Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2022.28190

250 (2022) 211–220
February

Factorial design and optimization of thermal activation of persulfate for stabilized leachate treatment

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Received 23 September 2021; Accepted 8 January 2022

ABSTRACT

Landfill remains as the most common municipal waste disposal method in the world. However, the production of leachate associate with landfill persists as a major drawback, which bring harmful effect to the environment. Persulfate oxidation is recently used for stabilized leachate treatment. Persulfate alone is still limited for leachate oxidation and an activation method is required to improve its performance. Accordingly, this study aims to investigate and compare the performance of persulfate subjected to thermal activation in treating stabilized leachate. Different experimental operational factors were considered and evaluated such as, $S_2O_8^{2-}$/chemical oxygen demand (COD) ratio, temperature, and reaction time. Experiments were designed and optimized by using response surface methodology, and results were analysed by using analysis of variance. The removal efficiencies for COD and colour using inactivation persulfate were reported only at 14% and 29%, respectively. However, the efficiencies were improved to 93.39% and 94.00% for COD and colour after thermal activation of persulfate under an optimum condition of 10 $S_2O_8^{2-}$/COD ratio, 80°C and 120 min. The maximum efficiency was achieved at the treatment cost of RM0.66 per litre of leachate.

Keywords: Persulfate oxidation; Organic degradation; Thermal activation; Landfill leachate; Experimental design

1. Introduction

In a recent report from the World Bank [1], landfill remains as the most common method for municipal solid waste management in global. It was well adopt in upper-middle-income country such as Malaysia. Despite the advantages of landfill such as cost conservative and easy operation [2], generation of leachate persist as a major drawback due to its negative impact to the environment [3,4]. Leachate is a highly polluted liquid, formed when water percolates through solid waste and carries organic, inorganic, heavy metals, and other impurities [5]. Generally, leachate is characterized in term of pH, dissolved oxygen (DO), total suspended solids (TSS), biological oxygen demand (BOD), chemical oxygen demand (COD), ammonium nitrogen (NH_3–N), total Kjeldahl nitrogen (TKN), heavy metal and others. Quality of leachate is affected by numerous factors such as climate, precipitation, landfill age and others [4]. The composition of leachate and standard effluent quality varies according to the rom location and the later differ by country legislation [6]. Treatment of leachate is necessary to ensure the end-product meets the limit set by authorities, to prevent environmental contamination. Generally, leachate treatment is categorized by biological,

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Presented at the 4th International Symposium on Green and Sustainable Technology 2021 (ISGST 2021), 3–6 October 2021, Ipoh, Malaysia

physical, chemical, or physicochemical processes. Integrated systems are usually adopted to maximize the efficiency of each process [4]. Various research, studies, and effort have been put into development or enhancement of new or current treatment processes. In recent year, advance oxidation process (AOPs) has shown promising result in degradation of recalcitrant and organic pollutants [7]. AOPs were often used as a pre-treatment or post-treatment for biological processes for a better removal rate of non-biodegradable pollutants [8]. AOPs involve two processes: generation of highly reactive free radical and chemical reaction with organic compound to achieve complete demineralization.

In the last decades, persulfate emerge as one of the popular oxidants used in AOPs [9]. Persulfates dissociate into persulfate anion ($S_2O_8^{2-}$, oxidation potential, $E°$ = 2.0V), and activated to produce stronger oxidant such as sulphate radical (SO_4^{-}, $E°$ = 2.6 V) and hydroxyl radical ($HO\cdot$, $E°$ = 2.8 V) with higher oxidation potential [10]. Various activation method can be adopted such as elevated temperature, sonication, pH, photo activation or using activator [9]. Among, thermal activated persulfate oxidation has a wide range of application, such as in in-situ chemical oxidation [11] and liquid waste treatment such as leachate treatment [12]. Thermal activation is simple in mechanism, produce clean oxidant radical without any additional chemicals [13], and has been reported to achieve higher performance than other persulfate activation mechanism [14]. In the design of leachate treatment, characteristic analysis is essential to understand the biological process that happened within the landfill and indicate the major pollutant to be treated [15]. Sahom landfill been operated for more than 27 years since 1992, it was considered an old landfill with stabilized leachate. As the year increases, composition of landfill change to a lower BOD/COD ratio and in increases of recalcitrant organic molecules [15,16]. Conventional biological treatment no longer meets a satisfactory treatment efficiency [16]. Physico-chemical treatment such as advance oxidation processes (AOPs) are used in treating toxic and bio-refractory compounds [7]. Persulfate is one of the oxidation agents used in AOPs, which can be activated by several methods to achieve higher treatment efficiency. Thermal activation is popular due to its simplicity and promising treatment performance [13]. In this paper, the performance of thermo activated persulfate oxidation on leachate sample was evaluated and optimized using response surface methodology (RSM). Economic appraisal and environment impact of effluent leachate were discussed along with some recommendation.

2. Materials and methods

2.1. Leachate collection and site location

Leachate samples were collected from Sahom landfill. Sahom landfill is located at Kuala Dipang in Perak and occupied a landfilling area of approximately 37 acres. The site receives municipal solid waste collected from around South Kinta Valley. Sahom landfill was an anaerobic landfill equipped with leachate collection system, leachate treatment pond and a composting centre. The leachate from Sahom landfill is categorized as a stabilized leachate with BOD_5: COD ratio of less than 0.1 [17]. Leachate samples were collected by using a pre-cleaned polypropylene bottle (PET). A total of 20 L sample was collected on the period between 19 October 2020 and 30 October 2020. The collected leachate sample was immediately transported back to the environmental Laboratory and stored in refrigerator under temperature of 4°C, to minimize any possible means on any chemical reactions and the biodegradation of the leachate sample. General characterization of leachate is presented in Table 1.

2.2. Experimental procedures

Preliminary tests for inactivated, and thermal activated persulfate oxidation on leachate samples were carried out to get a basic understanding on the contaminant removal performance and select range of parameters to be used in experimental design. With the results obtained, design of experiment (DoE) was set by using RSM with central composite design (CCD). Analysis and evaluation of respond data were then carried out using analysis of variance (ANOVA) to obtain the optimum conditions. Comparison of optimum conditions from experimental data were performed and results obtained were then compared with previous studies. All chemicals used in experiments are in analytical-reagent grade. The pH of leachate sample was conditioned by using 1 N nitric acid (HNO_3) or 1 N sodium hydroxide (NaOH). Sodium persulfate ($Na_2S_2O_8$) purchased from Sigma Aldrich Co., with molecular weight of 238.1 g/mol and purity >98%. For preliminary tests, three groups of experiments were performed for each activation mechanism. Under inactivated persulfate oxidation, a 100 mL of leachate sample was poured into 250 mL capacity Erlenmeyer flask, conditioned to desired pH, then added with designated persulfate dosage and swirl for 60 min using orbital shaker

Table 1
Characteristic of raw landfill leachate with Standard Discharge Limit (Environmental Quality (Control of Pollution from Solid Waste Transfer Station and Landfill) Regulations, 2009) [18]

Parameter	Range	Average	Standard Discharge Limit
Temperature, °C	27.7–32.2	30.0	40
pH	7.69–8.30	8.00	6.0–9.0
DO, mg/L	0.73–4.48	2.53	–
TDS, mg/L	1,835–1,977	1,907	–
EC, ms	1.977–2.131	2.054	–
Salinity, PSU	1.948–2.130	2.041	–
Resistivity, W	252.7–272.7	262.8	
Turbidity, NTU	23–47	35	–
Colour, Pt/Co	294–493	396	100
BOD, mg/L	20.07–69.13	45.17	20
SCOD, mg/L	140–170	159	–
TCOD	193–243	209	400
BOD/COD ratio	0.08–0.36	0.11	–
SS, mg/L	30–310	158	50
NH_3–N, mg/L	130.142–130.645	130.98	5

(Straits Scientific, Malaysia). Three groups of experiments were performed by adjusting different operational parameters: pH (4 and 9), rotation speed (100 and 200 rpm) and $S_2O_8^{2-}$/COD ratio (0.8–26.3). Bathing water must be refilled from time to time to ensure water level higher than solution water level in Erlenmeyer flask. Three groups of experiments run with operation parameter: ratio (0.2–7.0), temperature (40°C–80°C) and reaction time (30–120 min). All experiments were tested for COD and colour removal efficiencies. For thermally activated persulfate oxidation, additional SS and ammoniacal nitrogen tests were performed during preliminary stage. Initial and final pH with temperature were recorded along to observe effect of persulfate on pH change and calculate energy consumption. After preliminary experiments, another 20 sets of experiments recommended by the RSM were performed, analysed, and optimized.

2.3. Design of experiment (DoE)

RSM is the use of mathematical and statistical techniques to study the response of interest (dependent variable) affected by several variable (independent variable) with the objective to optimize the response [19]. On the basis of modelling and analysis of interaction between independent variable, it serves the advantages of time and cost conservation by minimizing the number of trials [20]. Before applying of RSM, design of experiment (DoE) must be set, which defines sets of combinations for all independent variables at various level. DoE for this research is based on second-order models: central composite design (CCD). After obtaining all response from experiment, results were evaluated and analysed to fit using a polynomial quadratic [Eq. (1)].

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{1\le i\le j}^{k} \beta_{ij} x_i x_j + \varepsilon \tag{1}$$

where y is response, x_i and x_j are operation variables, β_0 is constant coefficient, k is number of variables, β_i, β_{ij} and β_{ii} represent coefficients of linear.

Fitness of experimental data were verified by the correlation coefficient (R^2), and statistical significance of model for each response was evaluated using ANOVA [21]. The necessary information to obtain include dependent variable, independent variable, and factor level. Based on the result from preliminary test, thermally activated persulfate oxidation process was designed and optimized. In DoE, dependent variables are response parameters which significantly affected by a shift in independent variables, and it is the interested parameters to measure the performance of the experiment. Two dependent variables selected as removal efficiency of COD and colour. The removal efficiency was calculated by using the following equation.

$$\text{Removal efficiency}\left(\%\right) = \frac{X_i - X_f}{X_i} \times 100 \tag{2}$$

where X_i and X_f is the initial and final concentration of COD and SS respectively.

Vice versa, independent variables are factors that significantly affect the values of dependent variables. Three most significant independent variables were $S_2O_8^{2}$/COD ratio (g/g), temperature and reaction time. Range of independent variables were tested and decided based on preliminary result, as illustrated in Table 2. Persulfate to COD ratio range between 0.2–10.0, temperature range between 20°C–80°C and reaction time range between 20–120 min. A dimensionless ratio was used to express persulfate dosage instead of conventional expression in concentration unit, to facilitate comparison between similar treatment method on different leachate sample [22].

2.4. Analytical study

The concentration of BOD_5 was determined using the method 5210B. The DO was measured using the DO meter (model 1000, YSI Inc., USA) [23]. COD concentration was determined using closed reflux colorimetric method (5220B-DR2500 HACH) [24]. Sodium sulfite and heating were used to eliminate the interference of remaining potassium persulfate on COD analysis [25]. Color concentration was measured using a DR 2600 HACH spectrophotometer. pH and electrical conductivity (EC) were measured using the portable digital pH/mV meter (model inoLab pH 720, WTW, Germany). TSS was measured using the method 2540C. NH_3–N concentration was measured by the Nessler methos using DR2500 spectrophotometer.

For this study, Design-Expert® Version 10 was used to generate DoE using CCD and optimization of process using RSM. After filled in all the necessary information into the software, DoE matrix of a total 20 set of experiments run with different combination of independent variables were generated.

3. Results and discussions

3.1. Thermal activated persulfate oxidation

A total of 12 set experiments on thermal activated persulfate oxidation was carried out, to determine effect of temperature, reaction time and $S_2O_8^{2-}$/COD ratio on COD and Colour removal efficiency, results as shown in Table 3. All set of experiments were fixed under pH4 condition.

From Group C1 results, COD, and colour removal efficiency increase (COD from –4.62% to 28.95%, colour from 20.73% to 70.22%) when temperature increase (from 40°C to 80°C). This indicated the effect of temperature as a significant parameter in activation mechanism of persulfate oxidation. Under an increasing reaction time (from 30 min to 120 min), the COD and colour removal efficiency increase from 21.93% to 32.68% for COD and 62.50% to 76.63% for colour. From Group C3 results, an increase in persulfate

Table 2
Independent variable and range of actual values

Factor	Range	
	–1 (low)	+1 (high)
$S_2O_8^{2-}$/COD ratio	0.2	10.0
Temperature, °C	20	80
Reaction time, min	20	120

Table 3
Preliminary test for thermal activated persulfate oxidation

Operation parameters			Results		
Reaction time	Temp.	$S_2O_8^{2-}$/COD ratio	Final pH	COD removal efficiency	Colour removal efficiency
min	°C			%	%
Group C1: different temperature					
60	40	0.8	3.70	0.0	20.73
60	60	0.8	3.38	0.0	30.18
60	80	0.8	3.00	28.95	70.22
Group C2: different reaction time					
30	80	0.8	3.13	21.93	62.50
60	80	0.8	3.00	28.95	70.22
120	80	0.8	3.01	32.68	76.63
Group C3: different ratio					
60	80	0.2	3.00	17.54	25.00
60	80	1.1	3.00	27.85	57.83
60	80	2.0	2.97	37.72	72.36
60	80	3.0	3.00	7.02	52.54
60	80	5.0	2.80	57.02	52.03
60	80	7.0	2.30	64.69	60.67

dosage indicated by $S_2O_8^{2-}$/COD ratio (from 0.2 to 7.0), shows a positive increasing effect on COD and colour removal efficiency trend. Additional test on SS and NH_3–N in Group C3 shows negative effect on their removal efficiency. Thermal activated persulfate oxidation will increase the SS in leachate sample, while effect on NH_3–N is in negative but the values is too small to be consider a significant effect. The removal efficiencies for COD and colour using inactivation persulfate were reported only at 14% and 29%, respectively. In overall, inactivated persulfate oxidation did not shows significant treatment efficiency.

3.2. RSM design matrix with results

Based on earlier RSM design matrix generated by using Design-Expert® software, version 10, results of COD and colour removal efficiency from experiments is tabulated into the matrix, as shown in Table 4. Analysis by ANOVA, model graph interpretation and optimization result were discussed in following section. Response data for COD removal efficiency ranged from 2.41% to 95.39%, while colour removal efficiency ranged from 23.58% to 94.00%. Lowest removal efficiency found under condition of 10.00 $S_2O_8^{2-}$/COD ratio, 30.0°C and 20 min, while highest removal efficiency found under condition of 10.00 $S_2O_8^{2-}$/COD ratio, 80.0°C and 120 min. The ANOVA for COD and colour removal is presented in Tables 5 and 6.

For COD removal efficiency, model's Prob. > *F* smaller than 0.05 indicate model are significant. In this case, significant model terms are *B*, *C*, *AB* and *AC*. There are 22.07% chance that lack of fit occurred due to noise, indicate lack of fit are not significant, the model is fitted. R^2 higher than 0.9 (R^2 = 0.9721) further confirm a good agreement between experiment data and model prediction. Predicted R^2 of 0.4804 is much different from adjusted R^2 of 0.9469, indicate a block effect in model or data, transformation is not needed, for meaningful data interpretation [26]. A C.V. value of 14.55% is slightly higher than 10%, but within an acceptable range (<20%). Adequate precision of 29.146 is greater than 4, indicate model can be used to navigate design space.

For colour removal efficiency, model's Prob. > *F* smaller than 0.05 indicate model are significant. In this case, significant model terms are *A*, *B*, *C*, *AB*, *AC* and *BC*. There are 53.76% chance that lack of fit occurred due to noise, indicate lack of fit are not significant, the model is fitted. R^2 higher than 0.9 (R^2 = 0.9820) further confirm a good agreement between experiment data and model prediction. Predicted R^2 of 0.8222 is close to adjusted R^2 of 0.9657 (difference < 0.2), no transformation of data is needed. A C.V. value of 5.56% is well within 10%, the model is reasonably reproductible. Adequate precision of 30.630 is greater than 4, indicate model can be used to navigate design space.

Normal probability plots and predicted vs. actual plots for COD and colour removal are shown in Figs. 1 and 2. For both COD and colour removal efficiency quadratic model, normal probability plot generally follow a straight line with little dispersion. The predicted vs. actual plot for COD showed a skewed data towards the right, which indicate a transformation recommendation for colour, predicted vs. actual plot showed a normal distributed response data.

3.2.1. Effect of operation parameter on COD removal efficiency

All experiments were performed at Ph4 condition as recommended by preliminary result. The interaction

Table 4
RSM design matrix with results

Std	Run	Factor 1	Factor 2	Factor 3	Response 1	Response 2
		A: $S_2O_8^{2-}$/COD ratio	*B*: temperature	C: reaction time	COD removal efficiency	Colour removal efficiency
			°C	min	%	%
1	10	0.20	30.0	20	35.96	34.96
2	4	10.00	30.0	20	2.41	23.58
3	15	0.20	80.0	20	39.91	45.53
4	1	10.00	80.0	20	64.04	90.04
5	12	0.20	30.0	120	30.70	36.38
6	14	10.00	30.0	120	8.33	46.34
7	9	0.20	80.0	120	35.53	40.04
8	3	10.00	80.0	120	95.39	94.00
9	20	2.65	55.0	70	32.46	52.44
10	8	7.55	55.0	70	27.85	69.82
11	2	5.10	42.5	70	12.28	56.10
12	18	5.10	67.5	70	34.87	73.27
13	16	5.10	55.0	45	25.88	62.40
14	19	5.10	55.0	95	34.43	71.44
15	5	5.10	55.0	70	25.44	64.94
16	13	5.10	55.0	70	25.66	60.77
17	11	5.10	55.0	70	28.95	69.00
18	7	5.10	55.0	70	23.03	60.26
19	17	5.10	55.0	70	17.98	65.85
20	6	5.10	55.0	70	25.44	66.06

Std = standard order.

Table 5
ANOVA for COD removal efficiency quadratic model

Source	Sum of squares	DF	Mean square	*F*-value	Prob. > *F*	Remarks
COD removal efficiency						
Model	7,226.931	9	802.9923	38.6629	<0.0001	Significant
A	78.11368	1	78.11368	3.761059	0.0812	
B	3,350.184	1	3,350.184	161.3064	<0.0001	
C	119.7781	1	119.7781	5.767138	0.0372	
A^2	32.9432	1	32.9432	1.586166	0.2365	
B^2	31.68282	1	31.68282	1.525481	0.2450	
C^2	32.9432	1	32.9432	1.586166	0.2365	
AB	2,446.931	1	2,446.931	117.8161	<0.0001	
AC	275.3011	1	275.3011	13.25534	0.0045	
BC	86.5651	1	86.5651	4.167982	0.0685	
Residual	207.6907	10	20.76907			
Lack of fit	140.202	5	28.04039	2.077414	0.2207	Not significant
Pure error	67.48871	5	13.49774			

R^2 = 0.9721, adjusted-R^2 = 0.9469, predicted-R^2 = 0.4804, C.V. = 14.55%, adequate precision = 29.146

Final equation in terms of coded factors:

$$\text{COD removal efficiency} = 25.57 + 3.03A + 19.85B + 3.75C + 13.29A^2 - 13.03B^2 + 13.29C^2 + 17.49AB + 5.87AC + 3.29BC$$

DF = degree of freedom.

Table 6
ANOVA for colour removal efficiency quadratic model

Colour removal efficiency						
Model	5,900.84	9	655.6489	60.51717	<0.0001	Significant
A	1,315.452	1	1,315.452	121.4178	<0.0001	
B	2,206.218	1	2,206.218	203.6366	<0.0001	
C	86.94377	1	86.94377	8.025013	0.0178	
A^2	53.75886	1	53.75886	4.962007	0.0500	
B^2	1.40596	1	1.40596	0.129772	0.7262	
C^2	7.169885	1	7.169885	0.661789	0.4349	
AB	1,247.461	1	1,247.461	115.1421	<0.0001	
AC	118.5237	1	118.5237	10.93988	0.0079	
BC	82.6344	1	82.6344	7.627253	0.0201	
Residual	108.341	10	10.8341			
Lack of fit	51.77018	5	10.35404	0.91514	0.5376	Not significant
Pure error	56.57078	5	11.31416			

$R^2 = 0.9820$, adjusted-$R^2 = 0.9657$, predicted-$R^2 = 0.8222$, C.V. = 5.56, adequate precision = 30.630

Final equation in terms of coded factors:

$$\text{COD removal efficiency} = 64.91 + 12.44A + 16.11B + 3.20C - 16.97A^2 - 2.74B^2 + 6.20C^2 + 12.49AB + 3.85AC - 3.21BC$$

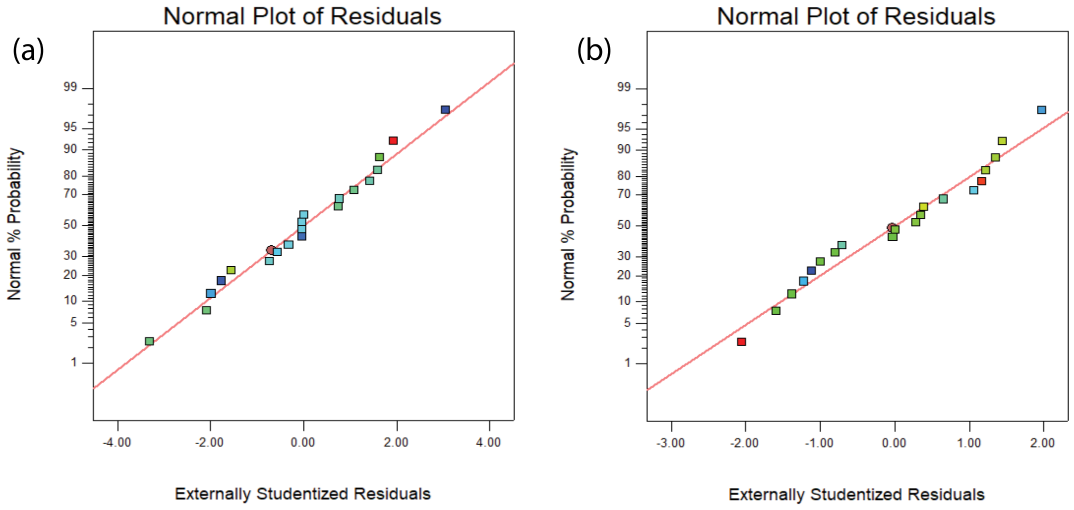

Fig. 1. Normal probability plot for quadratic model of: (a) COD removal efficiency and (b) colour removal efficiency.

between temperature and $S_2O_8^{2-}$/COD ratio showed a positive effect on COD removal efficiency (Fig. 3). Simultaneous increases in temperature and ratio causes increase of organic compound oxidation, due to the synergistic effect of increasing persulfate dosage and more generation of sulphate radicals as energy is provided [27]. This observation agreed by most literatures such as treatment on petrochemical wastewater [28], nanofiltration concentrated leachate [29] and membrane bioreactor leachate effluent [30]. The reaction time factor only showed effect on temperature and $S_2O_8^{2-}$/COD ratio after 70 min, as shown in the addition COD removal efficiency (additional red zone) in Fig. 4. Increased of reaction time led to increase contact time between sulphate radicals and organic compound [29].

Temperature is seen as a key factor in thermal activated persulfate oxidation, as described in Fig. 4. At 30°C, low COD removal efficiency were observed (dark blue to blue colour indicate lowest range of response value) regardless of change in time and $S_2O_8^{2-}$/COD ratio. As temperature increased, green and red colour start to show on surface graph indicating an increase of COD removal efficiency. Interactive between increasing reaction time and ratio showed a positive effect on the response under high temperature, in agree with result from Chen et al. [30]. According to Huling and Pivetz [9], a minimum temperature of 35°C to 40°C is needed in activation of persulfate anion to generate sulphate radical, which explain on the low COD removal efficiency in Fig. 4. Under mild temperature, persulfate oxidation took longer time to achieve desire removal efficiency as describe in most ISCO treatment [13].

Limited synergistic effect can be observed from interaction between reaction time and temperature change. As

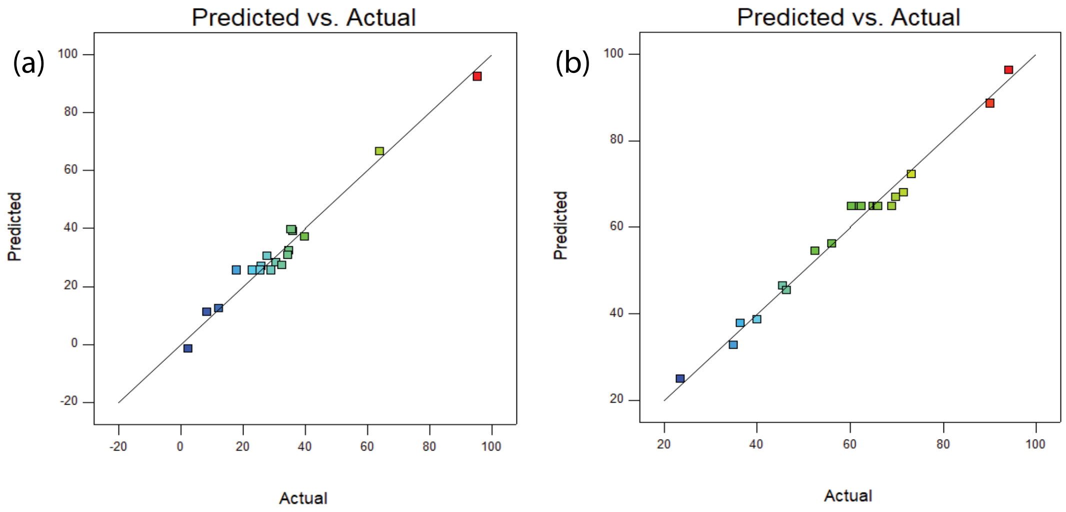

Fig. 2. Predicted vs. actual plot for quadratic model of: (a) COD removal efficiency and (b) colour removal efficiency.

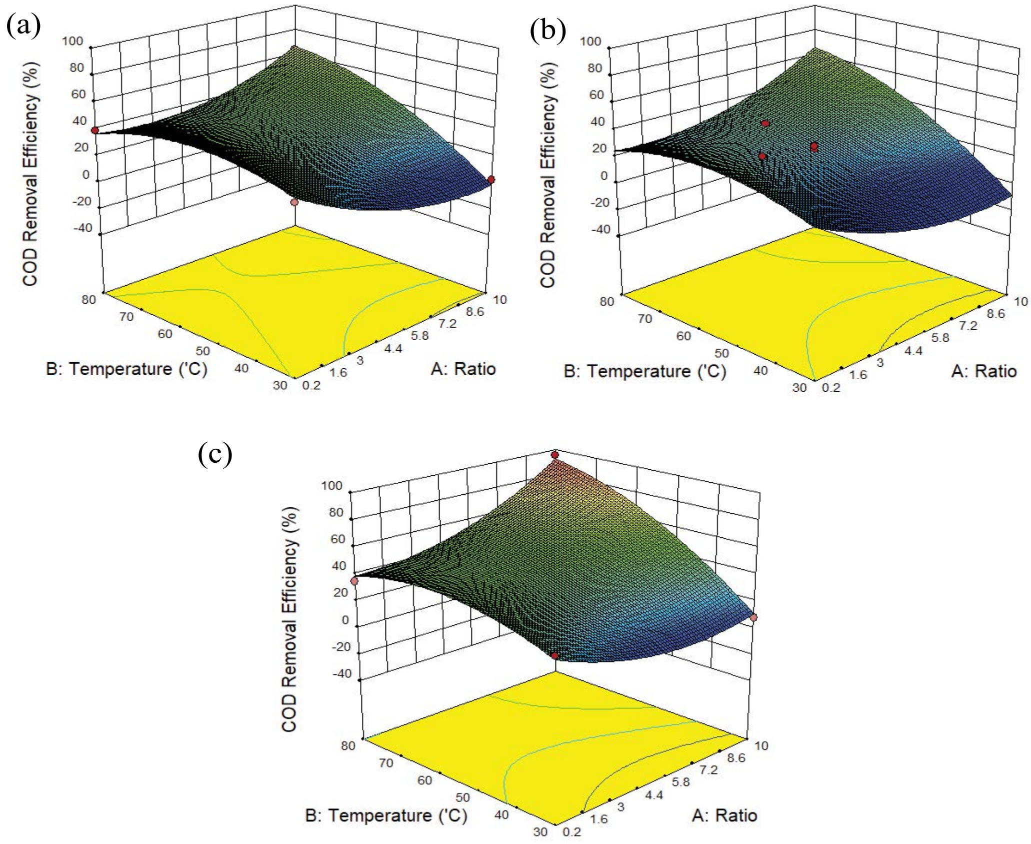

Fig. 3. Effect of temperature and $S_2O_8^{2-}$/COD ratio on COD removal efficiency at (a) 20 min, (b) 70 min and (c) 120 min.

$S_2O_8^{2-}$/COD ratio increase, COD removal efficiency increases as shown by increased green and red colour on surface graph. Under low ratio, increase of time and temperature did not result in major change of COD removal efficiency. As described by Huang et al. [27], sufficient amounts of persulfate are required to sustain degradation of contaminants. Effect of temperature is greater than that of reaction time. For example, at highest ratio, colour change along increasing reaction time is limited, while diverse colour change can be observed from increasing temperature (from blue to green finally red). Once again confirm significance of temperature factor in activation mechanism of sulphate radicals for organic compound oxidation treatment. The results in accordance with Chen et al. [30], and Guvenc [29].

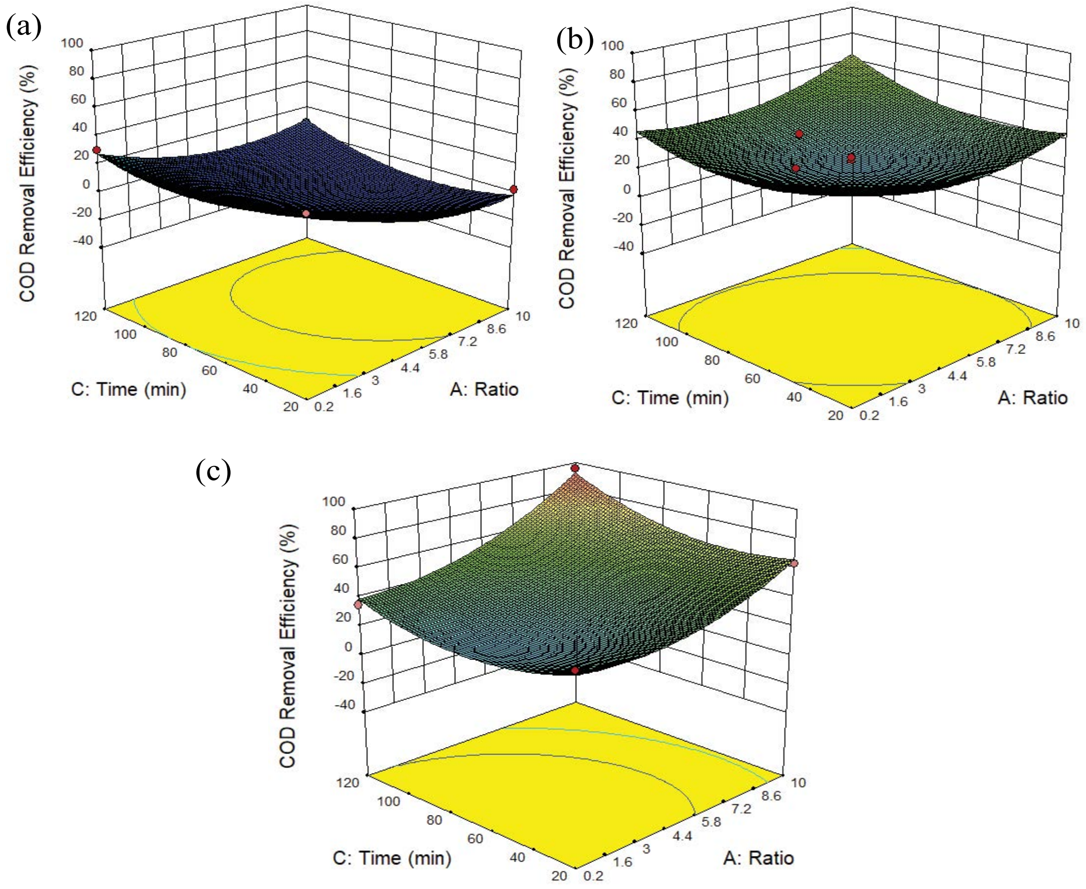

Fig. 4. Effect of reaction time and $S_2O_8^{2-}$/COD ratio on COD removal efficiency at (a) 30.0°C, (b) 55.0°C and (c) 80.0°C.

3.2.2. Effect of operation parameter on colour removal efficiency

Colour removal efficiency increased by the synergistic effect from elevated temperature and increasing $S_2O_8^{2-}$/COD ratio, as shown in Fig. 5. As describe earlier, increase temperature provide more energy for activation of persulfate, at the same time increase kinetic energy to allow more collision and reaction between oxidants and contaminants [11,31]. The same observation applied by Ahmadi et al. [31] on the degradation of Acid Blue 92. From Fig. 5, change in reaction time did not result in significant increase of colour removal efficiency. According to Dominguez et al. [13], with amount of persulfate oxidant higher than stoichiometric amount required for mineralization of contaminants, reaction time needed can be reduced. This might be able to explain situation in this case, where increase of temperature and ratio to their maximum (80°C and 10 ratio) is sufficient to mineralize most of the colour compound in leachate sample within 20 min, where further extend the reaction time become redundant. Since leachate colour is mainly contributed by organic matter and insoluble particles, the tread of colour removal efficiency is like COD removal efficiency as shown in Fig. 5.

The effect of increasing reaction time and ratio on colour removal efficiency is greatly influenced by increasing temperature. As showed by colour change, under higher temperature condition, increasing ratio significantly increase colour removal efficiency (from blue to red), in accordance with literature by Genç and Durna [12]. However, increasing reaction time did not show any relationship with the increasing ratio, as the colour removal efficiency across time change remain almost consistent under vary ratio.

3.2.3. Optimization

Process optimization by using RSM provide multiple combination sets of operation parameters which yield the maximum response value. The set with highest desirability was chosen as ultimate optimum condition, where comparison between predicted and actual optimum responses are shown in Table 7. The results of experiments result are in good agreement with predicted response. Thermal activation persulfate oxidation can achieve 93.39% COD and 94.00% colour removal efficiency at optimum condition 10 $S_2O_8^{2-}$/COD ratio, 80°C and 120 min.

3.2.4. Economic appraisal and environmental impact evaluation

Under optimum condition of 10 $S_2O_8^{2-}$/COD ratio, 80°C and 120 min, cost of sodium persulfate dosage and electricity cost for heating were calculated as below. By referring

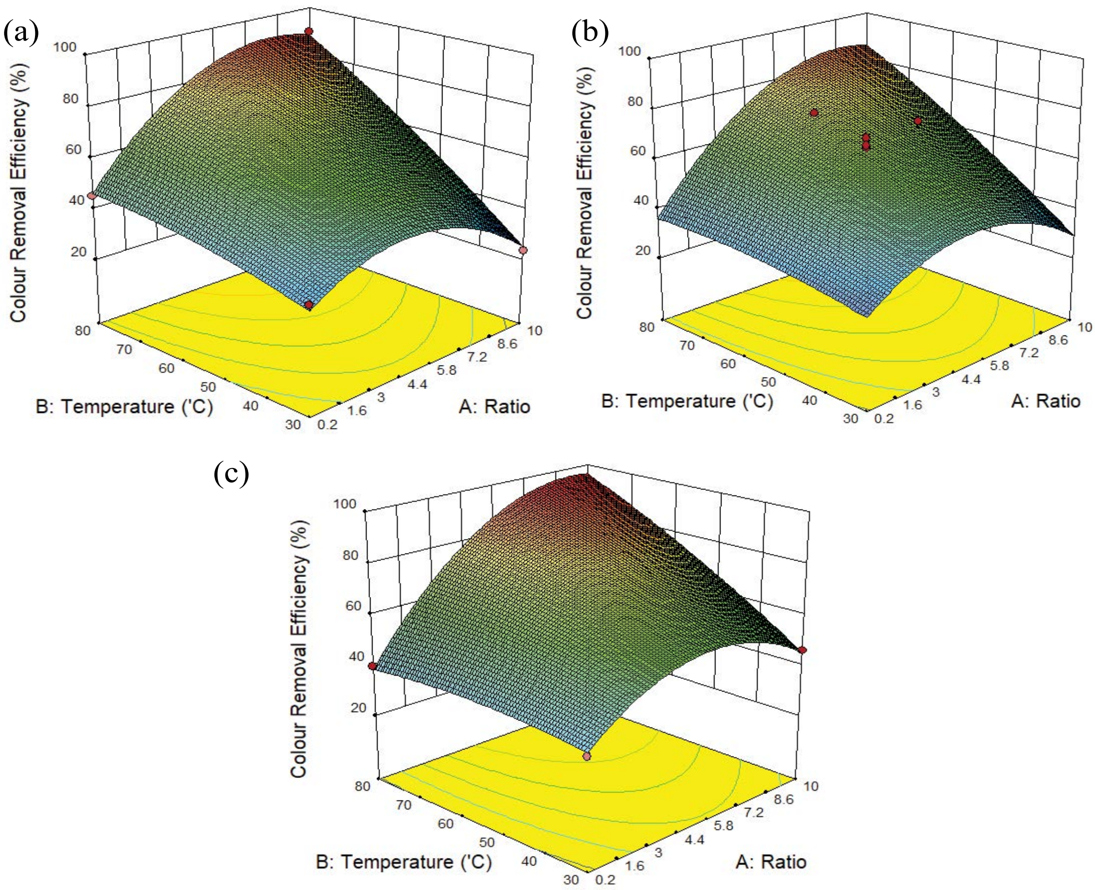

Fig. 5. Effect of temperature and $S_2O_8^{2-}$/COD ratio on colour removal efficiency at (a) 20 min, (b) 70 min and (c) 120 min.

Table 7
Response under optimum conditions

	$S_2O_8^{2-}$/COD Ratio	Temperature (°C)	reaction time (min)	COD removal efficiency (%)	Colour removal efficiency (%)
Goal/limit boundary	In range: 0.2–10	In range: 30–80	In range: 20–120	Maximize	Maximize
Predicted optimum condition and response	10	80	120	92.40	96.23
Actual condition and response	10	80	120	95.39	94.00

to sodium persulfate wholesale price of RM4.14 per kg and Malaysia's electricity tariff of RM0.365/kWh, total cost for thermal activated persulfate oxidation was RM0.67 per litre of leachate. Actual dosage and electrical consumption might be lower according to leachate influent quality. The total cost for sodium persulfate used in leachate treatment is calculated by 0.01 RM/L and the cost of electricity is 0.66 RM /L. The total cost for leachate treatment using thermal activation of persulfate oxidation was 0.67 RM/L. The final leachate effluent quality under maximum removal rate for COD and colour were 11 mg/L and 29.5 Pt/Co respectively, under conditions pH1.97 and 80°C. Both pollutant parameters have reached the Standard Discharge Limit of 400 mg/L and 100 Pt/Co (Environmental Quality (Control of Pollution from Solid Waste Transfer Station and Landfill) Regulations, 2009). However, pH adjustment and cooling services required after the treatment to readjust pH and temperature. According to Chen et al. [22], thermal activated persulfate oxidation will increase total dissolved solids (TDS) and nitrate nitrogen due to the degradation mechanism of persulfate. Possible production of toxicity sulphide hydrogen from sulphate and algal bloom due to excess nutrients must be consider for remediation.

4. Conclusion

Thermal activated persulfate oxidation showed promising results in treating landfill leachate. experiments were designed by using RSM and analyst with ANOVA. From the results, operation factor of $S_2O_8^{2-}$/COD ratio, temperature and reaction time were proven to be significant on the removal efficiency of COD and colour. Quadratic model surface graph generated by RSM reveal interaction and effect of factors on leachate treatment efficiency. Temperature and $S_2O_8^{2-}$/COD ratio showed strong synergistic effect on COD and colour removal efficiency, where temperature is the most significant factor to determine the treatment efficiency due to activation mechanism. Nevertheless, increase of $S_2O_8^{2-}$/COD ratio, temperature and reaction time increased removal efficiency of COD and colour. Under optimum condition of 10 $S_2O_8^{2-}$/COD ratio, 80°C and 120 min, removal efficiency of COD and colour achieved 93.39% and 94.00% respectively. Total cost for thermal activated persulfate oxidation on leachate was calculated as RM0.67 per litre of leachate. Final quality of leachate at 11 mg/L COD and 29.5 mg/L colour meet Malaysia Standard Discharge Limit under Environmental Quality Act. However, low pH and high temperature of leachate effluent must be adjusted before releasing into water bodies. This research performance is limited to Sahom landfill only, as no other source of leachate is used in the experiments. Nevertheless, the results and discussion are in agreement with most literature and can be used as reference for future studies.

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