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OPTIMIZATION OF REACTION PARAMETERS BY APPLYING CENTRAL COMPOSITE DESIGN (CCD) TO THE ADVANCED OXIDATION TREATMENT OF WWTP EFFLUENTS BY UV/H_2O_2

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Abstract: In this research the removal of effluent organic matter (EfOM) by advanced oxidation processes (UV/ H_2O_2) was evaluated. The target EfOM samples were the output of electro-membrane bioreactor (EMBR) pilot facility located in Wastewater Treatment Plant in the city of l'Assomption (Quebec). To optimize the treatment conditions, a response surface methodology (RSM) was applied. By using RSM and central composite design (CCD), the effect of operational parameters including H_2O_2 concentration (0.0 -12 Mm), aeration rate (0.0- 4 L/min) and pH (3-11) on treatment performance was investigated. The regression analysis of variance (ANOVA) with R^2 value of 0.98 confirmed the reliability of predicted quadratic polynomial model which had a good fitness to the experimental values. Experimental results revealed the significant influence of aeration, H_2O_2 concentration and pH on removal rate of EfOM. However, the pH values and aeration rate should not increase more than specific values and H_2O_2 consumption could be decreased by optimization of two other operational parameters, i.e. pH and aeration. Furthermore, by applying optimum condition, the results showed significant removal of total organic carbon (TOC) more than 90% in several samples. This study showed a significant influence of operating parameters on TOC (EfOM) removal in effluent by using UV/ H_2O_2 advanced oxidation system. The application of central composite design based on response surface methodology had an important role to find optimum conditions. Decrease of organic matter in effluent is an important step to produce drinking water directly from sewage. **Keywords:** Effluent tertiary treatment, Central composite design, Response surface methodology, Effluent organic matter, UV/H_2O_2.

1 INTRODUCTION

1.1 EfOM

Researchers were reported several pharmaceuticals and emerging contaminants (ECs) in drinking water output treatment facilities amongst water treatment units (Pal et al. 2010, Machado et al. 2016, Wert et al. 2007). One of the main causes of the presence of these pollutants in water bodies, is the discharge of wastewater effluent in to the surrounding surface water sources which are treated inefficiently (Naidoo and Olaniran 2013). Effluent organic matter (EfOM) mainly consists of a mixture of pharmaceutical active compounds (PhACs), endocrine disrupting chemicals (EDCs), proteins, lipids, polysaccharides, humic materials and polyphenols which are named as dissolved organic matter (DOM) (Ilani, Schulz, and Chefetz 2005, Imai et al. 2002). DOM can contribute to color, taste and odor of water and forming by-products (BPs) during the water treatment and therefore affect the quality of water (Matilainen et al. 2002, Owen et al. 1995).

1.2 AOPs

Therefore, due to the occurrence of ECs and DOM in water resources and their impact on the environment, there is an urgent need for investigation and application of new technologies to remove them (Wert et al. 2007). Many technologies have been examined for the removal of ECs from water streams and surface waters and effluent wastewater. Amongst these technologies, advanced oxidation processes (AOPs), such as UV/H_2O_2 system, have been identified as an effective technology to decompose recalcitrant ECs (Bui et al. 2016, Kim et al. 2008, Wols et al. 2013). Although UV oxidation processes present a viable and promising technology to remove micropollutants, there is a rising concern about the potential production of degradation by-products (BPs) and increasing potential hazard and toxicity (Ijpelaar, Harmsen, and Heringa 2007, Owen et al. 1995). Researchers implied that by increasing oxidant dose (H_2O_2 and air in this case) the possibility of by-products formation will be increases (Ijpelaar, Harmsen, and Heringa 2007). Therefore, optimization of reaction has an important role to control and minimize by-products formation.

1.3 RSM and CCD

In AOPs, operational conditions such as oxidant dose, UV dose, reaction time, the nature and concentration of target pollutant and other factors have very important effect on reaction efficiency. Finding the optimum condition in such treatment methods that have several variables is very difficult even by conducting numerous experiments to include the effect of all variables. On the other hand, conducting numerous experiments would lead to increased time and cost but not to the explore interaction between variables. In order to find the effect of independent variables to the removal efficiency, response surface methodology (RSM) and central composite design (CCD) are found to be effective methods (Myers 2009). In RSM one of the goals is designing the experiments to obtain the minimum number of test runs. In this research the second order polynomial equation is applied and CCD is one of the most popular class of second-order designs. CCD evolves using sequential experimentation by two-level factorial to fit a second-order response surface (RSM) to the designed variables. Many researches have been designed the chemical and electrochemical experiments by applying RSM (Li et al. 2010, Zhang Junwei et al. 2010, Sarrai et al. 2016). However, these process such as catalytic based AOPs and Photo-Fenton using Box-Behnken designs (BBD) or CCD on synthetic samples to remove different pollutants. To our knowledge, there is no report available using CCD focusing on real wastewater effluent removal by UV/H2O2 AOP. The main objective of this study is using RSM and CCD to optimize operational parameters for degradation of EfOM by UV/H_2O_2 AOP treatment method. To verify the model which was developed by RSM, the predicted results were evaluated by actual test results. Furthermore, the effect of operational parameters including pH, time, H_2O_2 dose and aeration to each other and on degradation efficiency was investigated.

2. Materials and Methods

2.1 Effluent Preparation

The effluent samples were collected from an electro-membrane bioreactor (EMBR) pilot plant located in l'Assomption city, QC, Canada and run by the Concordia University in Montreal (Belanger 2016). The details of this facility are reported elsewhere (Elektorowicz et al. 2017).

2.2 Chemicals, AOP System

Hydrogen peroxide 30% and other analytical grade chemicals (chloridric acid and sodium hydroxide for pH adjustments) were prepared from Fisher Scientific. Experimental AOP setup consisted of stainless steel (316) tubular 3.1 L reactor with 42 cm length and 10 cm diameter equipped with a LP-UVC 40-Watt lamp having 10.5 mW/cm^2 intensity (Trojan Company validated UV Lamp, ON, Canada). To deliver the effluent samples to the reactor and also adjusting desired flow rates, a peristaltic pump with a Tygon ELFL (06440-35) tubing was used. The system was completed with a 4-L Erlenmeyer reservoir allowed the effluent samples to receive an adequate H_2O_2 dose, mixing the solution, and aerated through nitrogen and oxygen counter current flows.

2.3 Semi-continuous Treatment and Analytical Methods

Before and after treatments, COD (chemical oxygen demand) and TOC (total organic carbon) were measured in a solution as indicators of the experiment performance. The tests were repeated two times for each sample. To verify analysis results, the COD/ TOC tests were conducted on wastewater effluent inorganics quality control standard solution with known TOC/COD concentrations (product # 2833249). For each test, 4 liters of effluent solution was continuously delivered to the reactor while proper adjustments were applied with respect to the pH value, H_2O_2 dose and aeration rate. The sampling of treated solution for COD and TOC analysis was conducted at 5 minutes' time intervals. For measuring COD and TOC, the ultra-low COD (TNT 820, Hach method 8000) and TOC (Hach method 10129) vials were used. The removal efficiency (R) was calculated based on equation [1], where C_t and C_o are the COD or TOC concentrations at time t and time zero, respectively.

[1] $R = (C_0 - C_t)/C_0 \times 100$

2.4 Experimental Design and Data Analysis

Three variables, namely the pH value, H_2O_2 dose and aeration rate, were operational parameters used to investigate organic matter removal efficiency. To design the experiments, the RSM based on fractional factorial, i.e. CCD, method was applied. Total 20 experiments defined by CCD method were conducted using the following ranges of three independent variables: 0.0 to 12 mM for H_2O_2, 3 to 11 for pH, 0.0 to 4 L/m for aeration rate. To virtually understand the behavior of AOP reactions, an empirical second order polynomial model was proposed (eq. [2]) to investigate and predict the effect of each independent variable on removal efficiency as well as an interaction between them (Myers 2009).

[2] $R\,(\%) = A_0 + A_1\,\mathcal{X}_1 + A_2\,\mathcal{X}_2 + A_3\,\mathcal{X}_3 + A_{12}\,\mathcal{X}_1\mathcal{X}_2 + A_{13}\,\mathcal{X}_1\mathcal{X}_3 + A_{23}\,\mathcal{X}_2\mathcal{X}_3 + \mathrm{A}_{11}\,\mathcal{X}_1^2\;\; \mathrm{A}_{22}\,\mathcal{X}_2^2 + \mathrm{A}_{33}\,\mathcal{X}_3^2$

In equation [2], R is response and $\mathcal{X}$ values representing the operational parameters as independent variables. A_0 is intercept coefficient, A_1 , A_2 , A_3 are linier coefficients, A_{12} , A_{13} , A_{23} are interaction coefficients between parameters and A_{11}, A_{22}, A_{33} are quadratic terms. The final response (i.e. TOC removal) for each independent variable (pH, H_2O_2, Air flow) was an estimated curvature model which can predict the effect of variables on treatment efficiency by UV/ H_2O_2 AOP. Independent variables were coded for low (-1), medium (0) and high (+1) levels as defined in Table 1.

Table 1: Independent variables correspond to coded values

Variable	Unit	[1]Min	[1]Max	[1]Coded low	[1]Coded high	Mean	[2] SD
H_2O_2 ($\mathcal{X}_1$)	m Mole	0	12	$-1 \leftrightarrow 3$	$+1 \leftrightarrow 9$	6	2.75
pH ($\mathcal{X}_2$)	-	3	11	$-1 \leftrightarrow 5$	$+1 \leftrightarrow 9$	7	0.84
Air ($\mathcal{X}_3$)	L/m	0	4	$-1 \leftrightarrow 1$	$+1 \leftrightarrow 3$	2	0.9177

[1] low and high coded values correspond to minimum and maximum experimental values
[2] Standard deviation

3. Results and Discussion

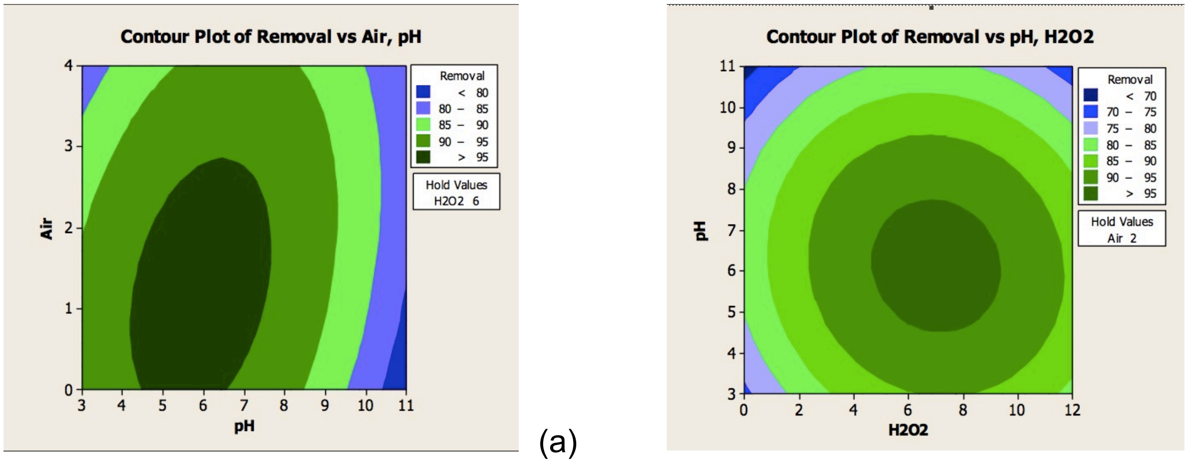
Twenty set of designed experiments as defined by CCD, were included in a matrix with independent variables having different values as presented in Table 2. The actual results for each set of experiments is shown besides the predicted responses by CCD. The quadratic terms and coefficients were estimated by analysis of variances. These terms and coefficients are included in the regression equation [3].

$$[3]\quad R\,(\%) = 55.9943 + 5.1136\ \mathcal{X}_1 + 7.6733\ \mathcal{X}_2 + 0.5909\ \mathcal{X}_3 - 0.0625\ \mathcal{X}_1\mathcal{X}_2 - 0.2083\ \mathcal{X}_1\mathcal{X}_3 + 0.4375\ \mathcal{X}_2\mathcal{X}_3 - 0.3081\ \mathcal{X}_1^2 - 0.6619\ \mathcal{X}_2^2 - 0.7727\ \mathcal{X}_3^2$$

Table 2: Independent variables and removal efficiencies; predicted compared to experimental

Run number	$\mathcal{X}_1$	$\mathcal{X}_2$	$\mathcal{X}_3$	Effluent removal efficiency (R%)	
				Predicted by model (%)	Experimental value (%)
1	9	9	3	88.4	87.5
2	3	5	1	90.8	92.1
3	6	3	2	89.7	88.7
4	3	5	3	88.9	90.4
5	6	7	4	91.4	93.3
6	6	7	2	95.9	96.5
7	6	7	2	95.9	96.5
8	6	7	2	95.9	96.5
9	6	7	2	95.9	96.5
10	6	11	2	80.9	83.4
11	12	7	2	88.2	89.6
12	9	5	3	91.8	91.4
13	9	9	1	89.3	88.6
14	6	7	0	94.2	93.7
15	9	5	1	96.1	98.1
16	6	7	2	95.9	96.5
17	6	7	2	95.9	96.5
18	3	9	1	85.4	86.4
19	3	9	3	87.1	85.8
20	0	7	2	81.4	81.9

Equation [3], can predict the removal of organic matter (EfOM) from effluent with respect to independent variables. Furthermore, the interaction between operational parameters, i.e. independent variables and their effect on the EfOM removal is expressed by polynomial quadratic equation. Table 2 shows very close numbers between the predicted removal efficiency and experimental results, which is a strong indicator for the method validation and significance of this model. Figure 1 depicted the counter plots of RSM for EfOM removal. In these plots. Figure 1.a. includes the effect of aeration rate and pH values, but Figure 1.b. presents the effect of pH and H_2O_2 dose. Both variables have significant impact on EfOM removal in addition to pH values. In the pH intervals between 4.5 and 7.5, EfOM has the highest removal comparing to other ranges. Furthermore, the maximum removals are fallen between 0 and 2.5 L/m of aeration rates beside the H_2O_2 dose of 4.5 to 8.5 mM.



(a) (b)

Figure 1: The counter plot of EfOM removal efficiency: a) pH and aeration rate b) pH and H_2O_2 dose

3.1 Reaction Optimization

The optimum values as predicted by CCD are highly close to the experimental results (Table 3). Therefore, there is a significance fit for polynomial quadratic equation model and experimental values. The regression analysis of variance, using ANOVA, with R^2 value of 0.98 confirmed the reliability of predicted quadratic polynomial model which had a good fitness to the experimental values.

Table 3: Optimum values (predicted/experimental) for maximum TOC removal by AOP UV/ H_2O_2

H_2O_2	pH	Aeration rate (L/m)	TOC removal (R%) Predicted by model /	Experimental
7.4	5.8	1.1	97.33	97.80

4. Conclusion

This study showed a significant influence of operating parameters such as pH, H_2O_2 dose and airflow, on the organic matter removal from wastewater treatment plant effluent by using UV/ H_2O_2 advanced oxidation system. It could be concluded that CCD method by RSM is an adequate approach to investigate optimal reactions where several variables are involved in the reaction mechanism. The method was applied to the effluents generated by membrane electro-bioreactor, which is an important step to produce drinking water directly from sewage.

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