

Study of the Effects of the Sulfate-Radical Sources for Wastewater Treatment using Response Surface Methodology

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Conventional wastewater treatment plants are mainly based on biological treatment technologies that do not suit for the removal of some organic pollutants in cold climate regions. Therefore, the research on complementary or post-treatment technologies such as advanced oxidation processes (AOPs) is important. AOPs are mainly based on the generation of hydroxyl and sulfate radicals for further oxidation of the pollutants. In this work, the sources of the sulfate radicals such as potassium persulfate ($K_2S_2O_8$), sodium persulfate ($Na_2S_2O_8$), and ammonium persulfate ($(NH_4)_2S_2O_8$) were compared in term of the total organic carbon (TOC) removal from the synthetic wastewater at low temperature. For this purpose, a three-level Box-Behnken design (BBD) in conjunction with the response surface methodology has been used. UV irradiation at 254 nm, the reaction time of 120 min, and Fe^{2+} dosage at 10 mg/L were used as hold values. According to the analysis of variance (ANOVA), the BBD-RSM models for TOC removal showed significant regression coefficients ($R^2 = 0.9753$, adjusted- $R^2 = 0.9309$, and predicted- $R^2 = 0.6221$). Pareto chart indicated that the concentration of the ammonium persulfate was the most significant factor at 12 °C.

1. Introduction

The amount of wastewater generated by the usage of water for human activities and industry is accelerating rapidly. According to the recent report 70% of the generated wastewater is treated in the high-income countries. On contrary, the portion of the treated wastewater was in the range between 38% and 8% for middle-income and low-income countries, respectively (Sato et al. 2013). The problems associated with the wastewater generation and treatment will intensify in the future due to the water scarcity and population growth. Therefore the swift actions must be made in order to create a wastewater treatment technique to produce a water of the certain quality. The treated wastewater could be used for irrigation, drinking, or for general use in human activities (Sato et al. 2013). The typical composition of the wastewater is complex and varies depending on the source of the wastewater. Municipal wastewater is generally consisted of inorganic compounds (nitrate, ammonia, chloride, carbonate, etc.) and organic contaminants (Mergenbayeva et al. 2021). Among them, organic pollutants of emerging concern such as pharmaceuticals, endocrine disrupting agents, pesticides and personal care products pose environmental risk (Kanafin, Satayeva, et al. 2021). The issue with emerging pollutants could be complicated as they tend to escape the conventional wastewater treatment plants based on biological treatment and, therefore, the development of the complementary methods of wastewater treatment is required (Mergenbayeva and Pouloupoulos 2022). There are a lot of different methods for wastewater treatment including but not restricted to membrane filtration, activated sludge process, and chemical treatment. Out of this, AOPs attract many researchers due to the high efficiency in dealing with recalcitrant organic pollutants and environmentally friendliness (Mergenbayeva and Pouloupoulos 2022). AOPs can be mainly described by the use

of oxidative radicals such as hydroxyl and sulfate (Lee, Von Gunten, and Kim 2020). Sulfate radicals are highly reactive and less affected by the presence of scavenging compounds. They can be generated by the activation of persulfate (PS) with ultraviolet light, ultrasound, microwave, heat, pH and transition metals (Anipsitakis and Dionysiou 2004). There are three compounds that are mainly used as a source of sulfate radicals: potassium persulfate, sodium persulfate and ammonium persulfate (Lee et al. 2020).

In this work, UV and Fe^{2+} were used to activate different sources of persulfate for the photo-Fenton-like oxidation of the synthetic wastewater. The study assessed the possibility of the use of persulfate in cold climate regions. The efficiency of the persulfate was studied in terms of TOC removal. Box-Behnken design in conjunction with response surface methodology was used to compare the efficiencies of the sulfate radical sources. To the best of authors' knowledge, there is no statistically significant studies on persulfate comparison for wastewater treatment at low temperature.

2. Materials and methods

2.1 Materials

Ammonium persulfate ($\geq 99\%$) and iron (II) sulfate heptahydrate (ACS reagent, $\geq 99\%$), peptone, sodium chloride, iron (III) chloride hexahydrate were purchased from Sigma Aldrich. Potassium persulfate ($\geq 99\%$) and sodium persulfate ($\geq 99\%$) were supplied by Reaktivsnab LLP. Lab lemco powder was obtained from Oxoid. D-Glucose, ammonium chloride, dipotassium phosphate, disodium phosphate, sodium bicarbonate and sodium chloride were supplied by Fisher Scientific. No additional purification of the reagents was conducted.

2.2 Wastewater composition

Synthetic wastewater was adapted from ISO11733 Standard and the composition is shown in Table 1 (ISO11733 2004). The average concentration of TOC was 178.5 ± 8.4 mg/L. The initial pH of the solutions was 7.5 ± 0.2 .

Table 1: Synthetic wastewater composition

Content	Peptone	Lab Lemco	Glucose	NH_4Cl	K_2HPO_4	Na_2HPO_4	NaHCO_3	NaCl	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$
mg/L	192	138	19	23	16	32	294	60	40

2.3 Analytical methods

The main analytical properties were obtained by analyzing the sample with Multi N/C 2100S (Analytik Jena AG, Germany). The properties include total carbon (TC), total inorganic carbon (TIC) and total organic carbon (TOC). pH control has been conducted using pH meter (Mettler Toledo, Five easy FE20). Using the data obtained on TC/TOC, the removal efficiency is deduced.

2.4 Photochemical treatment experiments

The batch photochemical reactor (Toption, China) with UV lamp (254 nm, 30W) and 400 mL vessel was used for photochemical treatment experiments. The full description and scheme of the reactor was previously provided (Kanafin, Makhatova, et al. 2021). All experiments were conducted for 2 hours with addition of Fe^{2+} (10 mg/L) at 12°C .

2.5 Statistical design

The statistical software Design-Expert (v.13) was applied to construct the experimental model. To find the primary significant effects, Box-Behnken design (BBD) has been constructed. The model included three different levels (-1, 0, +1) with three different corresponding variables: concentration of potassium persulfate (KPS), sodium persulfate (NaPS) and ammonium persulfate (NH_4PS) (Table 2). BBD experimental matrix consisted of 15 experiments. Response surface methodology (RSM) aided to maximize TOC removal in synthetic wastewater. Applying the Minitab Software (19.0), Pareto graphical chart was constructed and interpreted in the results section.

Table 2: BBD factors and levels

Factors	Levels		
	-1	0	+1
NH_4PS , mM	0	25	50
NaPS, mM	0	25	50
KPS, mM	0	25	50

3. Results and Discussions

3.1 ANOVA results

15 experiments were conducted using BBD. The experimental matrix design and obtained results are demonstrated in Table 3. All experiments lasted 120 min with the addition of Fe^{2+} (10 mg/L).

Table 3. Experimental matrix design and results.

Run	NH_4PS , mM	NaPS , mM	KPS , mM	TOC removal, %
1	0	25	50	23.15
2	50	0	25	61.60
3	50	50	25	62.16
4	25	0	50	40.57
5	25	25	25	62.90
6	25	0	0	32.49
7	0	50	25	54.43
8	25	25	25	65.61
9	0	25	0	32.35
10	0	0	25	24.74
11	25	50	0	52.37
12	25	25	25	64.01
13	50	25	0	53.70
14	25	50	50	57.22
15	50	25	50	54.01

Non-coded empirical relationship between the response and independent variables was expressed in the following second-order polynomial function (Eq. 1):

$$Y = 9.8442 + 1.41235 A + 1.00069 B + 1.09515 C - 0.014642 A^2 - 0.006864 B^2 - 0.022754 C^2 - 0.011652 AB + 0.00382 AC - 0.001292 BC \quad (1)$$

where Y = TOC removal (%), A = NH_4PS , B = NaPS , C = KPS , respectively. Positive sign of the coefficients indicates the synergistic effect from the factors and interactions, whereas the negative coefficients represent an antagonistic effect (Chen et al. 2016). In this case, the increase of concentrations of all three persulfates had positive effect on TOC removal. ANOVA was used to check the adequacy of the model (Table 4).

Table 4: ANOVA results

Removal	Source	Sum of Squares	Degrees of Freedom	Mean Square	F-Value	p-Value
TOC	Model	2981.69	9	331.30	21.97	0.0017
	Error	75.40	5	15.08		
	Lack of fit	71.69	3	23.90		
	Pure error	3.71	2	1.86		
Adeq. precision = 12.9852						
$R^2 = 0.9753$						
Adj- $R^2 = 0.9309$						
Pred- $R^2 = 0.6221$						

Regression coefficients (R^2 and Adj- R^2) were close to 1 and had small discrepancy between them. F-value (21.97) was high and p-value was less than 0.05. The mentioned parameters indicated that the model was significant. Adequate precision (12.9852) was much higher than 4, therefore, the model can be used to navigate within the design space (Li et al. 2019). Actual versus predicted values and normal probability plot is depicted on Figure 1.

Figure 1a shows good correlation between the predicted and actual removal values (%). Fig 1b implies that the residuals follow the normal distribution. As the model has been identified as the significant, Pareto analysis has been conducted to find the significant factors (Figure 2).

Pareto analysis revealed that ammonium persulfate was more efficient sulfate radical source followed by sodium persulfate and potassium persulfate.

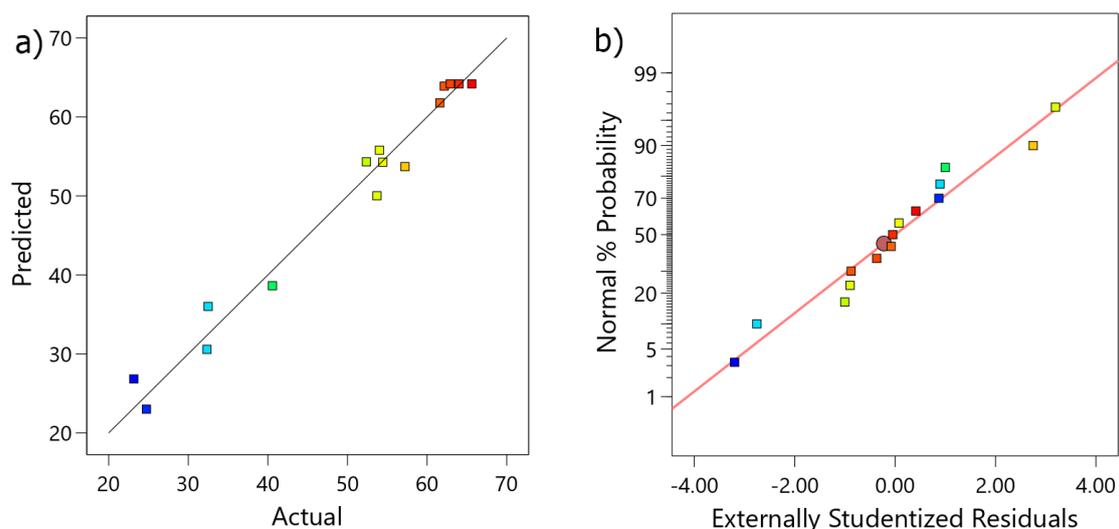


Figure 1: a) Predicted vs. actual removal values (%), and b) normal probability vs. externally studentized residuals values.

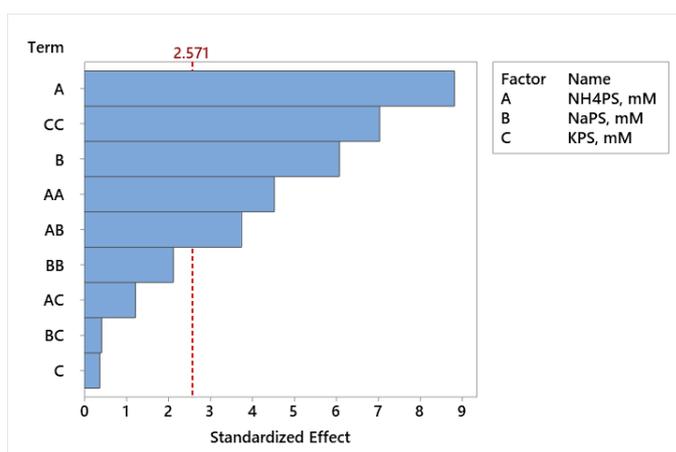


Figure 2: Pareto graphic analysis for photo-Fenton-like oxidation of the synthetic wastewater.

3.2 Visualisation and validation of the RSM regression model

3D plots of the RSM-BBD model based on the results of 15 experiments are demonstrated in Figure 3. Sulfate radicals are less affected by scavenging agents, therefore, they are more efficient when dealing with complex wastewater (Kanafin, Satayeva, et al. 2021). Previously, potassium persulfate has been successfully applied for the treatment of the real municipal wastewater (Kanafin, Makhatova, et al. 2021). Complete mineralization of TOC has been achieved using potassium persulfate (30 mM) and Fe^{2+} (224 mg/L) at pH 7.7 under UVC (Kanafin, Makhatova, et al. 2021). Ammonium persulfate has the lowest molecular mass and the highest water solubility (850 g/L) which gives its edge at wastewater treatment at low temperature (Izadifard et al. 2017). Moreover, the presence of the nitrogen source may be beneficial if the bioremediation is followed after persulfate oxidation (Izadifard, et al. 2017). Unlike hydroxyl radical based AOPs, sulfate radicals can oxidize ammonium and convert it to a higher valence state (N_2) (Deng and Ezyske 2011). However, this causes competition between organic pollutants and ammonium ions. Moreover, it has been reported that the concentration of ammonia nitrogen more than 100 mg/L is hazardous for living organisms (Zhang et al. 2010). Therefore, the additional treatment should be used after treatment with ammonium persulfate.

Izadifard et al. (2017) used 3 g/L of ammonium persulfate under UVC and achieved 90% sulfolane degradation after 60 min of the experiment (Izadifard et al. 2017). Wu et al. compared the efficiencies of the ammonium persulfate and sodium persulfate for the perfluorooctanoic acid (PFOA) degradation (Wu et al. 2018). Authors reported that the sodium persulfate had slightly better removal and explained it with the competition between ammonium and PFOA (Wu et al. 2018).

The optimum conditions for TOC removal were calculated by Design-Expert (Table 5).

Table 5: Optimum conditions found by RSM, and experimental validation for TOC removal

Time (min)	pH	Fe ²⁺ , mg/L	NH ₄ PS, mM	NaPS, mM	KPS, mM	Actual TOC removal (%)	Predicted TOC removal (%)	Error (%)
120	7.6	10	28.35	45.71	30.48	66.01	68.14	2.13

The predicted conditions for 68% TOC removal found by RSM were at the concentrations of (NH₄)₂S₂O₈, Na₂S₂O₈ and K₂S₂O₈ of 28.35 mM, 45.71 mM and 30.48 mM, respectively. The actual TOC removal was 66% indicating high goodness-of-fit of the RSM model.

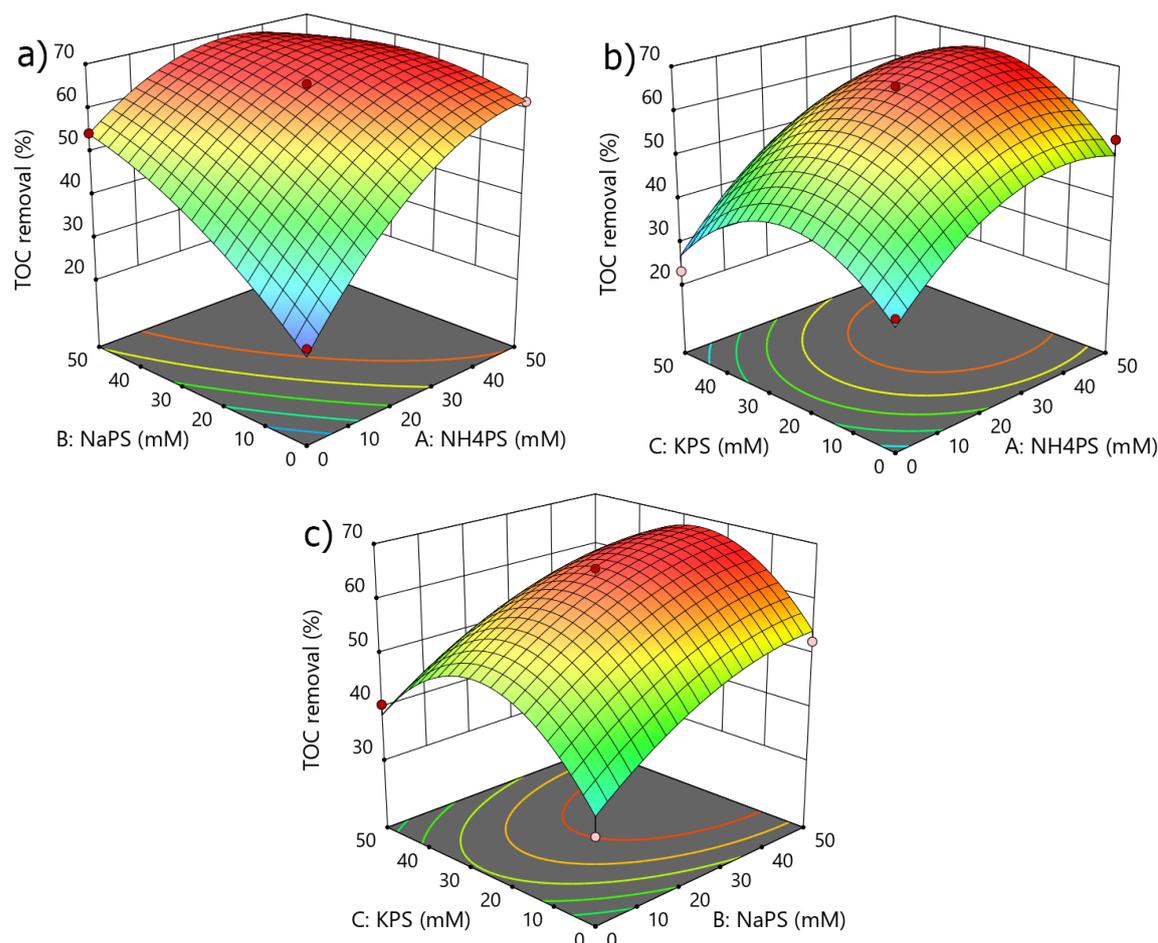


Figure 3: 3D plots of TOC removal as a function: (a) NH₄PS (mM) and NaPS (mM), (b) NH₄PS (mM) and KPS (mM), and, (c) KPS (mM) and NaPS (mM).

4. Conclusions

In this study, three sources of sulfate radicals, namely, ammonium, sodium and potassium persulfates were evaluated for the use for photo-Fenton-like oxidation at low temperature. RSM-BBD model had high accuracy and ANOVA analysis revealed that ammonium persulfate was the most significant factor. This could be linked with the high water solubility of the ammonium persulfate. However, excessive concentration of ammonium is hazardous for living organisms, therefore, ammonium persulfate oxidation should be followed with biological treatment.

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