Application of Box–Wilson experimental design method for the photodegradation of bakery's yeast industry with UV/H_2O_2 and UV/H_2O_2/Fe(II) process

Ebru Ç. Çatalkaya *, Füsun Şengül

Department of Environmental Engineering, Dokuz Eylül University, Kaynaklar Campus, Buca-Izmir, Turkey

Abstract

Decolorization and mineralization of bakery's yeast industry effluent by photochemical advanced oxidation processes (AOPs) utilizing UV with hydrogen peroxide and Photo-Fenton, were investigated in a laboratory scale photo-reactor equipped with a 16 W low-pressure mercury vapor lamp. The Box–Wilson experimental design method was employed to evaluate the effects of major process variables (e.g. pH, oxidant dose, and irradiation time) on the decolorization efficiency. Response function coefficients were determined by regression analysis of the experimental data and prediction results agreed with the experimental results. The optimum hydrogen peroxide concentration and irradiation time were found to be 5 mM and 50 min at pH 3, respectively, for UV/H_2O_2 process. In the Photo-Fenton process application, maximum decolorization efficiency (96.4%) was obtained at the optimum reaction conditions that were 100 mM H_2O_2 and 1 mM Fe(II) doses at pH 3, and 10 min of irradiation time.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Bakery's yeast industry; Box–Wilson design; Decolorization; Photo-Fenton process; UV/H_2O_2 process

1. Introduction

Bakery's yeast, a fermented product used in the preparation of bread, is manufactured by the aerobic fermentation of selected strains of *Saccharomyces cerevisiae*. Bakery's yeast products are made from strains of this yeast selected for their special qualities relating to the needs of the baking industry. The production of bakery's yeast using sugar beet molasses, which are markedly colored by high-molecular weighted melanoidin-type dark brown colorants, includes operations and processes, such as molasses preparation, fermentation, separation and drying of the yeast [1].

The effluent of bakery's yeast industry is a major source of pollution as it has a high biological oxygen demand. In addition to high BOD, an effluent from the bakery's yeast industry contains high chemical oxygen demand (COD), total Kjeldahl nitrogen (TKN), dark color, and non-biodegradable organic pollutants. There are basically two types of wastewater; one is high strength process wastewater that originates from yeast separators and processes, such as centrifuges and rotary vacuum filters, and the other one is low and medium strength process wastewater that originates from floor washing and equipment cleaning. High strength process wastewater that is high in COD and color can be treated anaerobically. Arhan et al. [2] have stated that the high strength wastewater following by anaerobic treatment stage was first combined with low strength wastewater and then sent to the aerobic treatment stage in the plant considered in their work [2].

Biological treatment of wastewater will eliminate important components of the organics in the wastewater. However, the biochemical decomposition by conventional treatment method may not be enough to complete color reduction. Although there is no effluent limitation set for color in the

* Corresponding author. Tel.: +90 232 412 7135;
fax: +90 232 4531008/1135.
E-mail address: ebru.cokay@deu.edu.tr (E.Ç. Çatalkaya).

regulations, it can be necessary to use more effective process for the reduction of color. Otherwise, ecosystems of streams can be seriously affected. In the past, refractory organics, which result color in wastewater, have been treated by adsorption onto activated carbon or by chemical coagulation [3,4]. However, these traditional methods mainly transfer the contaminants from wastewater to solid wastes.

In recent years, advanced oxidation processes (AOPs) have emerged as potentially powerful methods that are capable of transforming the pollutants into harmless substances [5] and that almost all rely on the generation of very reactive free radicals, such as the hydroxyl radical, $OH^{\bullet}$ (redox potential = 2.8 V) [6]. When generated, these radicals react rapidly and usually indiscriminately with most organic compounds, either by addition to a double bond or by abstraction of a hydrogen atom from aliphatic organic molecules [7]. The resulting organic radicals then react with oxygen to initiate a series of degradative oxidation reactions that ultimately lead to mineralization products, such as CO_2 and H_2O [8]. Therefore, advanced oxidation is a potential alternative to decolorize and to reduce recalcitrant organic compounds from polluted water.

Although AOPs have these advantages, one common problem in all AOPs is the high electrical energy demand for UV lamps, which causes high operational costs. Minimization of the required irradiation time, thus, the energy consumption by optimization of the other reaction conditions, such as operational pH, chemical types, chemical concentrations, and pollutant/oxidant ratio, therefore, is very important. For this aim, the Box–Wilson experimental design was used in order to find optimum reaction conditions and to investigate the effects of important process variables on color removal performance in this work.

The Box–Wilson experimental design is a response surface methodology used for evaluation of a dependent variable as functions of independent variables [9,10]. The objectives of this study were therefore to investigate the effectiveness of advanced oxidation by applying UV with hydrogen peroxide and Photo-Fenton processes for decolorization, and the residual total organic carbon (TOC) removal of biologically pretreated bakery's yeast industry (BYI) effluents using Box–Wilson experimental design method. Fe(II) and H_2O_2 doses, pH and reaction time were considered as independent variables while color removal efficiency was considered as dependent variable in the Box–Wilson statistical design method. In addition to color removal efficiency, TOC has also been determined in order to evaluate the mineralization rate, as an important indicator of the treatment effectiveness.

2. Experimental

2.1. Reagents

Characterization of bakery's yeast wastewater used in the study is listed in Table 1.

Table 1
Characterization of effluent of bakery's yeast industry used

Parameter	Unit	Value
pH	–	7.85
COD	$mg\,L^{-1}$	800
TOC	$mg\,L^{-1}$	200
Color (Abs)	m^{-1}	1.900

Ferrous ($FeSO_4 \cdot 7H_2O$) used as source of Fe(II), was analytical grade and purchased from Merck. Hydrogen peroxide solution (35% (w/w)) in stable form, H_2SO_4 (98–99%) and NaOH were all provided from Merck. An amount of $1000\,mg\,L^{-1}$ Fe(II) stock solution was prepared for further dilution to obtain a solution of desired concentrations. Fe(II) stock solution was stored at dark place to prevent oxidation of Fe(II). The pH of aqueous solutions was adjusted using either sodium hydroxide or sulfuric acid where needed. In order to prevent further oxidation of organics, excess H_2O_2 should be removed. For this aim, MnO_2 was added to collected aqueous samples. Distilled water was used in cleaning and experimentation.

2.2. Photo-reactor

All experiments were performed in a well stirred, batch, cylindrical photo-reactor with a total volume of 2.2 L. The reactor is made of glass and does not contain any metal parts. The outside of the reactor was covered with an aluminum sheet. The upper part of the reactor has inlets for feeding reactants, and ports for measuring temperature and withdrawing samples. The reactor was open to air and a teflon-coated magnetic stirring bar was placed at the bottom of the reactor to provide a proper mixing. The UV irradiation source was a 16 W low-pressure mercury vapor lamp (maximum emission at 254 nm) encased in a quartz tube. Since the light source produces heat, the lamp was surrounded with a water-cooling jacket to conduct experiments at room or controlled temperatures; the lamp was axially centered and immersed in the reactor. Fig. 1 shows the schematic diagram of the laboratory-scale photochemical installation used in the study.

2.3. Experimental procedure and analytical methods

For a standard reaction run, 2 L of the wastewater sample was used. Required amounts of sulfuric acid or sodium hydroxide solution were added to the sample in order to obtain the desired pH in the solution. Following the pH adjustment of bakery's yeast effluent, it was poured into the reactor. For runs using UV/H_2O_2 system at different pH values, different amounts of hydrogen peroxide were injected into the reactor before the initiating of each run. For runs using the Photo-Fenton process, the pH value of the solution was first adjusted to 3 by the addition of H_2SO_4 solution, and then a given weight of iron salt was added. The iron salt and wastewater were mixed very well before the addition of a given volume of hydrogen peroxide. The time at which the
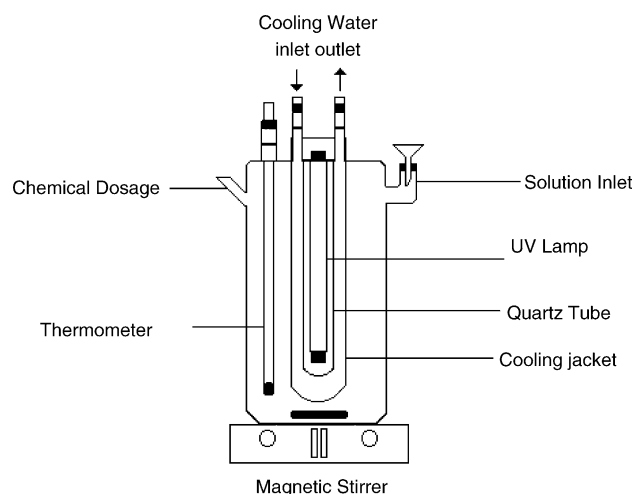
Fig. 1. Shematic diagram of the laboratary scale photochemical installation.

ultraviolet lamp was turned on was considered as time zero or the beginning of the experiment, which was taking place simultaneously with the addition of hydrogen peroxide. The temperature of the solution was kept constant at $25 \pm 2\,°C$ throughout all experiments.

Each run in this study was performed two times and each sample was analyzed twice to confirm the results. In the case of an error higher than 5%, a third run was also conducted to fit at least two values. The average values derived from the repeated experiments were used in this study, the results of which were within 5% of each other. Samples were taken at predetermined reaction times to measure absorbance, TOC, and pH. The samples were analyzed immediately to avoid further reaction. Color measurements were executed at 366 nm. Absorbance of effluent was evaluated for calculating color removal efficiency. A spectrophotometer of Novaspec II (Pharmacia Biotech.) was used to measure the absorbance. TOC measurements were carried out using a DOHRMAN

DC 190 model TOC analyzer. pH was measured by using a NEL pH 890 pH meter.

2.4. Box–Wilson experimental design

The Box–Wilson statistical experimental design was employed to determine the effects of operating variables on color removal efficiency and to find the combination of variables resulting in maximum color removal efficiency. The Box–Wilson design is a response surface methodology, which is an empirical modeling technique, devoted to the evaluation of the relationship of a set of controlled experimental factors and observed results. Basically this optimization process involves three major steps: performing the statistically designed experiments, estimating the coefficients in a mathematical model, and predicting the response and checking the adequacy of the model.

For UV/H_2O_2 process, the significant variables like pH, H_2O_2 concentration, and reaction time were chosen as the independent variables and designated as X_1–X_3, respectively. pH (X_1) varied between 3 and 11, while H_2O_2 concentration (X_2) was ranged from 5 to 100 mM, and the reaction time (X_3) was ranged from 10 to 150 min.

For Photo-Fenton process, the significant variables like ferrous concentration, H_2O_2 concentration, and reaction time were chosen as the independent variables and designated as X_1–X_3, respectively. The ferrous concentration (X_1) varied between 1 and 5 mM, while H_2O_2 concentration (X_2) varied between 5 and 100 mM. The reaction time (X_3) was ranged from 10 to 150 min.

The experimental conditions determined by the Box–Wilson statistical design method for the both processes are presented in Table 2. The experiments consist of six axial (A), eight factorial (F), and central points (C). The central point was repeated four times resulting in 18 experiments in total. Computation was carried out using multiple regression analysis that uses the least squares method. The following response function was utilized in the correlating of the color removal

Table 2
Experimental conditions according to a Box–Wilson statistical design for UV/H_2O_2 and $UV/H_2O_2/Fe(II)$ processes

Experimental no.	UV/H_2O_2			$UV/H_2O_2/Fe(II)$		
	pH	t (min)	H_2O_2 (mM)	t (min)	H_2O_2 (mM)	Fe(II) (mM)
A1	11	80	52.5	150	52.5	3
A2	3	80	52.5	10	52.5	3
A3	7	150	52.5	80	100	3
A4	7	10	52.5	80	5	3
A5	7	80	100	80	52.5	5
A6	7	80	5	80	52.5	1
F1	4.7	119.5	80	39.5	80	4.16
F2	9.3	39.5	80	119.5	80	1.84
F3	9.3	119.5	25	119.5	25	4.16
F4	9.3	39.5	25	119.5	25	1.84
F5	4.7	39.5	80	39.5	80	1.84
F6	4.7	119.5	25	39.5	25	4.16
F7	9.3	119.5	80	119.5	80	4.16
F8	4.7	39.5	25	39.5	25	1.84
C	7	80	52.5	7	80	52.5

efficiency (Y) with other independent parameters (X_1–X_3). A SCIENTIST computer program was employed for the determination of the coefficients of Eq. (1) by regression analysis of the experimental data:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3$$
$$+ b_{23}X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 \qquad (1)$$

where Y is the predicted yield, b_o the constant, b_1–b_3 the linear coefficients, b_{12}, b_{13}, and b_{23} the cross product coefficients, and b_{11}, b_{22}, and b_{33} are the quadratic coefficients.

3. Results and discussion

TOC and color removal efficiencies obtained from the experiments that consisted of six axial (*A*), eight factorial (*F*), and central points are summarized in Table 3. The observed color removal efficiencies were compared with the predicted ones obtained from the response function.

The observed color removal efficiencies varied between 6% and 41%, 20% and 82% for UV/H$_2$O$_2$ and UV/H$_2$O$_2$/Fe(II) processes, respectively. In terms of TOC, the removal efficiencies ranged from 3% to 27% for UV/H$_2$O$_2$ process, while the efficiencies ranged from 38% to 70% for UV/H$_2$O$_2$/Fe(II) process.

Experimental results were evaluated using a SCIENTIST regression analysis program to determine the coefficients of the response function (Eq. (1)). The calculated coefficients given in Table 4 were used for the calculating of predicted values of color removal efficiencies. The correlation coefficients (R^2) between the observed and predicted values were 0.980 and 0.985 for UV/H$_2$O$_2$ and UV/H$_2$O$_2$/Fe(II) processes, respectively. These results indicated excellent agreements between the observed and predicted values of color removal efficiencies. The effects of the operating variables on the color removal performance of the system were determined by the obtaining projections of the response functions on certain planes of the known parameter values.

3.1. UV/H$_2$O$_2$ process

Chemical oxidation using ultraviolet radiation in the presence of hydrogen peroxide is a very promising technique. The $^{\bullet}$OH radicals produced through UV/H$_2$O$_2$ system as shown in the reaction (i) are highly powerful oxidizing species. Hydroxyl radicals can oxidize organic compounds (RH) producing organic radicals (R$^-$), which are highly reactive and can be further oxidized:

$$H_2O_2 + h\nu \rightarrow 2^{\bullet}OH \qquad (i)$$

3.1.1. Effect of initial pH

In order to determine the effect of pH on color removal efficiency at a H$_2$O$_2$ concentration of 5 mM, some experiments

Table 4
Coefficients of the response function

Coefficients	Values	
	UV/H$_2$O$_2$	UV/H$_2$O$_2$/Fe(II)
B$_0$	0.972635	0.9
B$_1$	−0.17069	0.00075
B$_2$	−0.001486	0.0021
B$_3$	−0.00889	−0.195
B$_{12}$	0.000427	−0.00001
B$_{13}$	0.00177	0.00008
B$_{23}$	0.000006	0.0019
B$_{11}$	0.004057	−0.00001
B$_{22}$	−0.00003	−0.00005
B$_{33}$	−0.00003	0.0048

Table 3
Observed and predicted color removal efficiency with TOC removal efficiencies

No.	Observed color removal efficiency (%)		Predicted color removal efficiency (%)		TOC removal efficiency (%)	
	UV/H$_2$O$_2$	UV/H$_2$O$_2$/Fe(II)	UV/H$_2$O$_2$	UV/H$_2$O$_2$/Fe(II)	UV/H$_2$O$_2$	UV/H$_2$O$_2$/Fe(II)
A1	39	41	38.5	44.6	3	58
A2	30	52	28	52.13	11	52
A3	13	55	11.1	55.7	27	70
A4	13	41	12.5	44.1	13	47
A5	26	20	24.5	23	22	63
A6	17	82	15.8	82.8	15	47
F1	6	40	6.6	40.25	22	48
F2	35	67	34.4	66.7	4	65
F3	14	31	14	28.7	3	55
F4	7	67	8.2	63.9	22	58
F5	12	75	13.9	74.4	8	49
F6	20	32	22.5	29.5	16	55
F7	41	37	42.9	34	5	65
F8	26	66	26.8	66.2	6	38
C1	28	50	26.8	51.01	3	45
C2	26	50	26.8	51.01	3	45
C3	28	50	26.8	51.01	3	45
C4	26	50	26.8	51.01	3	45

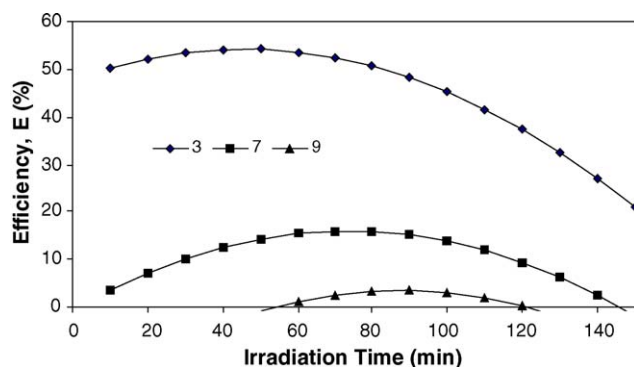Fig. 2. Variation of decolorization efficiency with time as a function of initial pH value ($H_2O_2 = 5$ mM).

Fig. 3. Variation of decolorization efficiency with time as a function of initial H_2O_2 concentration (pH 3).

were executed. Fig. 2 depicts the variation of color removal efficiency with the irradiation time at constant H_2O_2 concentration of 5 mM (optimum concentration); but, at different pH values. Maximum removal efficiency was obtained as 54.5% in 50 min at pH 3. However, high reaction times above 50 min caused lower efficiencies, probably because of intermediates production. The color removal efficiency decreased at neutral and basic pH value. Data for pH 11 were not given in Fig. 2, because, the color removal was not observed at pH 11. This observed decrease was probably due to the fast decomposition of hydroxyl radicals and hydrogen peroxide at high pH [11].

For the mineralization of bakery's yeast wastewater via ultraviolet radiation with hydrogen peroxide process, optimum pH value was found as 3.

3.1.2. Effect of initial H_2O_2 concentration

While it was possible to achieve 54.5% removal in 50 min at a hydrogen peroxide concentration of 5 mM (Fig. 2) at pH 3, color removal in 50 min at a hydrogen peroxide concentration of 100 mM at pH 3 was not observed. The decrease in removal efficiency at high oxidant concentrations is thought to be due to the side reactions taking place between the $^\bullet$OH radicals and the excess H_2O_2. In addition to this, high reaction times above 50 min caused lower efficiencies, probably because of production of intermediates. However, at pH 11, 72% color removal in 110 min at an oxidant concentration of 100 mM was also possible. This means the maximum color removal was possible at a hydrogen peroxide concentration of 100 mM after 110 min at a high pH value; but, there was still residual hydrogen peroxide in the solution. Although obtained color removal efficiency at low pH, low H_2O_2 concentration, and short reaction time is smaller than one at high pH, high H_2O_2 concentration, and long reaction time, this gives the engineer the opportunity to make a cost evaluation of the system. One can design a small volume reactor (short reaction period), which means low investment costs. In addition to this, this reactor uses fewer chemicals and decreases the operational costs. Depending on the data that can be obtained from the response function; an optimization can be made for the system to be cost-effective (Fig. 3).
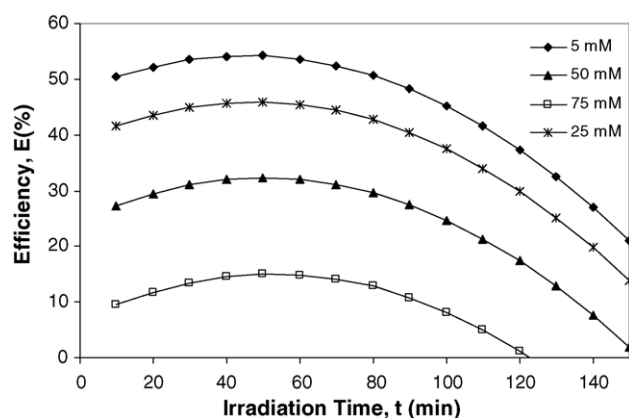
Evaluation of the results by means of mineralization efficiency, within the 150 min of irradiation at pH 3, H_2O_2 concentration was increased from 5 to 100 mM, decolorization efficiency also increased from 35.1% to 72.2%.

3.2. UV/H_2O_2/Fe(II) (Photo-Fenton process)

Recently, the Photo-Fenton reaction has been investigated as another photo-oxidative method [12]. The efficiency of the Photo-Fenton system is based on the hydroxyl radical generation by a mixture of H_2O_2 and Fe(II) ions (Fenton reaction) as shown in reaction (ii):

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

Beside this, another reaction producing additional hydroxyl radicals and regenerating Fe(II) ions takes place under the illumination (Photo-Fenton reaction) (reaction iii):

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe(II) + H^+ + {}^\bullet OH \qquad (iii)$$
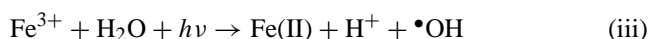
The reaction time needed for the Photo-Fenton process is extremely low and depends on the operating pH value and the concentrations of H_2O_2 and iron added.

Although 55% color removal of bakery's yeast industry was possible to achieve with UV/H_2O_2 process at low hydrogen peroxide concentrations, the time required for the complete disappearance of color was quite long (50 or 110 min according to applied pH value). Besides, the maximum mineralization efficiency was only around 35%. Therefore, in order to shorten the required irradiation time and enhance the degradation and mineralization efficiency, a number of experiments designed by Box–Wilson method, were carried out with UV/H_2O_2 process in the combination with Fe(II) catalyst, namely the Photo-Fenton process. All runs were carried out at an initial pH of 3.

3.2.1. Effect of initial Fe(II) concentration

Fig. 4 depicts the variation of color removal efficiency with irradiation time at constant H_2O_2 concentration of
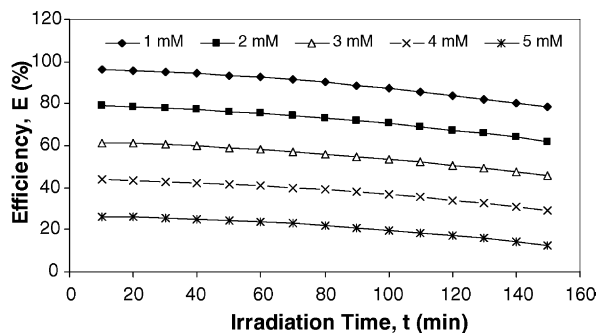
Fig. 4. Variation of decolorization efficiency with time as a function of initial Fe(II) concentration (H_2O_2 = 100 mM, pH 3).

Fig. 5. Variation of decolorization efficiency with time as a function of initial H_2O_2 concentration (Fe(II) = 1 mM, pH 3).

Fig. 6. Variation of decolorization efficiency with initial ferrous concentration for initial H_2O_2 concentration (t = 10 min, pH 3).

100 mM while, ferrous concentrations varied between 1 and 5 mM. Decolorization rate with this process was higher than UV/H_2O_2 process. Maximum color removal efficiency (96.4%) was achieved within the first 10 min of irradiation at an initial H_2O_2 concentration of 100 mM and Fe(II) concentration of 1 mM.

However, increasing the initial ferrous ion concentration enhanced the oxidation up to a certain point at which ferrous ion started to inhibit the color removal efficiency, and thus, after reaching the maximum efficiency that can be achieved at a certain Fe(II) concentration and irradiation time, the decreasing trend of predicted efficiency increased with the increasing of Fe(II) concentration. At Fe(II) concentrations higher than 1 mM, treatment efficiency was decreased as shown in Fig. 4.

Evaluation of the results by means of mineralization efficiency, within the 150 min of irradiation at a H_2O_2 concentration of 100 mM, Fe(II) concentration was increased from 1 to 5 mM, mineralization efficiency also decreased from 47.5% to 8.02%. It seemed that at a Fe(II) concentration higher than the optimum one, the initial formation rate of hydroxyl radicals originated mainly from the decomposition of H_2O_2 was so high that many of the hydroxyl radicals were consumed by the side reactions before they could be utilized effectively for the treatment of bakery's yeast wastewater.

3.2.2. Effect of initial H_2O_2 concentration

In the Photo-Fenton process, within the first 10 min of irradiation at a Fe(II) concentration of 1 mM, H_2O_2 concentration was increased from 5 to 100 mM, and decolorization efficiency also increased from 76.4% to 96.4%. Fig. 5 depicts the variations of the decolorization efficiency with the irradiation time at constant Fe(II) concentration of 1 mM; however, different H_2O_2 concentrations varied between 5 and 100 mM. The increasing trend of the predicted efficiency amplified with the increasing of H_2O_2 concentration as observed in Fig. 5.

When H_2O_2 concentration was increased from 5 to 100 mM, mineralization efficiency decreased from 64.7% to 47.5% within the 150 min of irradiation at a Fe(II) concentration of 1 mM.
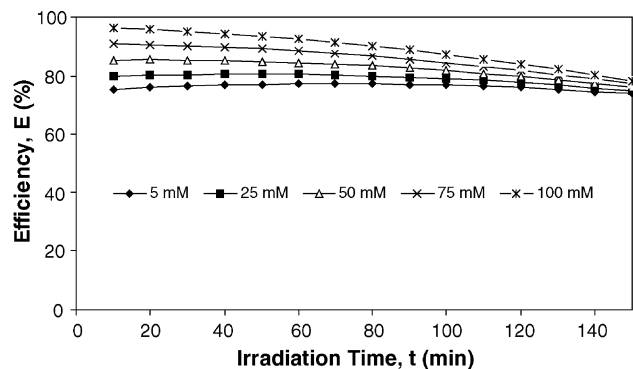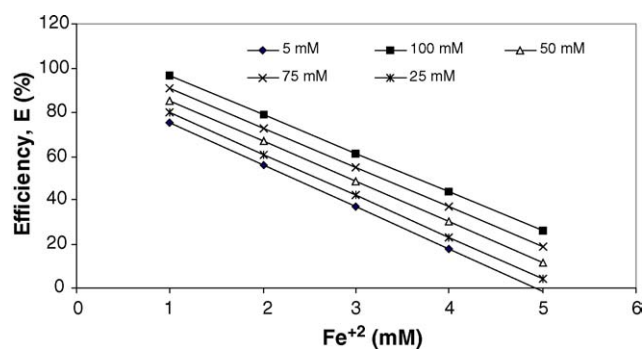
3.2.3. Effect of irradiation time

Maximum decolorization efficiencies were achieved within the first 10 min of irradiation at different H_2O_2 and Fe(II) concentrations. The fast degradation in the 10 min was the most probably due to the attack of $^\bullet$OH radicals produced via reaction (iii). However, a decrease in predicted efficiency increased with the increasing Fe(II) concentration at irradiation time of 10 min and pH 3, was observed from Fig. 6.

Fig. 6 depicts the variations of the decolorization efficiency with Fe(II) concentrations at constant irradiation time of 10 min and the H_2O_2 concentrations varied between 5 and 100 mM.

4. Conclusion

The most important factors affecting the performance of UV/H_2O_2 and UV/H_2O_2/Fe(II) processes are the hydrogen peroxide and ferrous concentration, which are added to wastewater. In order to determine the effects of oxidant dosage, reaction time, and pH in advanced oxidation processes, a Box–Wilson statistical experimental design was used by considering the pH, oxidant, reaction time as independent. The objective functions were the color and TOC removal efficiencies.

Decolorization and mineralization of bakery's yeast wastewater by the UV/H_2O_2 process and Photo-Fenton process was investigated using the Box–Wilson experimental design. Statistical analysis using response surface methodology appears to be a valuable tool for studying the optimization of the process variables of UV/H_2O_2 and Photo-Fenton processes.

In the Photo-Fenton process, 55% of color removal efficiency obtained by UV/H_2O_2 process was increased to 96.4%. In addition, irradiation time required for color removal was decreased from 50 to 10 min. Mineralization of the effluent of bakery's yeast wastewater also enhanced from 35.1% to 64.7% using Photo-Fenton process.

References

[1] T. Sahki, Y. Michiki, A. Itomine, K. Murakami, S. Fujit, Studies on the colored components in cane final molasses, in: Proceedings of the Research Society of Japan, Sugar Rafineries Technologists, vol. 40, 1992, pp. 58–63.

[2] Y. Arhan, T. Ciftci, I. Ozturk, Settling and dewatering characteristics of sludge from bakery's yeast production wastewater treatment, Water Sci. Technol. 34 (3–4) (1996) 459–467.

[3] S. Madaeni, The application of membrane technology for disinfection, Water Res. 33 (1999) 301–308.

[4] Y. Magara, S. Kunikane, M. Itoh, Advanced membrane technology for application to water treatment, Water Sci. Technol. 37 (10) (1999) 91–100.

[5] S. Esplugas, P.L. Yue, M.I. Pervez, Degradation of 4-chlorophenol by photolytic oxidation, Water Res. 28-6 (1994) 1323–1328.

[6] S.J. Masten, S.H.R. Davies, The use of ozonation to degrade organic contaminants in wastewaters, Environ. Sci. Technol. 28 (1994) 180A–185A.

[7] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of data constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals in aqueous solutions, J. Phys. Chem. Ref. Data 17 (1988) 513–586.

[8] O. Legrini, E. Oliveros, A.M. Braun, Photochemical processes for water treatment, Chem. Rev. 93 (1993) 671–698.

[9] G. Annadurai, R.Y. Sheeja, Use of Box–Behnken design of experiments for the adsorption of verolix red using polimer, Bioprocess Eng. 18 (1998) 463–466.

[10] D. Mantha, Z. Aslam Basha, T. Panda, Optimization of media composition by responce surface methodology for the production of tartaric acid by gluconobacter suboxydans, Bioprocess Eng. 19 (1998) 285–288.

[11] H. Christensen, K. Sehested, H. Corfitzen, Reactions of hydroxyl radicals with hydrogen peroxide, J. Phys. Chem. 86 (1982) 1588–1590.

[12] G. Ruppert, R. Bauer, G.J. Heisler, The Photo-Fenton reaction an effective photochemical wastewater treatment process, J. Photochem. Photobiol. A: Chem. 73 (1993) 75–78.