Sustainable Environment Research xxx (2017) 1–7

Contents lists available at ScienceDirect

Sustainable Environment Research

journal homepage: www.journals.elsevier.com/sustainable-environment-research/

Original Research Article

Removal of anionic surfactant sodium dodecyl sulfate from aqueous solutions by $O_3/UV/H_2O_2$ advanced oxidation process: Process optimization with response surface methodology approach

Ayla Arslan [a,*], Eylem Topkaya [a], Deniz Bingöl [b], Sevil Veli [a]

[a] Department of Environmental Engineering, Kocaeli University, Kocaeli 41380, Turkey
[b] Department of Chemistry, Kocaeli University, Kocaeli 41380, Turkey

ARTICLE INFO

Article history:
Received 6 June 2017
Received in revised form
25 September 2017
Accepted 16 November 2017
Available online xxx

Keywords:
Advanced oxidation
Anionic surfactant
Central composite design
Ozone
Response surface methodology
Sodium dodecyl sulfate

ABSTRACT

This study investigates the removal of sodium dodecyl sulfate (SDS) by $O_3/UV/H_2O_2$ process. Response surface methodology based on central composite design was used to assess the effects of process parameters including initial pH, H_2O_2 concentration, ozone dosage and reaction time on SDS removal. Analysis of variance showed that all parameters had significant effects on SDS removal. SDS removal increased significantly with increasing pH, ozone dosage and reaction time. Quadratic model was used for the response variable, i.e., SDS removal, and the predicted removal was 96%. Optimum conditions were obtained based on the performance of $O_3/UV/H_2O_2$ process in reaction time of 55 min, initial pH of 7.0, 10 mM H_2O_2 concentration and 10 mg L^{-1} ozone dosage. The model predictions were in an agreement with the experimental data with a deviation less than 2%.

1. Introduction

Surfactants play active role in personal care hygiene products and household cleaning [1]. According to the chemical structure, surfactants are classified as anionic, cationic, amphoteric (zwitterionic) and nonionic surfactants [2]. Surfactants are organic polar compounds comprising at least one hydrophobic and one hydrophilic group of molecules [1]. Surfactants are widely used in almost every industry [2]. Sodium dodecyl sulfate (SDS) is an anionic surfactant and used in household detergents, in shampoos and in toothpastes [3]. Surfactants are among widespread xenobiotics that may enter waste streams and the aquatic environment. They are responsible for the foams in rivers and treatment plants and they decrease water quality. Therefore, surfactants are harmful to human beings and ecosystems [4]. Conventional treatment methods are insufficient for the treatment of wastewater containing high concentrations of surfactants. SDS removal from wastewater by adsorption has been previously reported [5–8]. Various forms of Advanced Oxidation Processes (AOPs) have been investigated for treating wastewaters containing surfactants. These include the use of peroxi-electrocoagulation [9], solar driven Fenton-like oxidation [10], and photocatalytic Fenton oxidation [11].

AOPs provide the almost complete mineralization of pollutants to inorganic compounds, CO_2 and H_2O [12]. AOPs including ozone-based homogeneous processes, such as O_3, O_3/UV and $O_3/UV/H_2O_2$ are used as viable alternatives. Ozonation has emerged as a treatment technology for the removal of contaminants in water through direct ozone reactions and the indirect, free radical (i.e. hydroxyl radical (HO•)) initiated oxidation reactions [13].

Zangeneh et al. [14] studied the performance of different AOPs (UV/H_2O_2, UV/O_3, H_2O_2/O_3 and $UV/H_2O_2/O_3$) treating linear alkyl benzene (LAB) production plant's wastewater. In this study, maximum reduction in total Chemical Oxygen Demand was 58% for $UV/H_2O_2/O_3$, 53% for H_2O_2/O_3, 51% for UV/O_3 and 49% for UV/H_2O_2 processes. The mineralization of the LAB in neutral pH is favored under the acidic and basic pH conditions. Ikehata and El-Din [4] reviewed the degradation of recalcitrant surfactants in wastewater by ozonation and AOP. They emphasized that AOPs with various combinations of ozone, hydrogen peroxide, UV light and iron salts were effective in degrading recalcitrant surfactants.

* Corresponding author.
E-mail address: ataberk@kocaeli.edu.tr (A. Arslan).

Peer review under responsibility of Chinese Institute of Environmental Engineering.

https://doi.org/10.1016/j.serj.2017.11.002

Beltrán et al. [15] studied Sodium Dodecylbenzenesulfonate (NaDBS) removal from aqueous solution and domestic wastewater by ozonation. They showed that pH and organic load of the aqueous solution are important parameters that influence NaDBS removal by ozonation.

Generally, the main purpose of the optimization is to determine the levels of independent variables resulting in a maximum (or minimum) response without spending too much time with many experiments on a particular area of interest. These processes can be accomplished using response surface methodology (RSM) approach, which includes central composite design (CCD), Doehlert matrix, and Box–Behnken design. Among them, the CCD is a standard RSM design widely used to fit a second-order model [16].

The aim of this study was to examine the treatability of SDS by ozone-based process by varying four influential variables (initial pH, H_2O_2 concentration, ozone dosage and reaction time). The mathematical model was developed to determine the effect of O_3/UV/H_2O_2 process parameters on SDS removal using RSM based on CCD.

2. Materials and methods

2.1. Materials

Sodium dodecyl sulfate ($C_{12}H_{25}NaO_4S$; 288.4 g mol^{-1}) was purchased from Merck. SDS aqueous solutions were prepared with pure water. The molecular structure of the SDS is given in Fig. 1 [17]. H_2O_2 (Merck, 30% w/w) was used as an oxidant. Initial pH values of solution were adjusted by 0.5 N NaOH and 0.5 N H_2SO_4.

2.2. Ozonation system

The experimental set-up consisted of ozone generator, ozone monitoring device and reaction tank, as detailed in our previous study [18] (Fig. 2). Ozone was generated from dried air in a Teknozone TKZ-25G model ozone generator. Ozone was injected into the solution throughout a diffuser placed at the bottom of the cylindrical reactor. The ozone monitoring device (TKZ-PPM51 model) is designed to measure dissolved ozone gas in water and work at on & off mode at the recommended set value. Two low-pressure mercury lamps (2 × 2.2 W) were placed in the reaction tank for UV light source. The ozonation experiments were conducted in a batch reactor with a volume of 2 L. The effluent ozone was absorbed by potassium iodide solution.

2.3. Analysis

The synthetic solution was prepared by selecting an appropriate concentration from our previously studies [19]. 1 L solution of 2.5 mg L^{-1} SDS concentration was added into the reactor. The O_3/UV/H_2O_2 experiments were performed with the addition of H_2O_2 prior to ozonation. Liquid samples were periodically taken from the reactor to determine the concentration of the detergent.

Fig. 1. Molecular structures of SDS [17].

Concentration of detergent was measured by using the methylene blue active substance analysis, according to the Standard Methods [20].

The removal efficiencies were estimated from detergent concentrations determined before and after ozonation experiments. In the experimental study, a spectrophotometer (HACH-LANGE Dr 5000) and a digital pH-meter (HACH, HQd) were also used.

2.4. Experimental design

Experimental designs are generally economical, that is they offer a large amount of useful information from a small number of experiments. RSM, a technique used to design the experiment, helps researchers to develop models, to evaluate the effects of various factors, and to reduce the number of experiments, as well as to obtain optimal conditions for the desired responses. CCD, a standard RSM design has widely been used for fitting a second-order model and it requires a minimum number of experiments to be performed. Response surface and/or contour plots are used to determine optimum conditions and to graphically illustrate the relation between different experimental variables and the responses. The model is represented by Eq. (1)

$$y_{1i} = b_0 + b_1X_{1i} + b_2X_{2i} + b_{11}X_{1i}^2 + b_{22}X_{2i}^2 + b_{12}X_{1i}X_{2i} + e_{1i} \quad (1)$$

where i is the number of factors considered; X_{1i} and X_{2i} is the input variable that has an influence on the response y_{1i}; b_0, b_1 to b_2, b_{11} to b_{22}, b_{12} are intercept, linear, quadratic, and interaction constant coefficients, respectively, and e_{1i} is a random error. To evaluation of fitted mathematical model it is used the analysis of variance (ANOVA) in the confidence interval of 95%. The quality of the fit polynomial model is expressed by the coefficient of determination, R^2. Model terms are assessed with P-value (probability) at 95% confidence level [16].

In this study, CCD with four-factors at five levels was applied using a statistical program package Minitab-16 for regression analysis of data obtained and to estimate coefficients of the regression equation. Table 1 shows the selected ranges for coded and actual values of the selected process independent variables for response variable, SDS removal (%).

3. Results and discussion

The CCD and RSM were used for designing experiments, modeling and determining optimum conditions. A mathematical model was derived to find the estimated optimal system response. Table 2 shows the arrangements of independent and dependent variables used in the statistical analysis of the present study. The SDS removal (%) was determined as the average of two parallel experiments. In order to minimize systematic errors, the experiments were performed in a random order.

The results obtained from CCD were evaluated by ANOVA. The ANOVA was carried out at 95% confidence level to check the fitting of the experimental values to the predicted ones. ANOVA is a statistical technique, and 'P' values are used to indicate whether the variables and their interactions play a statistically significant role on response. If the P values are less than 0.05, these effects are considered significant. In this study, the statistical insignificant ones ($P > 0.05$) were removed from the model, and factors and the related interactions found statistically significant were included in the model. Therefore, a new ANOVA was then performed for the reduced model considering the statistically significant effects in the confidence interval of 95% (Tables 3 and 4). In both tables, all P-

Please cite this article in press as: Arslan A, et al., Removal of anionic surfactant sodium dodecyl sulfate from aqueous solutions by O_3/UV/H_2O_2 advanced oxidation process: Process optimization with response surface methodology approach, Sustainable Environment Research (2017), https://doi.org/10.1016/j.serj.2017.11.002