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Photochemical Treatment of Slaughterhouse Wastewater by UV/H_2O_2 with Effluent Recycle

A statistical experimental design approach

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***Abstract*—The UV/H_2O_2 process is optimized for slaughterhouse wastewater (SWW) treatment using a continuous-flow photoreactor with effluent recycle. A four factors at five levels central composite design (CCD) with response surface methodology (RSM) is used to maximize total organic carbon (TOC) removal and minimize H_2O_2 residual. The effects of the influent TOC concentration, H_2O_2 dosage, feed flow rate, and effluent recycle on the photolytic treatment of SWW are also investigated. Statistical modeling is used to predict the percent TOC removal and H_2O_2 residual as the response variables. Results show that recycle ratio is significant in minimizing the H_2O_2 residual and its cross-factor interactions with other variables demonstrate a significant effect on percent TOC removal. The statistical models are validated at the optimum operating conditions based on the results of the design of experiments (DOE). The model predictions are found to be in agreement with observed values, indicating that the proposed model could be used to describe the photochemical degradation of SWW using a continuous-flow UV/H_2O_2 photoreactor with effluent recycle.**

***Keywords*—slaughterhouse wastewater (SWW), advanced oxidation processes (AOPs), effluent recycle, UV/H_2O_2, central composite design (CCD), design of experiments (DOE)**

I. Introduction

Different advanced oxidation processes (AOPs) have been examined for the treatment of slaughterhouse wastewater (SWW) such as gamma radiation, ozonation, and UV/H_2O_2 [1–3]. The latter has been found to be effective for the treatment of SWW, being up to five times faster in inactivating and inhibiting pathogens as well as in degrading organic matter when compared to other technologies with removal efficiencies of up to 90% achieved by the UV/H_2O_2 process in terms of chemical oxygen demand (COD), biochemical oxygen demand (BOD), and total organic carbon (TOC) [3–9].

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AOPs are multifactor systems due to the cross-factor interaction of different parameters including concentration of organics, light intensity, oxidant dosage, output power, pH, and reaction time. The optimization of multiple factors by conventional methods requires a large number of experiments, materials, and time. Besides, factors such as recycle ratio (ratio of recycle flow rate to the main feed flow rate) and H_2O_2 residual (toxic to microorganisms in biological post-treatment), are not extensively studied. Thus, this system is required to be evaluated in terms of individual and interactive effects of the different parameters by means of the design of experiments (DOE) to identify the significant factors that influence the system [10].

Furthermore, the response surface methodology (RSM) is recognized to be statistically reliable for systematical multifactor analysis in wastewater treatment processes. RSM considers both individual and cross-factor interactions to achieve optimum responses with the minimum number of experiments [10–12].

In this study, the effects of the influent TOC concentration, feed flow rate, H_2O_2 dosage, recycle ratio, and their cross-factor interaction on the treatment of SWW using a continuous-flow UV/H_2O_2 photoreactor with effluent recycle were investigated. DOE was used to optimize the photochemical treatment of SWW by maximizing the removal of TOC and minimizing the H_2O_2 residual simultaneously. The optimal values of the model factors were obtained using a central composite design (CCD) of four factors at five levels with RSM. Statistical models were developed to predict both percent TOC removal and H_2O_2 residual as response variables and validated by an additional set of experiments at optimum conditions.

II. Materials and Methods

A. *Materials*

SWW samples were taken from selected slaughterhouses in Ontario, Canada. Distilled water (DW) was used for sample TOC level adjustment. A hydrogen peroxide solution (30% w/w) was purchased from Sigma-Aldrich and used as received.

B. *Experimental setup and procedure*

A laboratory scale photoreactor with continuous flow and effluent recycle was used. Fig. 1 depicts the schematic diagram of the UV/H_2O_2 process with effluent recycle. The

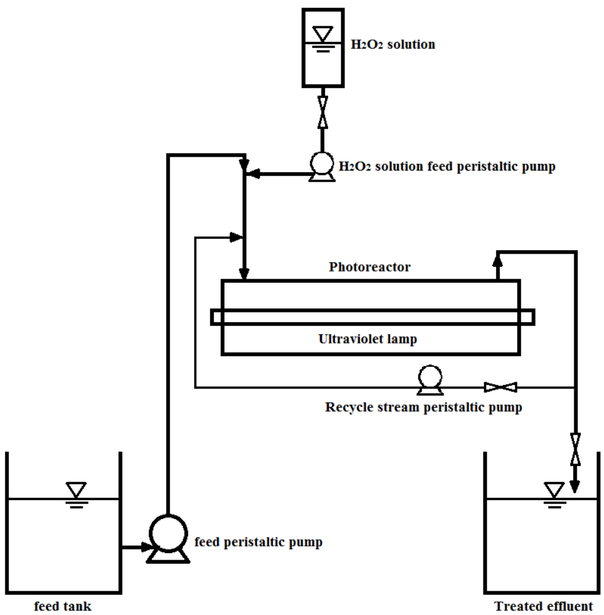

Figure 1. Schematic diagram of the laboratory-scale single lamp continuous UV/H_2O_2 photoreactor with effluent recycle.

cylindrical photoreactor (Siemens Inc., Barrier SL-1S, Markham, ON) had an operational volume of 1.35 L with an external diameter of 8 cm and a length of 34 cm. A UV-C lamp (output power of 6 W, and 254 nm wavelength) covered with a quartz sleeve (2.5 cm diameter), to prevent fouling and maintain a uniform UV radiation, was inserted into the center of the photoreactor. The following procedure was used for each experiment:

(i) The UV lamp was powered on 30 min prior starting each experiment for light intensity stabilization. (ii) SWW samples were filtered to separate the wastewater liquid portion from the solids. (iii) Filtered samples were diluted to reach the desired influent TOC concentration in a 6-L solution. (iv) The solution with the desired TOC concentration was fed to the photoreactor by a variable speed peristaltic pump to adjust and control the feed flow rate. (v) An adequate H_2O_2 dosage was calculated based on the material balance for each experiment and simultaneously fed to the system by a secondary peristaltic pump. (vi) A recycle stream was controlled by a third peristaltic pump to adjust the desired recycle ratio. (vii) Effluent samples were taken until the system reached steady state conditions at 15-minute intervals.

TOC concentration was analyzed using an automated TOC analyzer (Teledyne Tekmar, Apollo 9000, Mason, OH). The H_2O_2 residual was measured with a UV-visible spectrophotometer (Biosciences, Ultrospec 1100 pro, Amersham, UK) at 454 nm using neocuproine and copper as reagents [13]. All experiments were repeated in triplicates and the average values were reported.

C. *Experimental design*

A CCD of four factors at five levels with RSM was used to maximize percent TOC removal and minimize H_2O_2 residual in the effluent of the UV/H_2O_2 process with recycle. The independent factors used for the DOE were the influent concentration of TOC (X_1), H_2O_2 dosage (X_2), flow rate (X_3), and recycle ratio (X_4). Whereas, the percent TOC removal (Y_1) and H_2O_2 residual (Y_2) were used as the process responses. Consequently, each factor was coded at five levels from −2 to +2, as shown in Table I.

TABLE I. INDEPENDENT VARIABLES WITH CODED LEVELS OF THE FOUR-FACTOR, FIVE-LEVEL CCD.

		Coded levels				
Independent variable	**Symbol**	**-2**	**-1**	**0**	**1**	**-2**
TOC_{in} (mg/L)	X_1	10	25	40	55	70
H_2O_2 dosage (mg/L)	X_2	300	600	900	1200	1500
Flow rate (mL/min)	X_3	15	45	75	105	135
Recycle ratio	X_4	0	0.2	0.4	0.6	0.8

Equation (1) was used to predict the system responses and estimate the parametrical coefficients as a quadratic model by correlating dependent and independent variables using the least-squares regression [10–12]:

$$Y = \beta_o + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^{k} \beta_{ij} X_i X_j + c \quad (1)$$

Where, Y is the predicted response, β_o, β_i, β_{ii}, and β_{ij} are the constant, linear, quadratic, and cross-factor interaction coefficients, respectively, X_i and X_j represent the independent variables, and k and c are the number of factors and the residual term, respectively.

The statistical software Design-Expert 9.0.4.1 was used for graphical and regression analysis to estimate the coefficients of the response functions. The significance of the model equations, independent variables, and factor interactions were examined by analysis of variance (ANOVA) at confidence intervals (CI) of 95% (α = 0.05). Three-dimensional (3D) surfaces and two-dimensional (2D) contour plots were obtained while keeping another factor constant in the quadratic models.

III. RESULTS AND DISCUSSION

A. *Experimental design and statistical analysis*

Table II shows the CCD with four factors at five levels of a continuous-flow UV/H_2O_2 photoreactor with effluent recycle for SWW treatment. The relationship between the input factors and the responses shown in Equation (1) was used to predict the response functions. Thus, the second-order polynomial Equations (3) and (4) were developed for the percent TOC removal (Y_1) and H_2O_2 residual (Y_2), respectively.

$$Y_1 = 71.53 - 3.34X_1 + 1.35X_2 - 1.77X_3 - 1.12X_4 + 0.62X_1X_2 + 0.77X_1X_3 - 1.52X_1X_4 - 1.76X_2X_3 + 1.69X_2X_4 + 2.02X_3X_4 + 0.42X_1^2 - 2.11X_2^2 - 0.50X_3^2 - 1.40X_4^2 \quad (2)$$

$$Y_2 = 1.77 + 0.02X_1 + 0.12X_2 + 0.13X_3 + 0.08X_4 - 0.05X_1X_2 - 0.06X_1X_3 - 0.06X_1X_4 + 0.11X_2X_3 - 0.15X_2X_4 - 0.06X_3X_4 + 0.12X_1^2 - 0.01X_2^2 + 0.01X_3^2 + 0.08X_4^2 \quad (3)$$

TABLE II. FOUR-FACTOR, FIVE-LEVEL CCD WITH THE OBSERVED PERCENT TOC REMOVAL AND H_2O_2 RESIDUAL.

Run	Independent coded variables X_1	X_2	X_3	X_4	TOC removal (%)	H_2O_2 residual (%)
1	1	1	1	1	66.12	2.03
2	-2	0	0	0	80.43	2.25
3	-1	-1	1	-1	69.21	1.63
4	0	0	0	0	71.9	1.82
5	1	-1	1	1	60.55	1.96
6	-1	1	-1	-1	77.45	1.78
7	0	0	0	0	71.96	1.75
8	-1	1	1	1	71.94	2.35
9	0	0	0	0	72.08	1.75
10	2	0	0	0	64.39	2.35
11	-1	1	-1	1	76.17	1.87
12	0	-2	0	0	60.15	1.55
13	1	1	-1	1	66.83	1.79
14	-1	-1	1	1	71.23	2.1
15	0	0	2	0	64.7	2.17
16	1	-1	1	-1	66.79	1.78
17	1	1	1	-1	64.31	2.42
18	-1	-1	-1	1	67.09	1.97
19	0	0	0	2	63.41	2.3
20	1	-1	-1	-1	68.77	1.71
21	0	0	0	0	72.31	1.77
22	1	-1	-1	1	56.72	2.21
23	-1	-1	-1	-1	74.31	1.36
24	-1	1	1	-1	63.31	2.48
25	1	1	-1	-1	72.44	1.94
26	0	0	0	0	70.72	1.77
27	0	0	0	-2	66.89	1.99
28	0	2	0	0	64.43	2.01
29	0	0	-2	0	72.81	1.61
30	0	0	0	0	70.19	1.77

ANOVA with 95% CI was applied to evaluate the statistical significance of the percent TOC removal and the H_2O_2 residual developed quadratic models. The statistical significance of each factor coefficient was determined by the Fisher's (*F*) exact test, comparing probability (*p*) values greater than *F*. The model *F*-values of 35.34 and 102.08 were obtained for TOC removal and H_2O_2 residual, respectively, indicating *p*-values of <0.0001. Thus, implying the models are significant.

The goodness of fit of the model was validated by the determination coefficient (R^2) and the adjusted R^2 that ensures an adequate variation of the quadratic model to the experimental values. The values of R^2 and adjusted R^2 were found to be 0.97 and 0.94 for the percent TOC removal and 0.99 and 0.98 for the H_2O_2 residual, respectively. Thus, high R^2 and adjusted R^2 values represent a high model accuracy. Furthermore, the adequate precision of the percent TOC removal and H_2O_2 residual were found to be greater than four (27 and 41, respectively). Thus, the model can be used to navigate the CCD design space [10–12]. Moreover, the lack of fit was calculated to measure how well the model fits the data. The lack of fit of the percent TOC removal and the H_2O_2 residual were found to be significant with *p*-values of less than 0.10 (0.13 and 0.12, respectively), indicating that the model fits the data well.

On the other hand, the correlation between observed and predicted values is shown in Figs. 2a and 2b for percent TOC removal and H_2O_2 residual, respectively. Thus, a straight line trend indicates a good agreement between observed and predicted values.

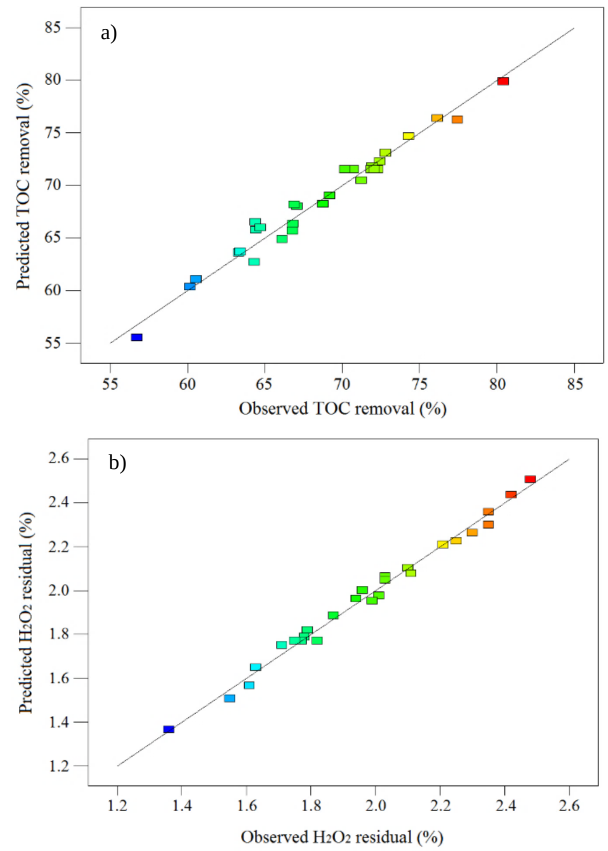

Figure 2. Observed experimental data versus predicted values for (a) percent TOC removal and (b) H_2O_2 residual.

B. *Individual effect and cross-factor interaction of model parameters*

The significance of each model factor was also performed using the *F* exact test and *p*-values for each factor including linear, quadratic, and cross-factor interaction. All four independent variables including influent TOC concentration (X_1), H_2O_2 dosage (X_2), flow rate (X_3), and recycle ratio (X_4), have significant effect on both responses, percent TOC removal and H_2O_2 residual, since their *p*-values are lower than 0.05.

On the other hand, only one interaction of model parameters did not indicate a significant effect on the percent

TOC removal, despite the fact that it was significant on the H_2O_2 residual simultaneously, this was the case of the cross-factor interaction of the influent TOC concentration and H_2O_2 dosage (X_1X_2). Conversely, the cross-factor interactions of the recycle ratio with other variables, including influent TOC concentration (X_1X_4), H_2O_2 dosage (X_2X_4), and flow rate (X_3X_4), showed a high significant effect on both TOC removal and H_2O_2 residual as illustrated in Figs. 3 and 4 for the TOC removal and the H_2O_2 residual, respectively.

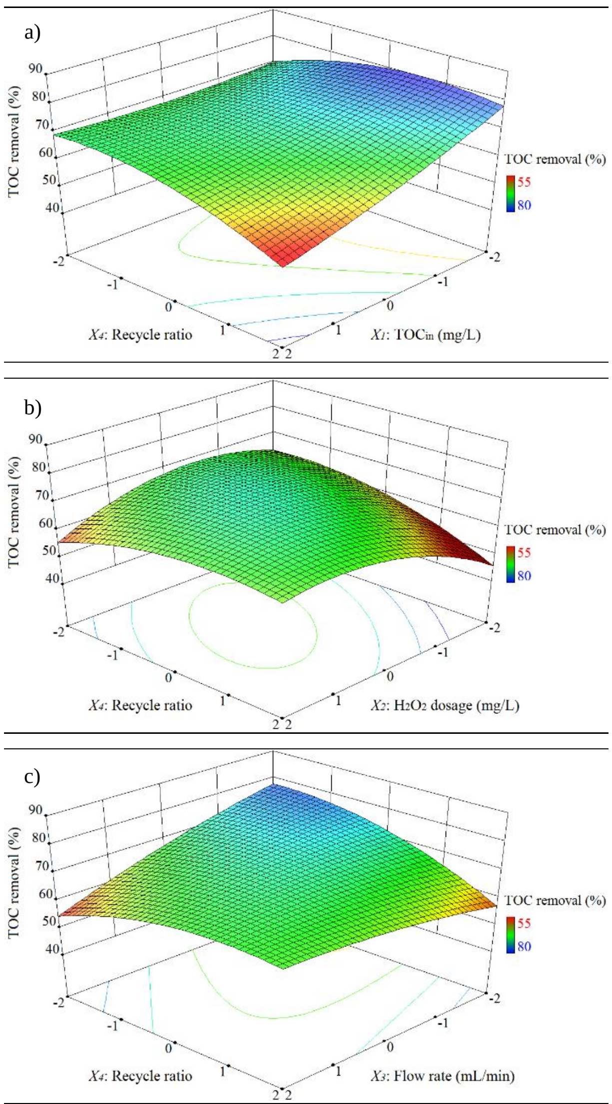

Figure 3. Interaction effects of different parameters on the percent TOC removal using 3D response surface and 2D contours: (a) influent concentration of TOC and recycle ratio (X_1X_4), (b) H_2O_2 dosage and recycle ratio (X_2X_4), and (c) flow rate and recycle ratio (X_3X_4).

C. ***Optimization of operating conditions***

RSM was used to determine the optimum conditions of the four independent variables to obtain maximum percent TOC removal and minimum H_2O_2 residual. Equations (2) and (3) were defined as objective functions for percent TOC removal and H_2O_2 residual, respectively, and the independent factors in their range were used as model constraints. Thus, the following optimum conditions to achieve a maximum TOC removal of 80% and minimum H_2O_2 residual of 1.4% were found: influent TOC of 24 mg/L, H_2O_2 dosage of 862 mg/L, flow rate of 15 mL/min, and recycle ratio of 0.2. The obtained optimal operating conditions were used in an additional run to validate the predicted values. Obtaining a TOC removal of 81% and H_2O_2 residual of 1.3% were obtained experimentally, confirming the reliability of the model.

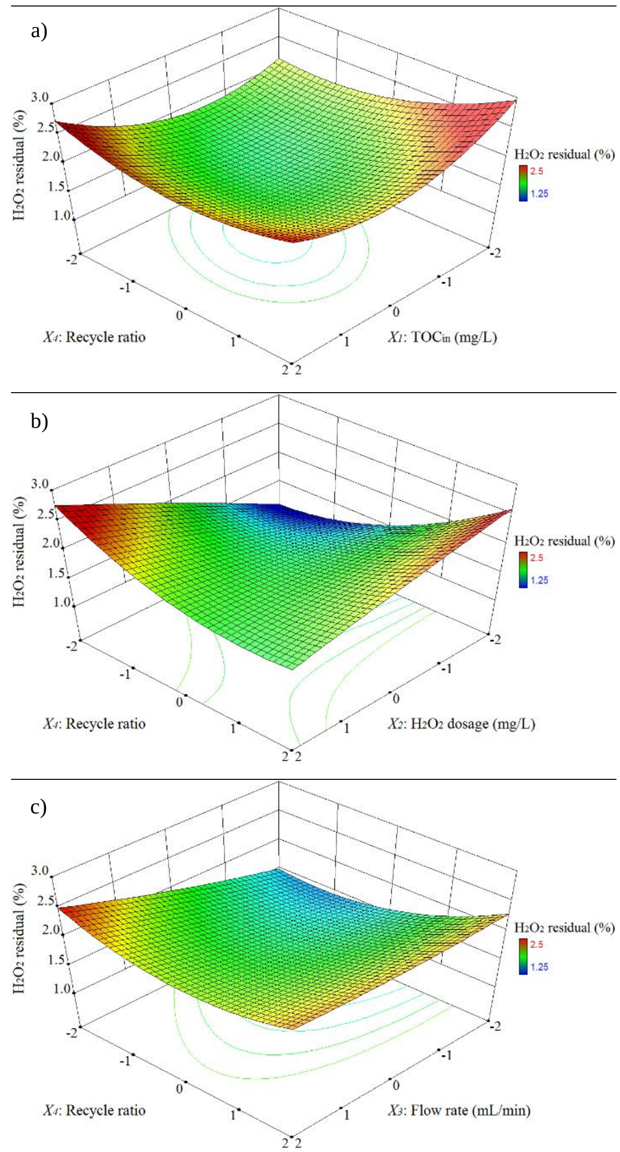

Figure 4. Interaction effects of different parameters on the H_2O_2 residual using 3D response surface and 2D contours: (a) influent concentration of TOC and recycle ratio (X_1X_4), (b) H_2O_2 dosage and recycle ratio (X_2X_4), and (c) flow rate and recycle ratio (X_3X_4).

D. ***CONCLUSIONS***

The cross-factor interactions of the recycle ratio with other variables, including the influent TOC concentration, H_2O_2

dosage, and flow rate, had significant effect on both TOC removal and H_2O_2 residual. Thus, an optimum recycle ratio was found to be significant to achieve maximum TOC removal with minimum H_2O_2 residual. The developed mathematical models provided a detailed exploration of the cross-factor interactive effects of the independent variables on the responses. Thus, the proposed models explaining the photochemical treatment of SWW by the continuous UV/H_2O_2 photoreactor with recycle could be used for future studies on process optimization, photoreactor design, modeling, and scale-up.

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