Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1103305

57 (2016) 19077–19086
September

Application of the central composite design for the treatment of soft drink factory wastewater in two-stage aerobic sequencing batch reactors combined with ozonation

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Received 12 August 2014; Accepted 15 September 2015

ABSTRACT

In current study, a two-stage aerobic sequencing batch reactor (SBR) at laboratory scale was used to investigate the removal of chemical oxygen demand (COD) of a soft drink factory wastewater. The experiment was settled in series and has been combined with ozonation unit as a middle step. We evaluated the effect of three significant independent variables on the process including: mixed liquor suspended solids in both SBRs (MLSS1 and MLSS2) and feed-gas/off-gas ozone concentrations. MLSS was limited to the 3,000, 4,500, and 6,000 mg/L, for both SBRs. Central composite design matrix (CCD) was used for the experimental design and response surface methodology (RSM) was employed to optimize the experiments. The results showed that using ozonation as a middle stage between two-stage SBR significantly affects COD removal of the soft drink factory effluent. In addition, multi-stage biological process revealed that MLSS in the first-stage SBR (i.e. MLSS1) influences the COD removal efficiency. We also found that due to a reduction in organic matter of effluent in first SBR, MLSS in the second stage SBR (MLSS2) is less important than MLSS1. Maximum COD removal efficiency (up to 95%) was obtained for the following conditions: MLSS1 6,000 mg/L, MLSS2 4,500 mg/L, and employing ozone. Based on a very good matching between predicted values of the RSM model and the experimental values ($R^2 = 0.989$ and Adj-$R^2 = 0.981$), we suggest that our model can be considered for future optimization of the COD removal.

Keywords: Soft drink wastewater; COD removal; SBR; Ozonation; Central composite design; Optimization

1. Introduction

Wastewater of food industries contains large amount of high concentration organic materials that can cause major environmental problems and also are risks to human health, and accordingly, wastewaters need special treatment before discharging into water resources [1,2]. Some of these organic materials resist to physicochemical treatments and are not easily biodegradable [3]. Hence, the treatment of wastewater

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containing toxic and refractory compounds has been considered as a challenging problem [4]. Recently, variety of biological and chemical processes have been widely used for the removal of chemical oxygen demand (COD) of wastewater, such as biological treatment, advanced oxidation processes (AOP), membrane filtration processes, and combination of biological and filtration processes [5]. The most effective treatments industrial wastewater are sequencing batch reactors (SBR) and activated sludge processing tanks, which have been employed as an aerobic biological system [6]. In SBR, reactors oxygen is dispersed through the wastewater to reduce COD and biochemical oxygen demand (BOD) which makes the effluent with good quality for discharging to surface waters. These simple configuration systems have high efficiency in COD and suspended solid removal [7]. Beside the easy operation and low costs and the capacity to handle hydraulic fluctuations makes this system very beneficial [8]. However, treatment using SBRs is not sufficient to remove surfactants and the recalcitrant COD fraction to levels for direct discharge to water resources or either a receiving environment. Therefore, additional steps such as AOPs are necessary. AOPs are an innovative technique for reducing the overall organic content of wastewater and production of hydroxyl radicals ($OH^{\bullet}$) which are very reactive and short-lived oxidants [9]. AOPs include numerous combinations of ultraviolet (UV) radiation/hydrogen peroxide, ozone/hydrogen peroxide, and UV radiation/ozone. [10,11]. In wastewater treatment applications, AOPs usually refer more specifically to a subset of such chemical processes that involve ozone (O_3), hydrogen peroxide (H_2O_2), and/or UV light [12,13]. Ozone is a most important alternative AOP in wastewater treatment and allows high removal efficiency of suspended solids (SS) and COD [14]. In comparison with other oxidizer, notable advantage of ozonation is that ozone is a strong oxidant and highly efficient, decomposes rapidly, and does not produce any secondary pollution [15]. Furthermore, combination of ozone with the biological processes in wastewater treatment removes COD and increases biodegradability of the wastewater [16,17]. SBRs and ozonation are among effective treatment methods and their efficiency to remove COD of effluents have been separately investigated by many researchers. This would result in a more efficient use of the integrating biological treatment and chemical oxidant. The efficiency of COD elimination in SBRs and in an aeration tank during the activated sludge process is affected by the concentration of mass liquid suspended solids (MLSS). The trend could be intensified with increasing MLSS, however, increasing the MLSS is not economically affordable. Minimizing experimentation, time, and costs for obtaining the desired COD removal depends on the optimization of the treatment process. Therefore, the experimental design of the most important variables affecting COD removal with respect to SBRs integrated with ozonation unit can be noteworthy. In the current study, in a novel approach and at a laboratory scale, we investigated the application of experimental design to optimize COD elimination from soft drink factory wastewater using a two-stage aerobic SBR combined with ozonation. Herein, the removal efficiencies of COD in the wastewater were optimized by RSM, which is a mathematical and statistical technique for designing experiments and characterizing the optimum conditions for desirable responses. The effects of various operating parameters including MLSS in both SBRs and also employing and non-employing conditions of ozonation were investigated.

2. Materials and methods

2.1. Experimental setups and operation

The schematics of lab-scale plant consisted of two-stages sequencing batch reactors (TSSBR) are presented in Fig. 1. The two-stage process is a combination of two independent SBR plants which work in series. Schematic diagram and real photograph of ozonation unit are shown in Fig. 2. Each SBR unit consisted of a cylindrical reactor with a working volume equal to 1 L. The SBRs are aerated through a sintered glass stone as oxygen which was supplied by infusion at a flow rate of 2 L/h. In order to support the

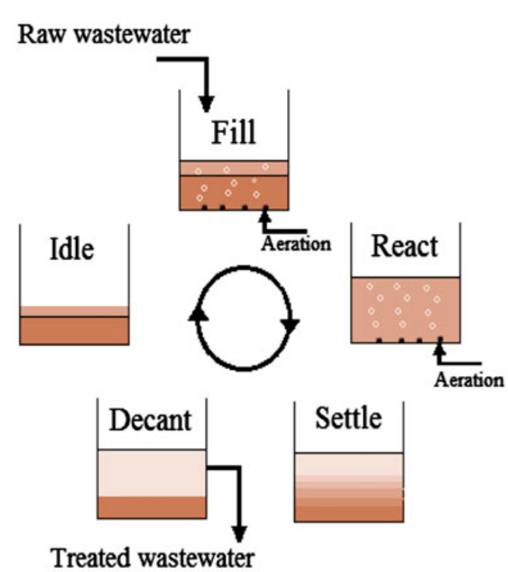

Fig. 1. Schematic diagram of the SBR process.

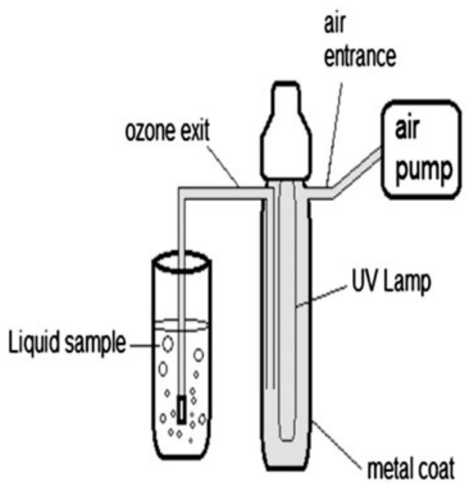

Fig. 2. Schematic of diagram the ozone process.

microbial growth, the porous stones were uniformly distributed close to the bottom of the each reactor in the liquid phase. Activated sludge from a soft drink wastewater treatment plant (located in Kermanshah in the west of Iran) was used as inoculums. In order to provide a suitable condition for micro-organisms growth, nutrients such as nitrogen and phosphorous entered into the reactors to obtain a COD:N:P ratio of about 100:7:1. During the first 9 d of operation, the biomass was permitted to acclimatize to the influent substrate. According to conventional SBR treatment systems, the operation of used SBRs consisted of the batch steps of fill, react, settle, decant, and idle in a cyclic operation with complete aeration during the reaction period to oxidize the organic matter. In which, all steps are accomplished in a single tank. Regarding to this point that the COD removal can affected by the increase in MLSS concentrations, the system was settled to operate at different MLSS concentrations, equal to 3,000, 4,500, and 6,000 mg/L. The ozone experiments were carried out in a bubble column reactor with working volume approximately 1 L. Producing ozone system was consisted of a stainless steel cylindrical vessel with a mercury vapor lamp (power of 300 W) inside the running length of the tube (Fig. 2). The ozone stream was fed into the wastewater through the bubble gas with a uniform flow rate about the 500 mg/h.

All experiments were performed at environment temperature, which is about 25℃. The initial COD of wastewater used in the process was 2,500 mg/L. Generally, plant operation is based on the succession of 24.5 h treatment cycles, each including three consecutive stages: a preliminary biological degradation (with a 12 h time lag), ozonation degradation (with a 0.5 h time lag), and finally the ozonated wastewater return to the SBR reactor for the final biological treatment in which the effluent from the first-stage process was fed in to the next stage process. Samples were taken from the end of every stage.

2.2. Ozonation process

The ozone experiments were carried out in bubble column reactor (working volume: 1 L). Producer Ozone was consisted of a stainless steel cylindrical vessel with a mercury vapor lamp inside the running length of the tube (Fig. 2). The lamp power is 300 W. The ozone stream was fed into the wastewater through a bubble gas.

2.3. Analytical methods

The ozone was bubbled into 2% KI solution, where the potassium iodide solution reacted with the excess ozone. The generating iodine was titrated using standard sodium thiosulfate, in the presence of starch as indicator. The quantities of unused ozone were determined, accordingly [18]. Analytical procedures followed in this study for MLSS determinations were those outlined in standard methods for the examination of water and wastewater [19].

2.4. COD test

In environmental chemistry, COD test is generally utilized to indirectly estimate the amount of organic compounds present in water [20,21]. COD is specified as the mass of oxygen required for the complete oxidation of an organic compound in water [22]. There has been suggested a standard method to determine the COD in wastewater. Principle of the standard COD test is that the organic matter present in sample gets oxidized completely by potassium dichromate ($K_2Cr_2O_7$) in the presence of H_2SO_4 and silver sulfate (Ag_2SO_4) [23]. In our experiment, the sample was refluxed with specific amount of potassium dichromate ($K_2Cr_2O_7$) in the sulfuric acid medium and the excess potassium dichromate was measured by titration ferroxine (Fe^{2+}) where ferroin was used as an indicator. In other word, the organic matter was oxidized over a 2-h heating period and after this time, the concentration of the remaining dichromate was measured by titration with ferroxine (Fe^{2+}). For the MLSS measurements, 50 ml of sample was filtered and placed in an oven at 103℃ for one hour and the biomass weight was found out by dry filter paper weight. The percentage of COD removal was calculated as follows:

$$\mathrm{COD}\,(\%) = \frac{C_\mathrm{i} - C_\mathrm{f}}{C_\mathrm{i}} \times 100 \tag{1}$$

where C_i and C_f are the initial and final concentrations of COD (mg/L).

2.5. Experimental design and optimization

The application of design of experiments (DOE) methods allowed us to quantify the effect of changes in wastewater treatment process conditions. Meanwhile, the optimization of COD removal conditions is particularly problematic for the development of economically feasible treatment processes.

Response Surface Methodology (RSM) is a body of techniques for DOE and, as an useful and efficient mathematical approach, has successfully been used in the optimization of the treatment process [24]. RSM can be applied to determine the relationship between the dependent (i.e. response) and independent (i.e. explanatory) variables, as well as to optimize the relevant processes [25]. One of the most popular response surface designs is the central composite design (CCD), which is an effective design method for constructing a second-order (i.e. quadratic) model for the response variable without any obligation to apply a complete three-level factorial experiment [26]. In the present study, we aimed to evaluate the application of RSM to design optimization of process variables relate to the degradation of COD concentration of soft drink wastewater. COD removal from soft drink wastewater was optimized via RSM packages in Design Expert 8.1. The design of runs was in accordance with CCD with bounds of the three independent parameters. Mass liquid suspended solid concentration in the first SBR reactor (MLSS1) and Mass liquid suspended solid in the second SBR reactor (MLSS2) were chosen as two independent variables in the degradation process and, ozone concentration was controlled as feed-gas and off-gas. Table 1 shows the arrangements of independent and dependent variables used in the statistical analysis of the present study. This setup allowed to develop an empirical equation as a function of MLSS in the first stage SBR (x_1), MLSS in the second stage SBR (x_2), and UV irradiation as on and off (x_3).

Table 1
Independent variables and their levels for the CCD used in the present study

Variables	Symbol	Coded variable levels		
		−1	0	+1
MLSS1 (mg/l)	X_1	3,000	4,500	6,000
MLSS2 (mg/l)	X_2	3,000	4,500	6,000
Ozone	X_3	Off	–	On

The CCD consists of 2^n factorial runs, $2n$ axial runs and six center runs, where n is the factor numbers. In the case of three factors, the full design matrix of 2^3 factorial points, 3 axial points, and 6 replications at the design center resulted in the total number of experiments equal to 20 ($=2^3 + 2(3) + 6$). The experimental data achieved from the CCD model experiments can be represented by the following equation [27–29]:

$$Y = b_0 + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} b_{ii} x_i^2 + \sum_{i=1}^{n-1}\sum_{j=i+1}^{n} b_{ij} x_i x_j + e_i \tag{2}$$

where Y is the response; b_0 is the constant coefficient; n is the number of studied factors; x_i and x_j are the factors; b_i, b_{ii}, and b_{ij} are the coefficients of linear, quadratic and first-order interaction, respectively, i and j are the index numbers of factor; and e_i is error. We also evaluated the significance of regression equation between dependent and independent variables using the analysis of variance (AVOVA). The polynomial model quality is expressed by the determination of coefficient such as R^2 and Adj-R^2. In order to perform the statistical calculations, x_i defines as a dimensionless value of the independent variable and the real value of an independent variable (X_i) is coded as x_i that given by [30,31]:

$$x_i = \frac{X_i - X_0}{\delta X} \tag{3}$$

where X_0 is the value of X_i at the center point, and δX is the step change. The experimental values vs. run numbers are shown in Fig. 3.

3. Results and discussion

3.1. Development of regression model equation

The resulted responses were evaluated via Design Expert. 8.1 using approximating models of COD concentration as dependent variables (i.e. Y). The complete design matrix together with the values of both responses based on the experimental runs is presented in Table 2. The first four columns show run numbers and experimental conditions of the runs as arranged by the CCD. In accord with the RSM results, polynomial regression modeling was carried out the responses of the fitting to uncoded values of the three different process variables, and the results were appraised. For COD removal, quadratic models were

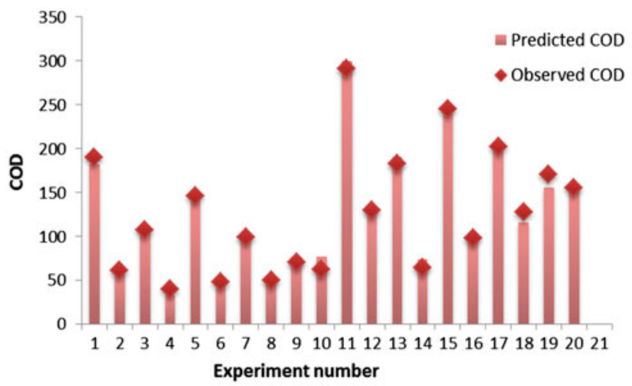

Fig. 3. Comparison between predicted and experimental COD.

suggested by the software and the predicted response (Y) for the effluent COD concentration of samples treated was obtained using Eqs. ((4) and (5)) as follows:

x_3 = on:

$$Y = 579.9 - 0.12438\,x_1 - 0.04971\,x_2 + 0.00000578\,x_1x_2 + 0.0000073\,x_1^2 + 0.000000746\,x_2^2 \quad (4)$$

x_3 = off:

$$Y = 7736 - 013916\,x_1 - 006038\,x_2 + 000000578\,x_1x_2 + 00000073\,x_1^2 + 0000000746\,x_2^2 \quad (5)$$

In this equation, Y is the effluent COD concentration for the treatment of soft drink wastewater; and x_1, x_2, and x_3 are the corresponding coded variables of MLSS1, MLSS2, and ozone, respectively. As we mentioned before coefficients of x_i, x_i^2, and x_ix_j refer to coefficient of linear, quadratic, and first-order interaction relationships, respectively. The results of regression models are represented in Table 3. Accordingly, we obtained a remarkably high value of discrimination coefficient (i.e. $R^2 = 0.989$, $p < 0.0001$) for the model which confirms a substantially strong relationship between the response variable (i.e. COD removal) and independent variables. In addition, an admissible agreement with the adjusted determination coefficient is essential. Consequently, we also found a high value of the adjusted determination coefficient (adjusted R^2), showing the high significance of the model [30].

3.2. Statistical analysis

The surface quadratic model for COD removal using ANOVA for all responses is summarized in Table 3. ANOVA is requisite to identify the significance and adequacy of the developed models. Polynomial models using a number of different degree models were employed for data fitting (Table 3). The quality fit of the polynomial model equation is expressed by the coefficient of determination R^2 and

Table 2
CCD experiments for treatment by combined SBR with ozonation

	Codified values			Experimental values			Effluent COD concentration (mg/l)
Experiment number	X_1	X_2	X_3	$MLSS_1$	$MLSS_2$	UV	
1	−1	−1	+1	3,000	3,000	On	190
2	+1	−1	+1	6,000	3,000	On	61
3	−1	+1	+1	3,000	6,000	On	107
4	+1	+1	+1	6,000	6,000	On	40
5	−1	0	+1	3,000	4,500	On	146
6	+1	0	+1	6,000	4,500	On	48
7	0	−1	+1	4,500	3,000	On	99
8	0	+1	+1	4,500	6,000	On	50
9	0	0	+1	4,500	4,500	On	70
10	0	0	+1	4,500	4,500	On	62
11	−1	−1	−1	3,000	3,000	Off	291
12	+1	−1	−1	6,000	3,000	Off	130
13	−1	+1	−1	3,000	6,000	Off	183
14	+1	+1	−1	6,000	6,000	Off	64
15	−1	0	−1	3,000	4,500	Off	245
16	+1	0	−1	6,000	4,500	Off	98
17	0	−1	−1	4,500	3,000	OFF	202
18	0	+1	−1	4,500	6,000	Off	127
19	0	0	−1	4,500	4,500	Off	170
20	0	0	−1	4,500	4,500	Off	155

Table 3
ANOVA regression model for COD degradation of soft drink wastewater

Source	df	Sum of squares	Mean squares	F-value	p-value
Model	8	93,097.52	11,637.19	125.712	<0.0001
X_1	1	43,320.08	43,320.08	467.968	<0.0001
X_2	1	13,467	13,467.00	145.478	<0.0001
X_3	1	31,363.2	31,363.20	338.803	<0.0001
X_1X_2	1	1,352	1,352.00	14.605	0.0028
X_1X_3	1	1,474.083	1,474.08	15.924	0.0021
X_2X_3	1	768	768.00	8.296	0.0150
X_1^2	1	1,259.524	1,259.52	13.606	0.0036
X_2^2	1	13.14881	13.15	0.142	0.7134
Residual	11	1,018.276	92.57		
Lack of fit	9	873.7762	97.09	1.344	0.4978
Pure error	2	144.5	72.25		
Cor total	19	94,115.8			

Notes: S = 9.621, PRESS = 3,723.698, R^2 = 98.9%, R^2_{pred} = 96%, and R^2_{adj} = 98.1%.

adjusted R^2. Parameters such as F-value, p-value, Lack of Fit, and R^2 are the measure of how the quadratic model fit the experimental values [30]. Based on our statistical analysis, the models were found to be highly significant ($p < 0.0001$), and the independent variables were significant at the 99% confidence level. The p-value (Eq. (5)), also demonstrated that the second-order polynomial model fitted the experimental results as well. x_1, x_2, x_1x_2, x_1^2, and x_2^2 were significant terms ($p < 0.05$), revealing that MLSS1, MLSS2, and the interaction effect of MLSS1 and MLSS2 are the key factors for the COD elimination. The models F-value of 125.712 in this table hints that the model is significant for the COD removal and there is only 0.01% chance that model F-values could occur due to noise. The "Lack of Fit F-value" of 1.344 demonstrated the Lack of Fit is not significant relative to the pure error. There was a 49.78% chance that a "Lack of Fit F-value" with this large value can be occur because of noise for COD removal. The diagnostic plot given in Fig. 4 was used for appraising the fitness of the regression model. Based on this figure, we found that the experimental values were distributed relatively close to the straight line, indicating a satisfactory correlation between these values, and accordingly, reliability and adequacy of experimental models for comparative responses were certified.

3.3. Effect of variables on COD removal

We investigated the effects of x_1, x_2 (i.e. $MLSS_1$ and $MLSS_2$), and x_3 (i.e. ozone) on COD removal efficiency. Fig. 5 depicts the variable interaction for MLSS1, MLSS2, and ozone dose as feed-gas or off-gas. According to this figure, the COD value reduces drastically as soon as the sludge is added. Considering the effect of increasing MLSS1, it seems that high liquor suspended solids (MLSS) concentration in SBR1 is beneficial to COD removal. In the begging, the MLSS of SBR1 and the microbial metabolism are low, and consequently, COD was quite high. After that, with a continuing increase in sludge, COD will be decreased. This reduction can be demonstrated by the following three reasons: (a) entrapment of COD in the flocs, (b) COD adsorption to the microbe surfaces, and (c) ingestion of COD inside the microbes [32]. However, in spite of COD reduction in wastewater, the treatment remains incomplete because of possibility presence of non-biodegradable in treating effluent.

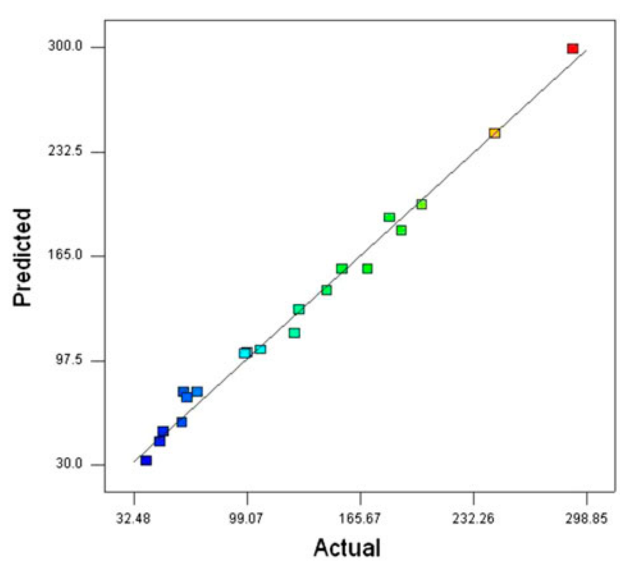

Fig. 4. The actual and predicted COD removal.

Therefore, for the removal of this non-biodegradable material, it is necessary to use ozone after biological treatment. In combined utilization of biological process and ozonation, ozone as chemical oxidation can change the molecular structure of compounds that are non-biodegradable and breakdown them into smaller molecules [14]. Accordingly, the material products generally have better and rather aerobic biodegradability than the original compounds. Indeed, the location of the ozonation unit in this process is very important. At the first stage, once the wastewater was treated using a biological process in SBR1, the organic material of it will be reduced, and subsequently, because of reducing receptive ozone material the value of required ozone is considerably decreased. Therefore, we suggest that using ozone as a middle step and after biological treatment is the best alignment with higher efficiency. According to Fig. 5(a) and (b), and as we expected, in the condition of ozone-feeding COD is lower than the state of no ozonation. For example, with MLSS1 equal to 4,500, COD at ozonation condition are approximately 2 times lower than that condition of no employing ozone, confirming that ozonation in this process is an effective method, which successfully can reduce organic matter and increase the COD removal efficiency. Referring to Fig. 6(b), an increase in MLSS2 has similar trend to MLSS1, but as far as the value of COD considerably decreased in SBR1, the effect of increase in MLSS2 is lower than that of MLSS1. It is important to keep in mind that the presence of SBR2 after the ozonation unit is necessary, and it is due to the purpose of eliminating the material in wastewater which change to biodegradable material through ozonation.

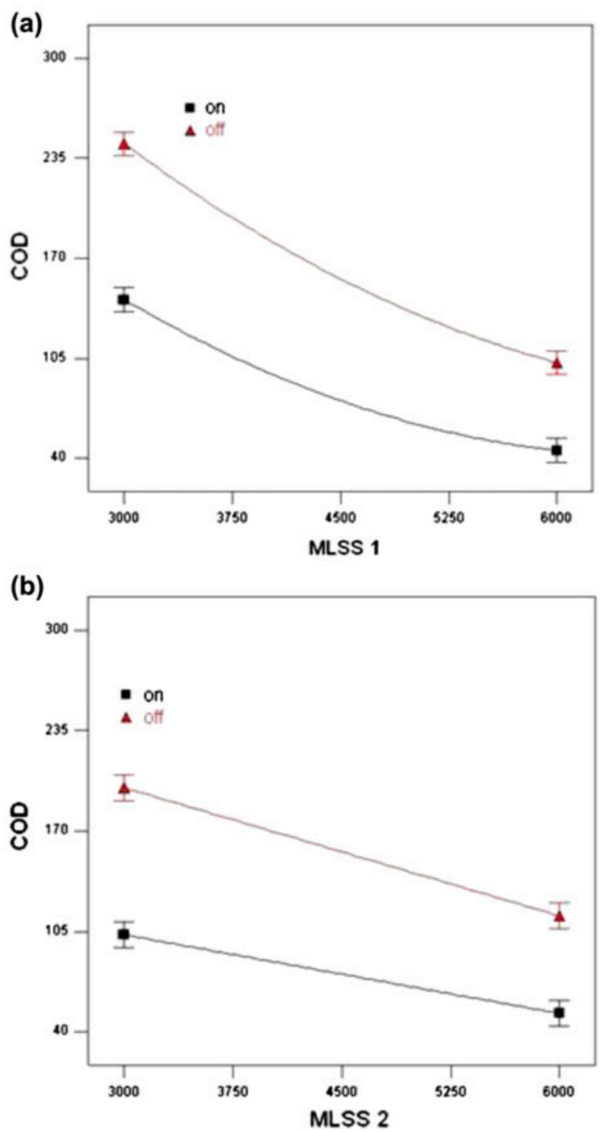

Fig. 5. Interactive effect of MLSS1 and ozone dose on COD, Interactive effect of MLSS2 and ozone dose on COD ((a) and (b)).

To investigate the integrated effect of MLSS1 and MLSS2, RSM was employed and the results were depicted as 3D plots. Fig. 6 demonstrates the effect of MLSS1 and MLSS2 on the COD uptake, in the condition of off-gas ozone concentration and implies that these parameters have considerable influence on the COD degradation. From the figure, the COD decreases with an increase in the MLSS1 and MLSS2. Generally, as the MLSS1 increases, higher microbial metabolism occurs, which could increase the consumption of organic matter. In addition, it is observed that when ozone not used, MLSS2 played an important role during COD reduction. Indeed, at any MLSS1 concentration, an increase in MLSS2 value from 3,000 to 6,000 g/l leads to decrease in COD, which it means increasing COD removal efficiency. Comparison between Figs. 6 and 7 implies that a combination of these two stages of SBRs system with ozonation is superior to using just a simple SBR process for the effective removal of organic matter from soft drink wastewater.

3.4. Optimization of experiment conditions

Optimization of the condition of COD removal in multi-stage treatment processes is more complex than single stage as the performance of both stages is combined. In the case study of this work, in order to obtain a large degree of depuration at the lowest operational costs, the ideal value of MLSS1 and MLSS2 must be determined by an optimization of the two-stage SBR and ozonation system. Because multi-stage activated biological process suppresses the production

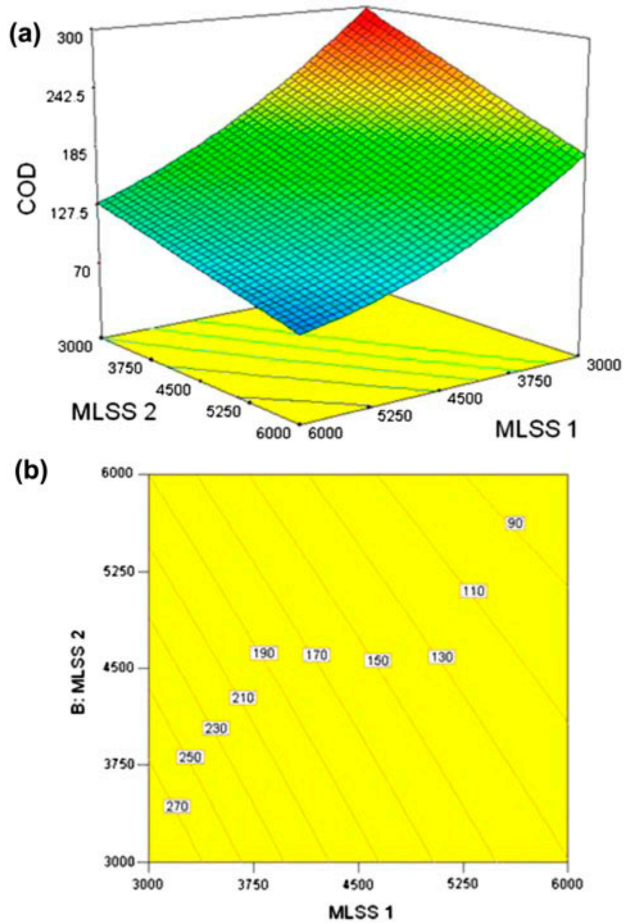

Fig. 6. Response surface and contour plots of COD removal rate without ozonation. Interactive effects of MLSS1 and MLSS2 on COD removal rate ((a) and (b)).

of extra sludge [33]. It decreases sludge disposal costs. CCD is used to optimize the parameters affecting the COD removal responses. The optimum treatment conditions are obtained using ozone and MLSS1 of 4,500 mg/L and MLSS2 at 3,000–4,500 mg/L. The optimum treatment showed COD removal up to 96%.

4. Conclusion

In this work, the optimization of two SBR processes combined with an ozonation unit with respect to COD removal for the treatment of soft drink factory wastewater was investigated. RSM was utilized to assess the interactive effects of three critical process parameters on COD removal and to optimize the experiments. Experimental findings revealed that using ozone as an oxidant in a middle stage between a two-stage aerobic SBRs is an effective treatment method for efficient COD removals from soft drink production wastewater.

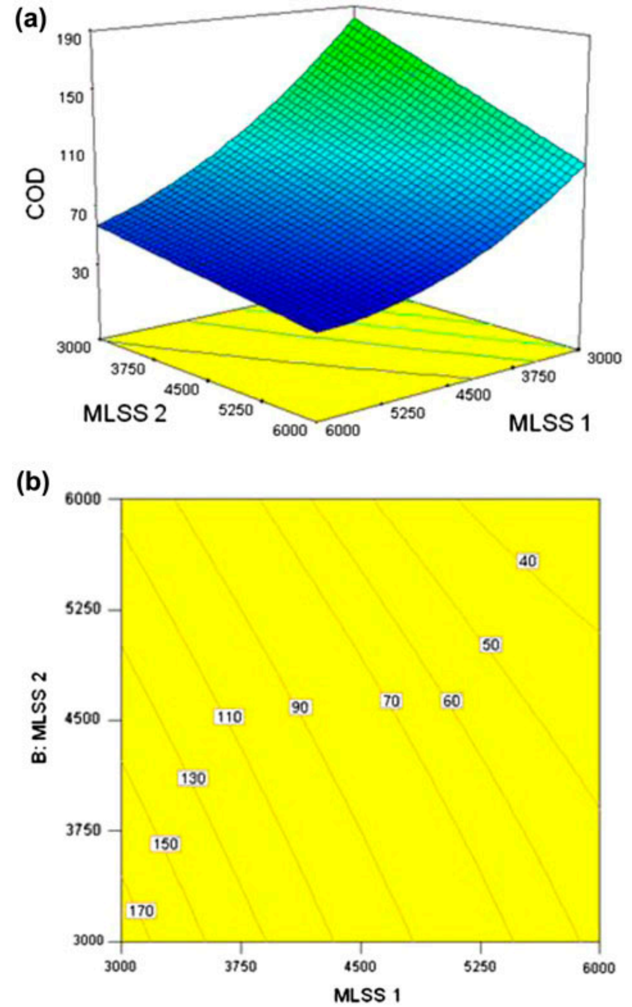

Fig. 7. Response surface and contour plots of COD removal rate with ozonation. Interactive effects of MLSS1 and MLSS2 on COD removal rate ((a) and (b)).

The proposed quadratic model fitted very well with the experimental data with $R^2 > 0.98$ for all responses. Statistical analysis of the data indicated that MLSS concentrations in first stage SBR had a significant effect on COD removal. The optimum process conditions for COD removal efficiency were up to 95% at 4,500 and 3,000–4,500 mg/L for MLSS1 and MLSS2 concentrations, respectively, and in the condition of feed-gas ozonation. Accordingly, we suggest RSM as an efficient method that could be effectively adopted to optimize multi-factor conditions in multi-stage SBR processes.

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