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A statistical experimental design approach for photochemical degradation of aqueous polyacrylic acid using photo-Fenton-like process

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A B S T R A C T

The present study investigates the degradation of poly(acrylic acid) in aqueous solution by a photo-Fenton-like process. Batch experiments are carried out to model and optimize the process. The effects of the initial concentration of poly(acrylic acid), the initial concentration of Fe^{3+}, and the H_2O_2 dosage as independent variables on the total organic carbon (TOC) removal as the response function are studied using response surface methodology (RSM). The significance of the independent variables and their interactions are tested by means of analysis of variance (ANOVA) with 95% confidence level. The statistical analysis of the results indicated satisfactory prediction of the system behavior by the developed model. The optimum operating conditions to achieve maximum TOC removal are also determined. The model prediction for maximum TOC removal is compared to the experimental result at optimal operating conditions. A good agreement between the model prediction and experimental results confirms the reliability of the developed model.

1. Introduction

Polyacrylic acid (PAA), one of the widely used synthetic water-soluble polymers, has broad applications in pharmacy, paint industry, dentistry, and hair-styling products [1]. Due to elevated volumes of production and consumption, the synthetic water-soluble polymers are constantly discharged into the aquatic environment. Therefore, they may have harmful effects on the wildlife and the human health as they are not amenable to biodegradation [2,3,4]. Also, due to their water solubility that makes them invisible, less attention has been centered on the degradation of this type of polymers [5]. In the recent decades, advanced oxidation technologies (AOTs) have been found as a promising alternative to degrade compounds that are not degradable by the conventional means [6,7,8,9]. Applications of AOTs for treating wastewater containing recalcitrant and inhibitory organics have risen drastically during the past few decades [10]. Among AOTs, the photo-Fenton process has been applied for the degradation of broad range of contaminants, predominantly refractory organic pollutants [3,11,12]. In the photo-Fenton-like process, H_2O_2 in a catalytic cycle reacts with iron ions as the catalyst. This process involves the production of reactive and non-selective hydroxyl radicals and can initiate the degradation reactions by reacting with the organic molecules. In photo-Fenton-like process, a powerful, non-selective source of oxidation ($^{\bullet}OH$) is generated from H_2O_2 in the presence of Fe^{3+} ions according to the following simplified reactions [3,13,14]:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \quad (1)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad (2)$$

$$Fe^{3+} + H_2O \xrightarrow{hv} Fe^{2+} + {}^{\bullet}OH + H^+ \quad (3)$$

$$H_2O_2 \xrightarrow{hv} 2{}^{\bullet}OH \quad (4)$$

The free radical species mediate fast degradation of target organic compounds [15,16]. Photo-Fenton processes have been rarely studied for degradation of high molecular weight compounds. On the other hand, the photo-Fenton-like process likewise other AOTs is a multifactor system that different factors such as the initial concentration of target compounds, the initial dosage of oxidants, pH and other operating conditions have effect on the process efficiency [17,18]. The optimization of the factors by classical methods needs extra time, materials, and large number of

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experiments. Also, classical methods fail to consider the combined effects of all the parameters involved. A statistical experimental design could overcome the limitations of conventional methods and consequently optimize the affecting factors [5,19]. Response surface methodology (RSM) as a reliable statistical tool in multivariate system fits the studied experimental domain in the theoretical design through a response function. In this study, the experimental design for the PAA photodegradation by photo-Fenton-like process is investigated in a batch recirculation system. The effects of the initial concentration of PAA, the initial concentration of Fe^{3+}, and the H_2O_2 dosage on the percent TOC removal were studied using a three-factor three-level Box-Behnken experimental design combined with RSM and quadratic programming. The optimal operating conditions to achieve maximum TOC removal were obtained and validated experimentally.

2. Materials and methods

2.1. Materials

PAA (35% wt) with an average molecular weight of 13×10^4 g mol^{-1}, H_2O_2 (30% wt), and $FeCl_3.6H_2O$ were purchased from Sigma Aldrich and were used as received. NaOH (99%) and H_2SO_4 (99%) used to adjust pH were supplied by EMD Chemicals and used as received.

2.2. Experimental setup and procedure

A laboratory-scale batch recirculation photoreactor providing uniform light distribution was used in this study. The system represents the simplest mathematical model for both mass and radiation balances. A small annular photoreactor (model SL-LAB from Siemens Inc.) with the annular space of 1.33 cm was used as part of a recycle system including a centrifugal magnetic pump (Model RK-72012-10 from Cole–Parmer), an all glass heat exchanger (for controlling the temperature), and a large volume tank with provisions for sampling and temperature measurements as presented in Fig. 1. The system was also equipped with a by-pass valve to control the flow rate and to provide a relief to the pump pressure. The lamp (model LP4130 from Siemens Inc.) sealed with the quartz sleeve was positioned at the centerline of the photoreactor with stainless steel housing. The pH was adjusted by adding few drops of 1N NaOH or H_2SO_4 as needed and it was measured by a portable pH meter (230A plus, Thermo Orion).

The following protocol was pursued in conducting each experiment. The PAA solution was diluted to achieve the desired PAA concentration in a 4-L solution. The lamp was turned on for 30 min before the beginning of each experiment to stabilize the light intensity. The solution was fed to the system and the temperature was kept constant at 25°C during each experiment by means of a heat exchanger. The samples were taken from the collection tank at different time intervals during a total reaction time of 120 min. The TOC concentration of the samples was monitored by a TOC analyzer (Apollo 9000, Teledyne Tekmar, USA).

3. Experimental design

The operating conditions to maximize the TOC removal in the photo-Fenton-like process was obtained using a three-factor three-level Box-Behnken experimental design combined with response surface modeling. The Box-Behnken design, a modified central composite design, is known as an independent, rotatable quadratic design having no fractional factorial points [9,20]. In this type of design, the variable combinations are at the center and the midpoints of the edges of the variable space [21]. Also, compared to other types of experimental design such as full factorial design, the Box-Behnken experimental design needs fewer runs [22]. In this study, the effects of three independent variables on the TOC removal were investigated. The independent variables were the initial concentration of PAA (A), the initial concentration of Fe^{3+} dosage (B), and the initial concentration of H_2O_2 (C) that were coded as −1, 0, and +1 as presented in Table 1. The total number of experiments (N) was 15 which could be calculated as follows:

$$N = k^2 + k + cp \quad (5)$$

where k is the number of factors and cp is the number of replicates in the central point. The critical experimental levels were chosen based on the preliminary experimental results and the literature values. Therefore, the data from Box-Behnken design was subjected to the following quadratic model which is a second order equation that correlates the dependent and independent variables:

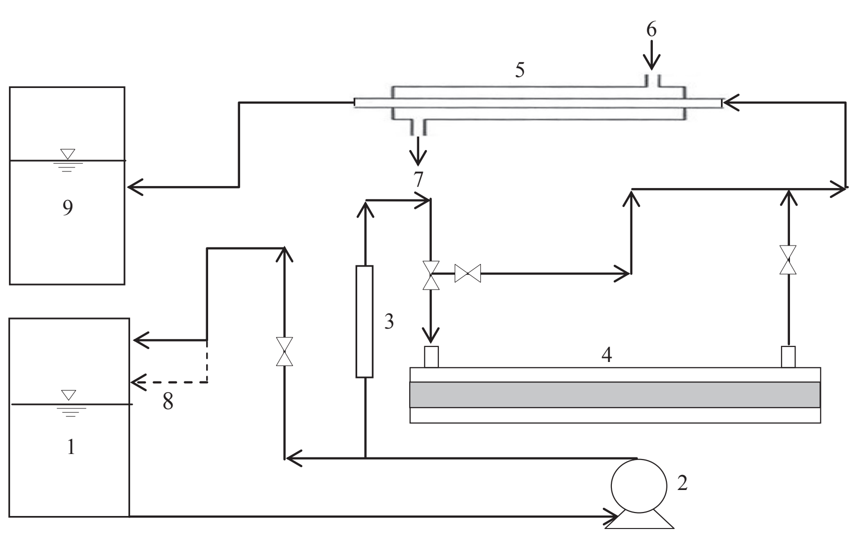

Fig. 1. Schematic diagram of the experimental setup batch with recirculation system: (1) Reservoir tank, (2) Pump, (3) Flow meter, (4) UV-C photoreactor, (5) Heat exchanger, (6) Cooling water in, (7) Water out, (8) Bypass, and (9) Collection tank.