowledge, there are only a few studies on Bisphenol A removal using electrochemical process. However, the reported studies suffered from low removal efficiency [25, 26]. Moreover, in the classical investigations, the optimization of the treatment process is based on varying one factor at the time which needs a large number of experiments where the other factors keep constant. However, the obtained results are not able to provide a satisfactory model for evaluating and predicting the main effects of parameters, their simultaneous interactions and quadratic effect to achieve the optimum condition for ECP process. Therefore, in the current work, RSM applied for optimization of the treatment procedure and reducing the number of experiments.

2. Material and methods

2.1. Chemicals and reagents

Analytical grade bisphenol A (purity >99% w/w), sodium sulfate (anhydrous, purity ≥99%), tert-butanol (anhydrous, purity ≥99.5%), sodium phosphate (purity ≥98%), and dichloromethane HPLC grade (purity ≥99.9%) were purchased from Sigma-Aldrich. Methanol HPLC grade (purity ≥98% v/v), sulfuric acid (purity ≥98% v/v), H_2O_2 (purity 30% w/w), sodium hydroxide (purity >98% w/w), sodium chloride (purity min. 99.5% w/w), sodium bicarbonate (purity ≥98% w/w), potassium nitrate (purity ≥99%) were purchased from Merck company. All solutions were prepared using deionized water.

2.2. Electrochemical peroxidation process

A cylindrical glass cell of 9 cm height with 7 cm internal diameter used as an electrochemical reactor. One pair of iron electrodes with dimensions of 5 × 0.5 × 0.1 cm installed parallel to each other were used as anode and cathode at a fixed distance of 3 cm apart. The volume of 250 mL sample with supporting electrolyte of Na_2SO_4, 5 mM were used throughout the experiment. The pH adjustment was carried out using a pH meter metrohm 827 pH/mV lab by addition of appropriate amounts of 0.1 M NaOH or H_2SO_4 solutions. The test solution gently stirred (200 rpm) during ECP run with the current density set at a given level using DC power supply and a hydrophilic PTFE syringe filter (0.45 μm pore size) was used for filtering the final suspension.

2.3. Removal efficiency evaluation

HPLC analysis was carried out using a KNAUER Smartline HPLC system, C_{18} column; 250 × 4.6 × 5 mm and a UV detector. The column temperature kept at 30 °C, the detection wavelength was set at 276 nm, and the injection volume was 20 μL for each analysis. For all HPLC analysis, a gradient program used at a flow rate of 1.0 mL min^{-1}, by combining solvent water and solvent methanol as follows: 35–80% (37 min) [27].

2.4. Response surface methodology

RSM as a statistical technique was applied to design some limited experiments for suggesting an effective treatment model based on ECP process [28, 29]. The significance of main variables including initial BPA concentration (X_1), current density (X_2), the H_2O_2 dosage (X_3), and their interactive influences investigated. The parameters variations and their levels summarized in Table 1.

To conduct a successful study, RSM is applied to generate a quadratic model to find a suitable approximation for the relation between independent main variables and response as expressed below [30]:

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i X_i + \sum_{i=1}^{n} \beta_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \beta_{ij} X_i X_j \quad (4)$$

where Y denote the predicted response which is removal percentage. X_i and X_j are the coded independent variables including initial BPA concentration, current density, and H_2O_2 dosage. The parameter β_0, β_i, β_{ii}, β_{ij} denote the model constant, the linear coefficient, the quadratic