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Application of the central composite design and response surface methodology to the advanced treatment of olive oil processing wastewater using Fenton's peroxidation

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Abstract

The central composite design (CCD) technique was used to study the effect of the Fenton's peroxidation on the removal of organic pollutants from olive oil mill wastewater (OMW). The ratio of hydrogen peroxide-to-Fe(II) (x_1) was between 1.67 and 8.33. Fe(II) concentration was constant at 0.03 M while the H_2O_2 concentration was set at three levels: 0.05, 0.15 and 0.25 M. Based on the molarity ratio, the selected ratio were in the low range of Fe(II)-to-H_2O_2 ratio ($\ll$1). While based on the wt/wt ratio, the tested Fe(II)-to-H_2O_2 ratios were in the range of $\leq$1:5. pH (x_2) was between 3 and 5. The concentration of OMW (x_3) was varied between 40 and 100%. The influence of these three independent variables on the four dependent variables, i.e. COD, total phenolics (TP), color and aromatocity removal was evaluated using a second-order polynomial multiple regression model. Analysis of variance (ANOVA) showed a high coefficient of determination (R^2) value of 0.902–0.998, thus ensuring a satisfactory adjustment of the second-order regression model with the experimental data. H_2O_2-to-Fe(II) ratio had significant effect on all the four dependent variables. The positive sign for the regression coefficient of this regressor variable indicated that the level of the pollutant removal increased with the increased levels of factor x_1 from 1.67 to 8.33 and this effect was the most pronounced for TP removal. pH had also significant effect on the pollutant removal and the effect was the most noticeable for TP reduction. The negative coefficient of this variable (pH) indicated that level of the pollutant removal decreased as the pH increased from 3 to 5. The negative coefficient of the interaction between variable x_1 and x_2 indicated that a simultaneous increase in H_2O_2-to-Fe(II) ratio with decrease in the pH of the reaction led to an increase in the COD, TP and color removal. Quadratic models were predicted for the response variable, i.e. pollutant removal, and the maximum model-predicted removals were 56, 100, 33 and 32% for COD, TP, color and aromatocity, respectively. Optimum conditions for this wastewater treatment was obtained based on the performance of the Fenton's peroxidation in the experiment where the H_2O_2-to-Fe(II) ratio was at its high level (8.33) and the pH and OMW concentration were 4 and 70%, respectively.

Keywords: Advanced oxidation process; Central composite design; Empirical modeling; Fenton's peroxidation; Olive oil mill wastewater; Response surface methodology

1. Introduction

Small olive oil mills process olives for the extraction of oil while large volumes of liquid wastewater are produced (olive oil mill wastewater, OMW 97 l/100 kg olives, when the conventional three-phase decanter is used) [1]. Phenolics present in OMW at high concentrations (1–10 g/l) are considered as the major recalcitrant compounds which possessing antimicrobial properties, and are difficult to

Abbreviations: CCD, central composite design; OMW, olive oil mill wastewater; COD, chemical oxygen demand; TP, total phenolics; ANOVA, analysis of variance; BOD, biological oxygen demand; AOP, advanced oxidation process; AST, advanced sludge treatment; RSM, response surface methodology; $OH^{\bullet}$, hydroxyl radical; TSS, total suspended solids; TKN, total Kjeldahl nitrogen; CV, coefficient of variance; PRESS, predicted sum of squares

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biologically degrade. Conventional biological processes for the purification of OMW are therefore inefficient. The OMW hence, constitutes a major environmental problem because of its high organic load. The chemical oxygen demand (COD) of this wastewater is in the range of 80–200 g/l while the biological oxygen demand (BOD) for OMW is in the range of 89–100 g/l [2]. These values are about 200–400 times higher than those of a typical municipal sewage [3]. Stringent environmental regulations impose increasing efforts toward the development of new technologies and methods for the reduction of the organics in wastewaters, such as OMW. Advanced oxidation processes (AOP) that utilize H_2O_2, O_3, or O_2 as the oxidant, are very promising techniques for the remediation of contaminated ground, surface, and wastewaters having non-biodegradable organic pollutants [4,5]. The AOPs involve the generation of the hydroxyl radical ($OH^{\bullet}$) that is a reactive intermediate and has a high oxidation potential [6]. One available technique in the area of AOPs is based on the Fenton's peroxidation which is considered as the iron-catalyzed H_2O_2 decomposition reaction. The Fenton's reagent is a mixture of ferrous salt and hydrogen peroxide.

Organic substances are oxidatively and non-selectively degraded by the generated hydroxyl radicals and although the Fenton's peroxidation mechanism of organics present in the wastewater is complex but the process has been used successfully to treat wide range of industrial wastewaters, including OMW and wastewater sludge (biosolids) [7–10]. Technical points and economic considerations of using advanced sludge treatment (AST) methods have been discussed thoroughly (biosolids) [10]. The Fenton's peroxidation mechanism of an organic compound is likely to occur in the several steps: generation of $OH^{\bullet}$ radical and its oxidative reaction with the organic compound, the direct action of H_2O_2 toward the pollutant, $OH^{\bullet}$ scavenging due to ferrous ions and H_2O_2 and reactions of Fe(III) with H_2O_2 with regenerations of ferrous ions and formation of hydroperoxyl radical ($HO_2^{\cdot}$), and reduction of Fe(III) to Fe(II) by $HO_2^{\cdot}$ [11].

Results reported by Beltran-Heredia et al. [8] showed that treating OMW by Fenton's peroxidation decreases COD by 33% while total phenolics (TP) were reduced by 93%. The H_2O_2 and ferrous ions concentration in this study were 0.78 and 0.055 M, respectively [8]. Similar findings were reported by Rivas et al. [12]. On the other hand, concentrations of ferrous ion and H_2O_2 used in the degradation of atrazine and metolachlor (two widely used herbicides) in the study conducted by Pratap and Lemley [13] were 0.0036 and 0.025 M, respectively. As pointed out by [7], the relationships between ferric, ferrous and H_2O_2 concentrations and the quantity of organic and inorganic compounds in the Fenton' peroxidation, can be quantified and this stoichiometric relationship has been used to classify the Fenton system. In this reaction mixture, at ratio of Fe(II)-to-H_2O_2 ≥ 2, when the organic compounds are absent, the reaction of $OH^{\bullet}$ is mainly with Fe(II), the rate of this reaction being ten times faster than that between $OH^{\bullet}$ and H_2O_2 [7]. The presence of organic compounds only affects the behavior of the ferrous ion in the solution and not H_2O_2, since the organic pollutant competes with Fe(II) for hydroxyl radical [7].

Conventionally, wastewater treatments, like many other industrial processes are optimized by using "one at a time" variation of treatment variables. Moreover, this method assumes that various treatment parameters do not interact and that the response variable is only function of the single varied parameter. However, the response obtained from a waste treatment method for example, results from the interactive influences of the different variables. When a combination of several independent variables and their interactions affect desired responses, response surface methodology (RSM) is an effective tool for optimizing the process [14]. RSM uses an experimental design such as the central composite design (CCD) to fit a model by least squares technique [15,16]. Adequacy of the proposed model is then revealed using the diagnostic checking tests provided by analysis of variance (ANOVA). The response surface plots can be employed to study the surfaces and locate the optimum. In several industrial processes, RSM is almost routinely used to evaluate the results and efficiency of the operations [17–21].

In the present work, a CCD in the form of a 2^3 full factorial design was used to develop mathematical equations, in terms of the pollutant removal, providing quantitative evaluation of the Fenton process used to oxidatively treat OMW. Hydrogen peroxide-to-Fe(II) ratio, pH and concentration of OMW (a real industrial wastewater) as the key parameters affecting the decomposition performance of the Fenton's reagent were studied in this evaluation.

2. Experimental

2.1. Olive oil mill wastewater and Fenton's peroxidation method

The OMW used in this study was obtained from an olive oil mill in the Roodbar region, home of the olive growing and processing sector, in the northern part of Iran. The three-phase centrifugation method has been used for the oil extraction. Fresh OMW was transported to our laboratory under refrigeration within 15 h of its production, and in order to conduct the tests with the same wastewater, appropriate amounts of OMW were distributed in 250 ml plastic bottles and stored at $-20\,^{\circ}C$ until use. At the time of use, the OMW sample was thawed in a refrigerator and filtered using Whatman filterpaper #2. The OMW at different initial concentrations, i.e. different COD concentrations were used. Fenton's peroxidation experiments were carried out batchwise in a 500 ml Erlenmeyer flask with continuous stirring (130 rpm) in a shaker incubator at $25\,^{\circ}C$. Total volume of the reaction mixture was 400 ml. The appropriate volume of the OMW was first added. Dilution of OMW when needed, was done using distilled water and in a way that sequential addition of the reagents, at the end could provide the desired