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Reprint of: Decomposition of PPCPs by ultrasound-assisted advanced Fenton reaction: A case study with salicylic acid☆

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ABSTRACT

The study is about the degradation of a widely used pharmaceutical and personal care product-salicylic acid by sonocatalysis, and the experimental design of the reaction system. The first part of the study consists of sonication (572 kHz) in the presence of zero-valent iron (ZVI) with or without H_2O_2 to select and optimize the operational parameters as frequency, time, initial solute concentration, dose of reagents and pH. The second part consists of the use of response surface methodology and multiple regression to develop an experimental design modeland to assess the individual and interactive effects of pH, power (P_o), ZVI dose and H_2O_2. The results showed that the optimal conditions predicted by the model without defining any restrictions are: pH = 2.0, P_o = 120 W, ZVI = 24 mg L^{-1}, which provide total salicyclic acid and 48% TOC decay. However, the prediction implies intensive consumption of energy and reagents, and must therefore be modified by restricting the value of TOC decay to a lower value and that of pH to a higher one. Cross-validation tests showed that the prediction accuracy of the model was considerably high with 5.0–9.4% deviation from the experimental data.

1. Introduction

PPCPs are pharmaceuticals and personal care products that are widely utilized by humans for personal health and cosmetic care, and by agribusiness for boosting the growth or health of livestock [1]. Most common of all are analgesics/anti-inflammatory drugs, antibiotics and bacteriostatics, antiepileptics, beta-blockers, blood lipid regulators, cytostatic drugs, oral contraceptives, antiseptics, musk fragrances and sun screen agents [1,2].

Upon consumption, PPCPs are readily discharged to sewage treatment facilities via excretion or wash waters. However, the majority of these compounds are resistant to biodegradation so that they bypass the sewage treatment facilities unchanged ending up either in receiving waters or the sewage sludge [3]. As such, they are frequently detected in freshwater systems at considerably high concentrations (ppm ranges) [4–6]. The environmental concern with the presence iof PPCPs in fresh water is that they are recognized with acute or chronic adverse effects on aquatic organisms and are of potential risk to humans if the reclaimed water is recycled and returned to the water supply [7].

Salicylic acid (SA), also known as 2-hydroxybenzoic acid is a widely used PPCP in pharmaceutical and cosmetic formulations. It is easily produced by hydrolytic deacetylation of acetylsalicylic acid, and used in ingredients of acne treatment, shampoos, facial cleansers and moisturizers. On the other hand, it is a bio-persistent compound with moderate toxicity to aquatic organisms, requiring therefore advanced water treatment options before discharge to a fresh water source. Advanced Oxidation Processes (AOPs), which are recognized with on-site generation of OH radicals in the reaction medium seem to be promising alternatives for the destruction of recalcitrant organic pollutants such as SA in water [8]. The most commonly employed lab-scale AOPs for removing SA from water are photocatalysis with TiO_2, electrochemical, Fenton, and wet air oxidation, and rarely ultrasonication [9–13].

The use of ultrasound in heterogeneous reactions provides unique advantages such as enhancement of mass transfer and chemical reaction rates, improvement of the catalyst surface, reducing of chemical consumption and sludge generation [14]. A very common catalyst for use in combination with ultrasound is zero-valent iron (ZVI) with its very reactive surface and ability to release Fe species in solution, thus initiating Fenton or Advanced Fenton reactions. A unique advantage of ultrasound in these systems is that one of the components of Fenton reagent (H_2O_2) is in-situ generated via combination of two hydroxyl radicals that form upon water pyrolysis in the collapsing cavity bubbles [15]. A summary of chemical reactions taking place during sonolysis of water in the presence of ZVI is given in the following [16,17]:

$$H_2O +))) \rightarrow HO^{\cdot} + H^{\cdot} \quad (1)$$

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$$2HO^{\cdot} \rightarrow H_2O_2 \quad (2)$$

$$HO^{\cdot} + H_2O_2 \rightarrow HOO^{\cdot} + H_2O \quad (3)$$

$$Fe^0 \text{ (surface)} +))) \rightarrow Fe^{2+} + 2e^- \quad (4)$$

$$Fe^0 \text{ (surface)} +))) \ ^{*}Fe^{2+} + 2e^- (4) \quad (5)$$

$$Fe^0 \text{ (surface)} + H_2O_2 \rightarrow Fe^{2+} + HO^{\cdot} + OH^- \quad (6)$$

$$Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + OH^- \quad (7)$$

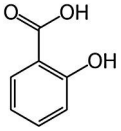
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO^{\cdot} + H^+ \quad (8)$$

The operation of sono-Fenton reactions requires consideration and optimization of the critical process parameters, namely pH, the dose of ZVI and H_2O_2 (if external addition is necessary), and the initial concentration of the reactants. In the past, the effect of these variables on the efficiency of the process and/or reaction kinetics have been investigated with focus on conventional "single-factor-at-a-time" method [18]. However, the method is inadequate with incomplete understanding of the behavior of the system, which is affected by multiple variables [19,20]. In addition, the "single-factor-at-a-time" method does not show the effect of interactions between parameters, and therefore cannot provide an accurate prediction of the system behavior [21]. The confusion may be avoided with the use of well-designed experimental systems and adequate multifactor models such as the "response surface methodology" (RSM), which is widely used to develop empirical models that accurately describe process behaviors and interactions between the variables [22]. No scientific work has been so far published on the use of RSM in the experimental design of a sonocatalytic reaction system to be used the degradation of PPCPs by advanced Fenton reactions.

This present study was aimed to investigate the degradability of salicyclic acid in water by advanced sono-Fenton reaction using zero-valent iron to predict the individual and interactive effects of process parameters on the efficiency of carbon mineralization. The method of prediction was based on the RSM methodology and multiple regression analysis. The reactions were run in a high-frequency reactor at various preset values of ZVI, H_2O_2, electrical power and pH, which were selected as the independent variables of the model. The response of the system to variations in these variables was selected as the reduction in total organic carbon (TOC), which is the dependent variable reflecting the efficiency of the system.

2. Materials and methods

Salicylic acid with properties and chemical structure as given was purchased from Sigma-Aldrich (> 99% purity) and used for preparing a stock solution of the compound. HPLC grade acetonitrile and phosporic acid were purchased from Merck (Istanbul). ZVI and hydrogen peroxide were obtained from Hepure (USA) and Merck (Istanbul), respectively. The chemical structure and some of the physical/environmental properties of SA are as given [23–25]:



Chemical Formula: $C_7H_6O_3$, MW: 138.122 g mol^{-1}, pK_a: 2.97, Water Solubility: 2240 mg L^{-1} (25 °C), EC50: 870 mg L^{-1} (Species: Daphnia magna, pH 7.45, 21 °C, 48 h), logKow: 2.26.

2.1. Experimental

Batch adsorption tests were carried out at 10 mg L^{-1} SA and varying concentrations of ZVI (2.5, 5, 10, 30, 50 mg L^{-1}) in a shaker at pH 3/3.5 and a mixing rate of 125 rpm for 60-min to asses the effect of catalyst dose on the degree of SA adsorption.

The ultrasonic devices were the following:

i) A multi-frequency plate type reactor with a 500-ml glass cell, and a 120 W generator connected to three piezoelectric transducers (22 cm^2) emitting at 572, 861 and 1164 kHz (Ultraschall/Meinhardt, Germany). The reaction volume was optimized at 250 mL, and the power density in it was estimated by calorimetry as 0.21 W mL^{-1}.
ii) A low-frequency horn connected to a 180 W generator and a piezoelectric transducer (1.13 cm^2) emitting at 20 kHz. The solution volume was 150 mL and the power density was estimated as 0.19 W mL^{-1}.

The reactor contents were sonicated for 45-min, during which samples were collected periodically for the analysis of SA, DOC/TOCand UV absorption. The optimum pH, frequency, initial solute and ZVI concentrations were selected based on the efficiency of mineralization.

2.2. Analytical

Salicylic acid was analyzed by a Shimadzu LC-20AT HPLC with a 20A UV–Vis photo diode array detector, an Inertsil ODS-3 V (C18) (Hypersil BDS), and a 250 mm × 4.6 mm column. The mobile phase was 20 mM phosphoric acid at pH 2.0 and acetonitrile (50:50). The concentration of the compound was also monitored spectrophotometrically at 297 nm using a UNICAM-Helios, Alpha/Beta double beam spectrophotometer. The degree of C-mineralization was evaluated by monitoring the reduction in organic carbon of the samples using a Shimadzu TOC-V CSH analyzer.

2.3. Factorial design and data analysis

Values of the model factors were selected using the central composite technique with a 4-factor-5-level inscribed composite, and the design matrix was generated by MATLAB 11.2 [26]. The open source R Gui software [27] was used for the statistical analysis of results and validation of the regression model.

3. Results and discussion

3.1. Control experiments

Batch adsorption data collected during 60-min contact of SA with ZVI in the absence of ultrasound showed that the compound weakly adsorbed on the metal surface and the degree of adsorption increased with increased concentrations of the adsorbent. Maximum SA adsorption was 13% at the highest dose of ZVI, while the percentage of DOC removed from solution under equivalent conditions was slightly larger (16.4%) as the evidence of oxidative degradation in the bulk solution or at the reactive metal surfaces. The data are presented in Fig. 1.

The second set of control experiments were carried out in the presence of SA and ultrasound only (no ZVI) to select the optimum values of pH, C_0 and frequency. The data were generated at three pH levels (3.5, 5.0, 9.0), four SA concentrations (2.5, 5, 8.75, 10 and 15 mg L^{-1}) and three frequencies (20 kHz, 572 kHz, 856 kHz). We found that the optimum concentration of SA was 10 mg L^{-1}, and low frequency irradiation (20 kHz) was considerably ineffective, as it provided almost no reduction in SA and TOC (data not given). The lack of sonochemistry under 20 kHz is due to the long collapse duration of the cavity bubbles that reduces the incidence of bubble collapse and facilitates radical combination reactions leading to reduced rate of $OH^{\cdot}$ ejection to the bulk solution.

Fig. 2 presents time-rate of SA decomposition and DOC decay observed during high frequency irradiation of 10 mg L^{-1} SA at the test pH levels. The data show that the rate of oxidation was a maximum at

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