



Effects of partial ozonation on activated sludge process for the minimization of excess sludge production during biological treatment

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ABSTRACT

Minimization of excess sludge production may be achieved by either changes in operational conditions or by the treatment of recycled activated sludge. It was investigated using ozone-treated return activated sludge in lab-scale activated sludge process operated continuously with optimum conditions determined using Box–Behnken experimental design method as 400 mg/L initial chemical oxygen demand concentration (COD_i), 25 h hydraulic retention time, and 25 d solid retention time, respectively. Batch experiments were carried out in order to determine the optimum ozone dose of 0.05 g O₃/g total solid considering disintegration degree (DD). Ozone reactor (OR) and control reactor (CR) were evaluated considering sludge reduction capacity, effluent quality, and sludge characteristics. About 61 and 40% reductions can be achieved in mixed liquor suspended solid concentration and observed sludge yield value in OR compared to CR, respectively. The effluent quality in terms of COD and NH₄-N removal in OR was not significantly affected by ozonation. The dewatering capacity was slightly weakened while little improvement was observed in filtering capacity in OR compared to CR, in terms of capillary suction time and specific resistance to filtration. Particle size changed and sludge destruction led to an increase of small particles.

Keywords: Sludge minimization; Ozonation; Cell lysis; Box–Behnken experimental design

1. Introduction

Conventional activated sludge process is commonly used biological treatment method with high excess sludge production. Huge amount of sludge produced during biological treatment becomes a

serious problem. Sludge treatment and disposal is an important drawback accounted for 25–60% of the total cost of wastewater treatment plant [1]. So, to develop methods of reducing excess sludge produced during wastewater treatment rather than the post-treatment become very important issue in the wastewater treatment technology [2–4]. Sludge reduction at the source is an ideal solution for sludge disposal problem.

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The researchers are forced by the stringent regulations to develop new methods regarding sludge treatment and disposal for the minimization of excess sludge production [3].

Minimization of the excess sludge production may be achieved by either changes in operational conditions (extended aeration, membrane bioreactor, improved aeration, chemical uncouplers, etc.) or by treatment of the recycled activated sludge (acid or base hydrolysis, thermal treatment, ozonation, mechanical disintegration, etc.). Changes in operational conditions are mainly focused on promoting disappearance of suspended organic matter by mechanisms such as maintenance, endogenous respiration, and decay of cells or grazing by higher organisms while the treatment of recycled activated sludge is focused on promoting lysis of biomass by adverse environmental conditions (pH, oxidant conditions, or temperature) [5].

Less excess sludge production is proposed using minimization techniques which include lysis-cryptic growth, uncoupling metabolism, and micro-fauna predation mechanisms [5–12]. Generally, sludge reduction technologies are based on lysis-cryptic growth. Lysis and biodegradation are the stages of lysis-cryptic growth. If the lysis stage is promoted, the sludge production can be reduced [3]. The disintegration methods induce microbial cells lysis and cell contents are released. The cell wall of micro-organisms can be disrupted with ozonation. The ozone-treated sludge containing soluble organics from the disrupted cells [4] is returned to the bioreactor for degradation. This extra organic substrate is reused in microbial metabolism and a part of the carbon is released as respiration product. The biomass production is reduced as a result of lysis-cryptic growth [13].

Sludge ozonation is one of the effective methods with the highest disintegration degree (DD) [14]. The minimization of excess sludge production can be achieved by partial ozonation of the returned sludge in an activated sludge process [15–17]. The ozone oxidation leads to sludge decomposition process described as floc disintegration, solubilization, and mineralization [18]. Sludge degradation in an aeration tank can be improved after ozonation and minimization of excess sludge production can be achieved recirculating the ozone treated sludge into the aeration tank [19]. Torregrossa et al. [20] compared the ozonation and oxic-settling anaerobic process considering excess sludge production and biomass activity. The results showed that both technologies could minimize the excess sludge production with a slight decrease of biomass respiratory activity.

Ozonation also changes the characteristics of the sludge. A large number of micro-particles dispersed

in the supernatant are generated in addition to soluble organic substances by floc disintegration and solubilization [21].

Since, minimization of the excess sludge production may be achieved by both changes in operational conditions (extended aeration) and by treatment of the recycled activated sludge (ozonation), in this study, the operational conditions of activated sludge process were determined using Box–Behnken statistical design program and then the partial ozonation was applied to one of the activated sludge process to promote cell lysis. The performances of ozone reactor (OR) and control reactor (CR) were monitored. Furthermore, the sludge reduction efficiency, effluent quality and sludge properties of both activated sludge processes were evaluated.

Briefly, this paper presents an overview of the application of sludge ozonation technologies in lab-scale plants as a solution of sludge problem at the source. Changes in the characteristics of activated sludge after ozonation, the impact of ozonation on sludge reduction, especially, settling properties and dewatering conditions were also evaluated.

2. Methods

2.1. Experimental system

A lab-scale setup consists of two activated sludge processes designed to conduct continuous disintegration experiments for the ozone application. Fig. 1 depicts a photograph of the experimental system. Each activated sludge process contained a 6L-bioreactor and a 3L-settling tank. For the start up of two processes, the activated sludge taken from treatment plant of a yeast production factory located in Izmir, Turkey was inoculated and cultivated with synthetic wastewater to domesticate two processes for approximately 30 days. The synthetic wastewater composed of diluted molasses, NH_4Cl , KH_2PO_4 , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, CaCl_2 , and FeCl_3 with a chemical oxygen demand concentration (COD)/N/P ratio of 100/5/1 was used throughout the study. A completely mixed reactor with diffused air was used to generate the sludge and the dissolved oxygen level was kept above $2\text{ mg O}_2/\text{L}$ by using of a porous stone diffuser delivering compressed air.

2.2. Optimization of operational parameters of activated sludge process: Box–Behnken statistical design program

All aerobic treatment systems are operated on some principles. Mixing regimes, solid retention time (SRT), and hydraulic retention time (HRT) are

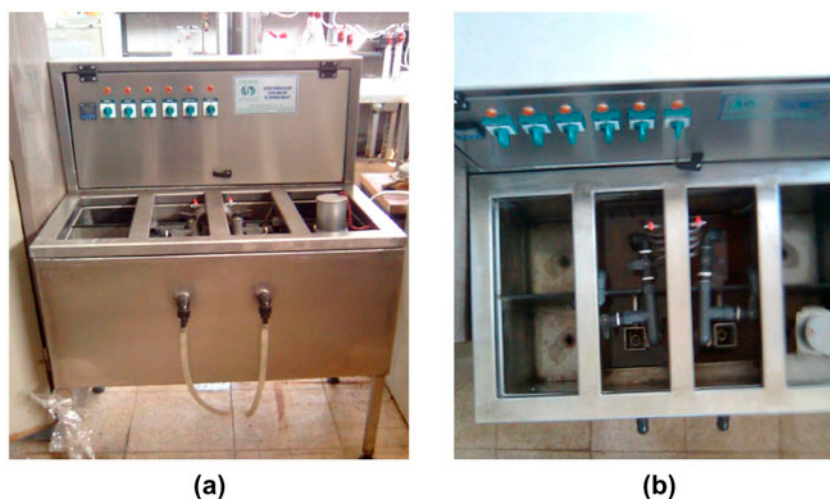


Fig. 1. (a) Experimental setup consists of two activated sludge processes and (b) Aeration and settling tanks of the activated sludge processes.

important factors for the activated sludge process. There are two parameters that relate to time in the system. The link between SRT and HRT is neither proportional nor linear and depends on the wastewater organic (COD or biochemical oxygen demand₅ [BOD₅]) concentration and the reactor suspended solids concentration (TSS) [22]. Due to this fact the optimum values of these parameters should be determined for the successful operation of activated sludge process. Box–Behnken statistical design program was used to determine the optimum operational parameters and minimize the number of parameters to be analyzed. Experiments were carried out according to the Box–Behnken statistical design program. The independent variables were chosen as (COD_i), HRT, and SRT. The low, center, and high levels of each variable designated as -1 , 0 , and $+1$, respectively are presented in Table 1.

HRT: 5–25 h, SRT: 5–30 d, and COD_i concentration (300–500 mg/L) were determined as variable parameters in order to represent the extended aeration activated sludge process (Table 1). Experimental data points used in Box–Behnken statistical design program are also given in Table 1. The mathematical relationship connecting the variables and the response can be calculated by the quadratic polynomial equation given below.

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 \quad (1)$$

where Y = predicted response, b_0 = constant, X_1 = COD_i (mg/L), X_2 = HRT (h), X_3 = SRT (days), b_1, b_2, b_3 = linear coefficients, and b_{12}, b_{13}, b_{23} = cross-product coefficients.

The design experiments were carried out for analysis using the Stat-Ease Design Expert 7.0.3 computer program for this study. Box–Behnken design requires 17 runs for a three-factor experimental design.

2.3. Continuous operation of activated sludge processes prior to modification

After the determination of optimum operational conditions of activated sludge process, two systems were operated in parallel with the optimum conditions during 45 days until the steady-state conditions. During 45 days, the effluent quality and sludge properties of the systems were monitored.

2.4. Determination of optimum ozone dose

Cost of producing and full-scale application of ozone in plants is the disadvantage of ozone usage. Since, the optimization of the sludge ozonation stage is one of the main research objectives, the efficiency of sludge solubilization is the most important parameter in evaluating the performance of sludge ozonation.

The necessary ozone dose for sludge reduction has been reported to range from 0.02 to 0.5 g O₃/g TSS [16,23–30].

In present study, when the steady-state conditions were reached, specific batch tests were carried out in order to investigate the biodegradability of disintegrated sludge and determine the optimum ozone dose. The sludge ozonation experiments were conducted for seven different ozone doses that ranged between 0.007 and 0.06 g O₃/g total solid (TS). About 400 mL of return sludge sample volume was used for

Table 1

The minimum and maximum values of the variable parameters and experimental data points for Box–Behnken statistical design program

The minimum and maximum values of the variable parameters				
Variable	Symbol	Coded variable level		
		Low level	Center level	High level
Solid retention time (SRT)	X_1	–1	0	+1
Hydraulic retention time (HRT)	X_2	5	17.5	30
Initial COD conc.	X_3	5	15	25
		300	400	500

Experimental data points for Box–Behnken statistical design program

	Factor 1 A: Initial COD (mg/L)	Factor 2 B: HRT (h)	Factor 3 C: SRT (day)
1	300.00	5.00	17.50
2	400.00	5.00	5.00
3	300.00	15.00	30.00
4	300.00	25.00	17.50
5	400.00	15.00	17.50
6	500.00	15.00	5.00
7	400.00	15.00	17.50
8	400.00	15.00	17.50
9	400.00	15.00	17.50
10	400.00	25.00	5.00
11	400.00	15.00	17.50
12	400.00	5.00	30.00
13	400.00	25.00	30.00
14	500.00	25.00	17.50
15	500.00	5.00	17.50
16	500.00	15.00	30.00
17	300.00	15.00	5.00

each experiment. Ozone was generated by a corona discharge of OZO 1VTT model ozone generator with a maximum ozone production capacity of 5 g/h. The ozone produced from pure oxygen with a purity of 99.5% was bubbled through the OR using a diffuser with the diameter of 15 mm and with the height of 25 mm. The OR was made of pyrex-glass with a total reactor volume of 2 L. Initial ozone dose (4.7 g/h) and residual ozone concentrations after reaction were measured by the standard potassium iodide absorption method [31].

After ozonation, the sludge and supernatant were analyzed in order to investigate the effect of ozonation on DD as an achievement of sludge solubilization at the end of the cell lysis for each ozone dose. The sludge lysis efficiency is represented by DD_{COD} by Zhang et al. [32] which is calculated as follow (Eq. (2)):

$$DD_{COD} = \frac{SCOD_{\text{ozone}} - SCOD_o}{TCOD - SCOD_o} \quad (2)$$

In Eq. (2), the supernatant COD of the ozonated and raw sludge sludge are represented by $SCOD_{\text{ozone}}$ and $SCOD_o$, respectively. TCOD is the total COD of raw sludge.

2.5. Modification of activated sludge process using partial ozonation

An activated sludge process coupled with ozonation for sludge reduction was proposed and developed by Yasui and Shibata [17]. Kamiya and Hirotsuji [33] reported that excess sludge production was reduced by 50% at an ozone dose of 0.01 g O_3 /g TSS in the aerobic tank. No excess sludge was produced when the ozone dose was kept as high as

0.02 g O₃/g TSS. Gardoni et al. [34] achieved a 17% of decrease in excess sludge production and a slight decrease in N and P removal efficiency in a full-scale wastewater treatment plant by ozonation.

Due to the fact that, in present study, the partial ozonation of return activated sludge process was conducted with determined optimum ozone dose. After the optimization study for ozone dose, one of the activated sludge process was modified by inserting ozonation stage. One of the systems named as OR was modified using partial ozonation. The flow rate of return sludge is 4 L/d in terms of HRT (25 h), volume of aeration tank (6 L), and recirculation ratio (0.7). So, the 20% of return activated sludge (0.2 Q_R) corresponded to 800 mL.

For ozone system, 800 mL return activated sludge was subjected to batch ozonation with optimum ozone dose during a month. The other unmodified system served as a control run (CR) and operated in parallel with the same conditions without ozonation. There was no excess sludge wastage from OR during the experimental period. The CR was performed for 25 d under SRT. The results of CR and OR were evaluated considering sludge reduction. Furthermore, sludge properties of ozonated sludge were investigated.

2.6. Analytical methods

The changes in carbon, nitrogen, and phosphorus in the supernatant after ozonation were evaluated. The sludge was centrifuged at 4,000 rpm for 30 min for the analysis of SCOD, TN, and TP. SCOD was measured according to Standard Methods using open reflux method [31]. TP and TN in the supernatant were measured using spectroquant kits numbered 14537 and 00616, respectively in a NOVA 60 photometer. TSS and VSS concentrations were also measured according to procedure given in Standard Methods [31]. Particle size distributions of sludge were monitored using Malvern Mastersizer 2000QM analyzer. Capillary suction time (CST) values were analyzed with a Triton A-304 M CST-meter. The Buchner funnel test was employed for the determination of specific resistance to filtration (SRF). All analyses were measured three times a week.

3. Results and discussion

3.1. Optimum operational parameters of activated sludge process

Box–Behnken statistical design program was used in order to determine the optimum operational conditions in the activated sludge processes. The

experiments were chosen using variable parameters and the obtained efficiencies from these experiments were based on a mathematical model. HRT, SRT, and initial COD concentration were chosen as variable parameters for the activated sludge process (HRT: 5–25 h, SRT: 5–30 d, and COD_i: 300–500 mg/L).

Seventeen experiments were carried out in two different activated sludge processes, simultaneously. The results of the experiments were obtained at least after two-week-operation period. During 2–3 weeks, COD concentration of effluent and influent was measured three times a week for each process.

The response function coefficients were determined using experimental data for each independent variable. The analysis of variance (ANOVA) program was used for the determination of most suitable response function and correlation of the experimental data. The results of the ANOVA test for COD removal are presented in Table 2. The quadratic model provided the best fit to the experimental data with the lowest standard deviation, the highest correlation coefficient (0.95), and the lowest *p*-value according to ANOVA test.

The estimated coefficients of the response functions are given in Table 3. The predicted values of the response functions and experimental data are given in Table 4. Using the equation obtained from the Box–Behnken statistical design program, the results of the variable range can be predicted. When the results of the experiments and the prediction are depicted in the figures, the optimum value of operational parameters can be obtained from the figures easily.

Response function predictions were in good agreement with the experimental data. Variations of percent COD removal with SRT at different HRT at constant initial COD concentration (300 mg/L) were depicted in Fig. 2(a). COD removal efficiency (%) increased with the increasing of SRT up to 25 days. Further increases in SRT caused slight decrease in COD removal efficiency for all HRT values. When the initial COD concentration was 300 mg/L, HRT = 25 h, and SRT = 25 d, the highest COD removal efficiency was obtained. The predicted COD removal efficiency was found as 99.93%. Due to this fact the optimum COD_i/SRT/HRT ratio was 300 mg/L/25 d/25 h.

Variations of COD removal efficiency (%) with SRT at different HRT at constant initial COD concentration (400 mg/L) were depicted in Fig. 2(b). When COD_i: 400 mg/L, HRT: 20 h and SRT: 25 d, percent COD removal was the highest. The predicted COD removal efficiency was found as 98.78% using the equation. Meanwhile, 20 h for HRT, 25 d for SRT and 400 mg/L for initial COD concentration could be chosen as the optimum values for operational parameters.

Table 2
ANOVA analysis for COD removal efficiency

Source	Sum of squares	df	Mean square	F value	p-value Prob > F	
<i>COD removal (%)</i>						
Mean vs. total	1.546E+005	1	1.546E+005			
Linear vs. mean	199.95	3	66.65	8.55	0.0021	
2FI vs. Linear	11.75	3	3.92	0.44	0.7313	
Quadratic vs. 2FI	76.70	3	25.57	13.89	0.0025	Suggested
Cubic vs. quadratic	11.86	3	3.95	15.41	0.0116	Aliased
Residual	1.03	4	0.26			
Total	1.549E+005	17	9111.14			
<i>Lack of fit tests</i>						
Linear	100.31	9	11.15	43.45	0.0012	
2FI	88.56	6	14.76	57.54	0.0008	
Quadratic	11.86	3	3.95	15.41	0.0116	Suggested
Cubic	0.000	0				Aliased
Pure error	1.03	4	0.26			
<i>Model summary statistics</i>						
Standard deviation		R^2	Adj. R^2	Press		
Linear	2.79	0.6636	0.5860	190.10		
2FI	2.99	0.7026	0.5242	368.74		
Quadratic	1.36	0.9572	0.9022	191.36		Suggested
Cubic	0.51	0.9966	0.9864	+		Aliased

Table 3
Response function coefficient for COD removal efficiency (%)

Coefficients	Value
b_0	107.1719
b_1	−0.09977
b_2	−0.2229
b_3	1.335136
b_{12}	0.001678
b_{13}	−0.00025
b_{23}	0.00132
b_{11}	7.5E−05
b_{22}	−0.0118
b_{33}	−0.02565

Variations of percent COD removal with SRT at different HRT at constant initial COD concentration (500 mg/L) were depicted in Fig. 2(c). When CODi: 500 mg/L, HRT: 25 h, and SRT: 25 d, the highest COD removal efficiency was obtained. The predicted COD removal efficiency was found as 99.2% using the equation. The conditions 20 h for HRT, 25 d for SRT, and 500 mg/L for initial COD concentration were

determined as the optimum values for operational parameters.

Consequently, three different initial COD concentrations were performed with Box–Behnken statistical design program. Each figure given in Fig. 2 agreed with the others regarding optimum operational conditions. About 400 mg/L of initial COD concentration was determined as the best representative value of COD concentration for domestic synthetic wastewater. About 25 h and 30 d were determined as optimum values for HRT and SRT, respectively. According to the experimental results, 20 h of HRT could be determined as optimum value; however, there was no significant difference between 20 and 25 h for the COD removal efficiency. When HRT was determined as 25 h, the flow of feed wastewater of the system per day was lower than the 20 h of HRT. Because of the lower synthetic wastewater demand, 25 h was determined as an optimum value for HRT.

3.2. Steady-State conditions of activated sludge process before modification

The steady-state conditions given in Table 5 were reached after 45 days of operation.

Table 4
Experimental and predicted COD removal efficiency (%)

		Exp.COD (%) COD removal (%)	Prd.COD (%)
1	1	100	99.42
9	2	87.5	86.77875
7	3	100	100.8713
3	4	100	98.4075
14	5	96.92	97.448
6	6	89	88.12875
16	7	96.88	97.448
13	8	97.7	97.448
17	9	97.92	97.448
10	10	88.5	88.79125
15	11	97.82	97.448
11	12	95.69	95.39875
12	13	97.35	98.07125
4	14	97.39	97.97
2	15	90.68	92.2725
8	16	97.76	92.2725
5	17	90	96.45875

3.3. Optimization of ozone dose

About 0.007–0.06 g O₃/g TS was applied to the return activated sludge and the SCOD concentrations of the supernatant of the ozonated sludge were measured and the results showed an increment with the increasing of the ozone dosage as given Table 6. It was concluded that ozonation resulted in cell lysis and the increase in SCOD was mainly due to cell lysis. The changes of DD with the increasing of the ozone doses were also given in Table 6. The DD increased with ozone dose increment but not linearly. A 10% sludge lysis was achieved at the ozone dose of 0.007 g O₃/g TS. The efficiency of sludge solubilization was only around 9.76% at an ozone dose of 0.007 g O₃/g TS. Thereafter, efficiency of sludge solubilization increased rapidly to around 56.19% at an ozone dose of 0.05 g O₃/g TS. When the ozone dose was 0.05 g O₃/g TS and the reaction time was 89 min, TSS and VSS decreased by 4,550 and 3,150 mg/L; the remaining TSS and VSS were 1,300 and 1,250 mg/L; the corresponding reduction ratio was 77.77 and 72.72%, respectively. The DD_{COD} was calculated as 56.14%.

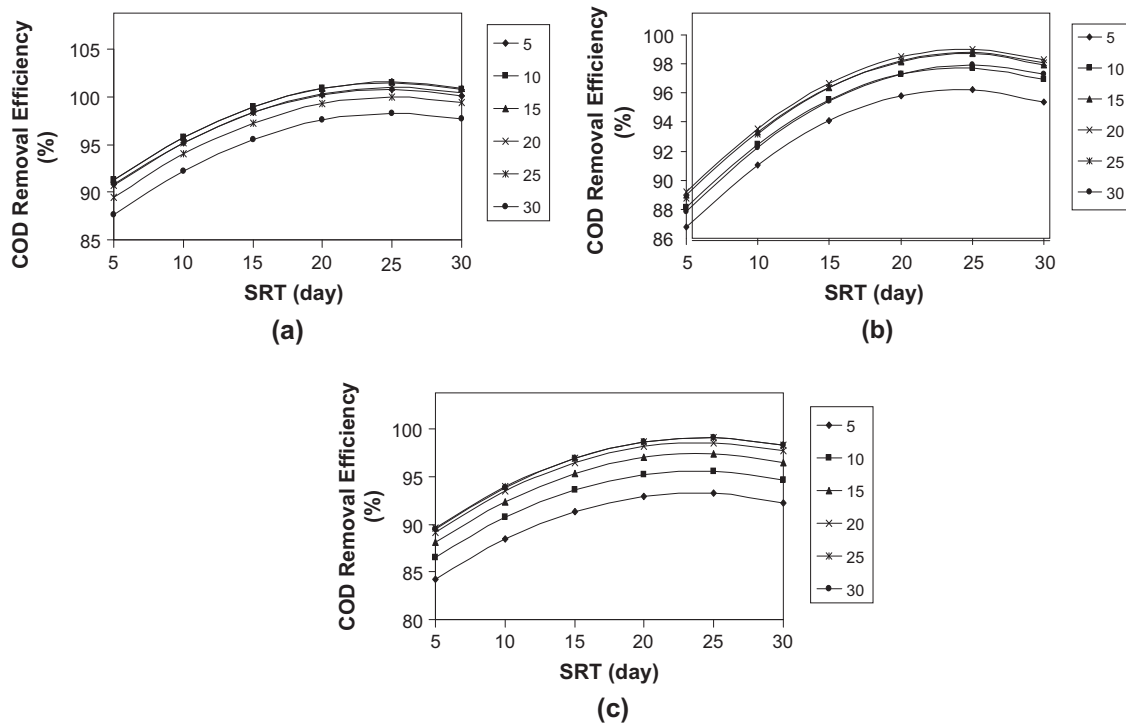


Fig. 2. (a) Variations of percent COD removal with SRT at HRT at constant COD_i concentration (300 mg/L), (b) Variations of percent COD removal with SRT at HRT at constant COD_i concentration (400 mg/L), and (c) variations of percent COD removal with SRT at HRT at constant COD_i concentration (500 mg/L).

Table 5

Steady-state conditions for activated sludge processes for stabilization period

Parameter	Reactor 1	Reactor 2
pH	7.62 ± 0.3	7.56 ± 0.28
T (°C)	23.2 ± 1.37	23.2 ± 1.42
Dissolved oxygen (DO) (mg/L)	2.57 ± 0.1	2.56 ± 0.09
Conductivity (μS/cm)	884 ± 52	950 ± 43
Oxidation–reduction potential ORP (mV)	176 ± 5	174 ± 8
MLSS (mg/L)	2088 ± 300	2,506 ± 350
MLVSS (mg/L)	1,769 ± 300	2,166 ± 350
COD removal (mg/L)	85.9 ± 5.3	87.8 ± 13
NH ₄ -N removal (mg/L)	84.42 ± 9	74.82 ± 5
PO ₄ -P (effluent) (mg/L)	5.93 ± 1	5.38 ± 2.5
NO ₃ -N (effluent) (mg/L)	5.27 ± 1.5	8.63 ± 1.32
CST (s)	11.8 ± 1.2	12 ± 1.7
SVI (mL/mgMLSS)	95.6 ± 5.8	88.2 ± 9.2
SRF (m/kg)	2.16 × 10 ¹³	2.2 × 10 ¹³

Demir and Filibeli [36].

Table 6

SCOD concentration, DD value, TSS, and VSS reduction for different ozone doses

Ozone dose (g O ₃ /g TS)	Ozonation time (min)	SCOD (mg/L)	DD (%)	TSS reduction (%)	VSS reduction (%)
0.007	12	656	9.76	38.46	42.04
0.013	23	1,248	18.57	49.57	56.81
0.02	34	1,536	22.85	67.52	68.18
0.025	45	2,320	34.52	68.37	69.31
0.03	56	2,480	36.90	70.08	69.31
0.05	89	3,776	56.19	77.77	71.59
0.06	111	3,840	57.14	77.77	72.72

3.4. Effects of ozonation on sludge reduction in continuous operation

It was confirmed that the biodegradability of the sludge was improved after ozonation. The effect of sludge ozonation on the minimization of excess sludge production was studied with the measurement of mixed liquor suspended solid (MLSS) and MLVSS concentration of aeration tanks. The ratio of VSS/TSS decreased from 78% in raw sludge to 73% in ozonated sludge with a dose of 0.16 g O₃/g TS [35]. Results of the present study showed that the excess sludge production was reduced by 71% at an ozone dose of 0.05 g O₃/g TS at the end of the operation. While the ozone dose was kept as high 0.05 g O₃/g TS, no excess sludge was produced. The changes of MLSS and MLVSS concentrations of the aeration tank were depicted in Fig. 3(a) and (b), respectively.

It can be seen from Fig. 3 that MLSS and MLVSS were always decreasing during ozonation. It can be deduced that the decrease of MLSS was mainly due to the decrease of MLVSS, because the decreased MLVSS accounted for main part of the lost MLSS.

A 71% MLSS reduction was achieved in OR. Similarly, Demir and Filibeli [36] reported that the results showed 66% of MLSS reduction with an ozonation of 400 mL of the return sludge corresponding to 0.1 Q_R that was discharged from the reactor at a dose of 0.05 g O₃/gMLSS. It was concluded from the results of previous study by Demir and Filibeli [36] and present study that when the volume of ozonated sludge increased, the MLSS reduction also increased due to the cell lysis.

MLVSS was decreased as seen in Fig. 3(b). It can be attributed to the circulation of ozonated sludge to the aeration tank. The MLVSS/MLSS ratio can be

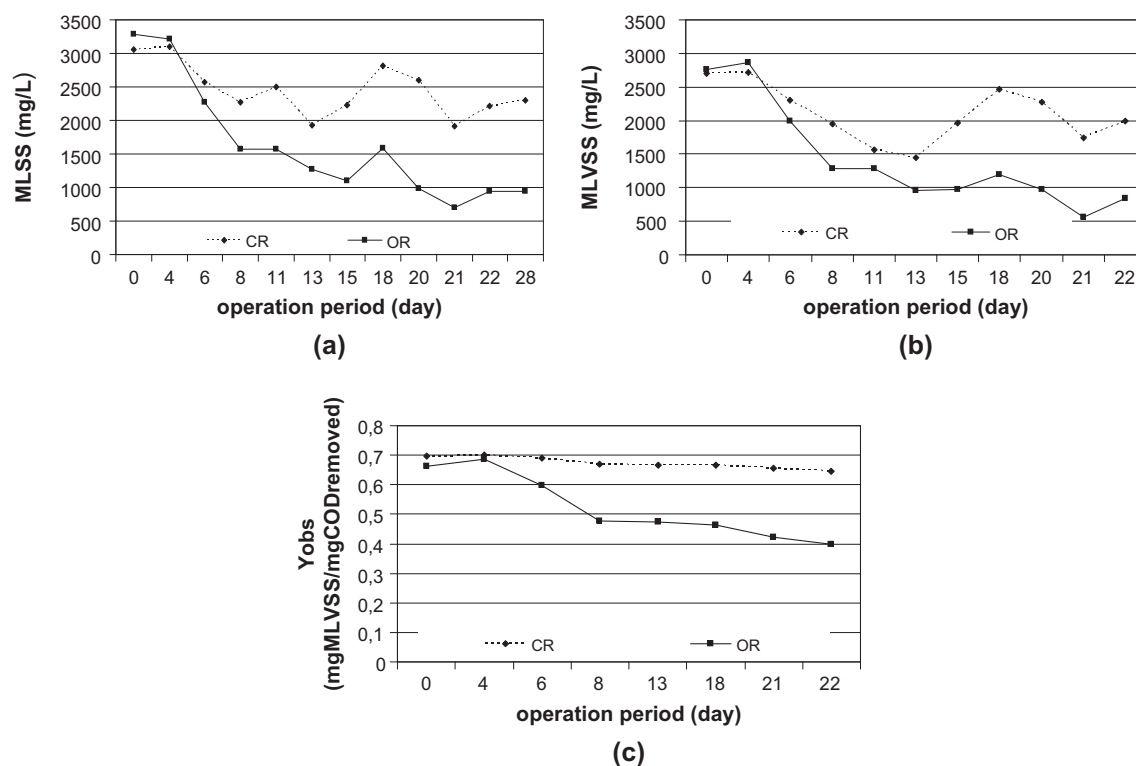


Fig. 3. (a) MLSS variation of aeration tanks for CR and OR, (b) MLVSS variation of aeration tanks for CR and OR, and (c) observed yield (Yobs) variation of for CR and OR.

obtained from Fig 3(a) and (b) for each day of the operation. At the beginning of the operation, the values of MLVSS/MLSS could be calculated as 0.84 for OR and at the end of the operation this value was decreased to 0.75. The average value of MLVSS/MLSS was 0.85.

The observed yield (Yobs) values of the reactors can be seen in Fig. 3(c). It can be realized that the ozonation could reduce Yobs in OR. Yobs values of OR were reduced from 0.66 to 0.4 mg MLVSS/mgCO₂-Dremoved. So, 39% Yobs reduction can be achieved in OR during the operation period. In CR, average 0.67 mgMLVSS/mgCODremoved of Yobs was observed during the operation period. It was stable due to the daily excess sludge wasting in CR. A 40% Yobs reduction could be achieved in OR without sludge wasting.

3.5. Effluent quality after ozonation in continuous operation

The influence of sludge ozonation on effluent quality in the biological treatment process is very important for the application of ozone for the sludge reduction. It was reported that ozonation of the returned activated sludge had no significant negative

impact on the final effluent quality [16,37]. Beside this, as a result of ozonation, inert dissolved and colloidal COD is released into the solution and leads to an increase in inert SCOD of the effluent during long-term operation [16,26,30,33]. In this study, the water treatment performances of two activated sludge processes are shown in Fig. 4. The effluent COD concentrations were always at satisfactory level for both activated sludge processes as illustrated in Fig. 4(a). After ozonation, the COD removal efficiency of OR slightly decreased after twentieth day of operation period. Kamiya and Hirotsuji [33] also reported that SS and SCOD in the effluent were always satisfactory at a level in a pilot-scale activated sludge system coupled with sludge ozonation for 112 days of operation without excess sludge wasting. From the literature, it can be concluded that the ozonation can change COD removal capacity and slightly increase of COD can be seen in the effluent [17]; however, Lee et al. [26] and Sakai et al. [16] reported that no obvious increase was observed in the effluent COD and BOD, respectively [38]. The differences between the results can be attributed to the using of different wastewater, different type of reactor, and operational conditions. The results of present study proved Lee et al. [26] and Sakai et al. [16] that there was no significant increase in effluent

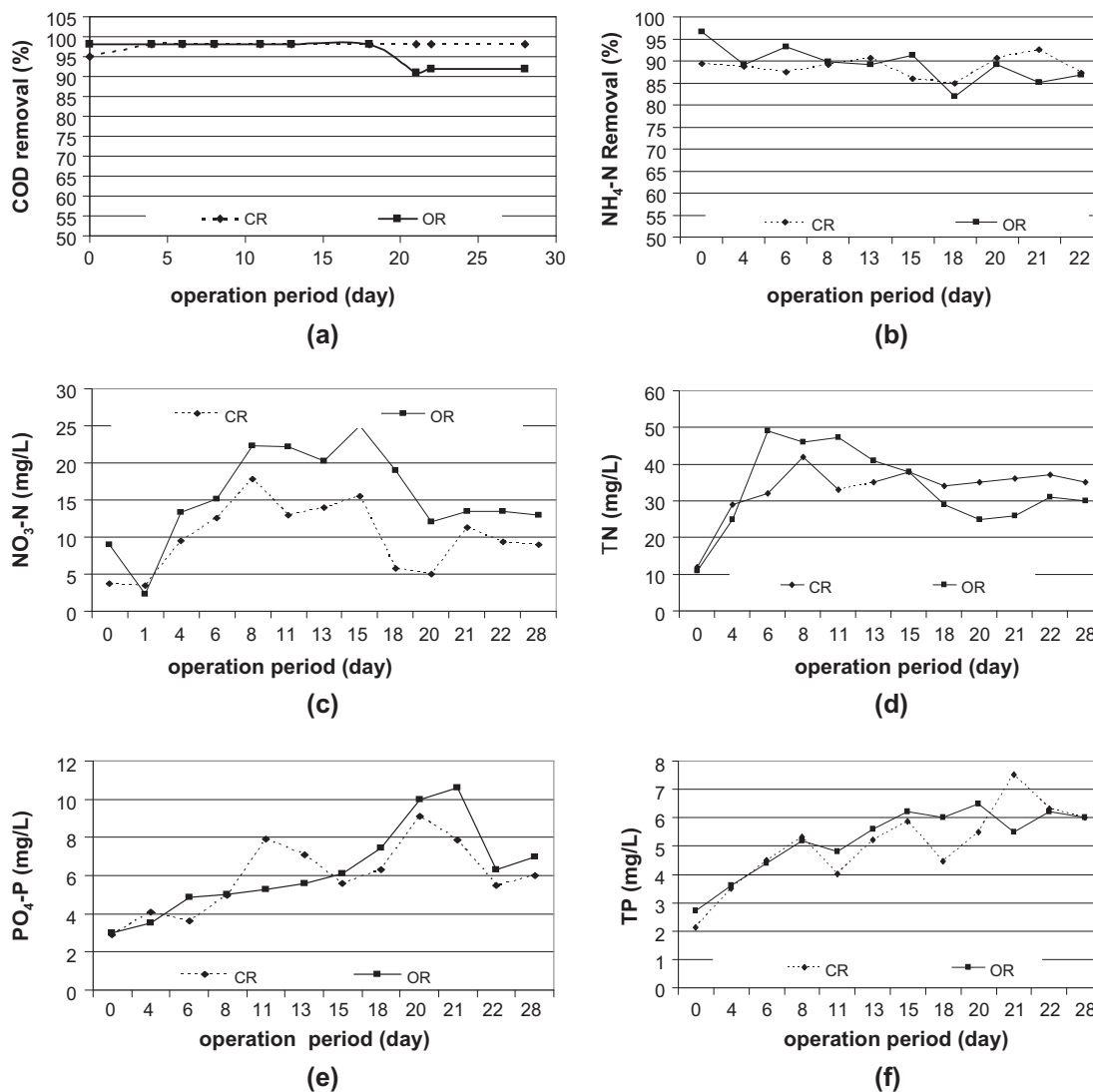


Fig. 4. Variation (a) COD removal efficiency (%), (b) $\text{NH}_4\text{-N}$ removal efficiency (%), (c) $\text{NO}_3\text{-N}$ concentration of effluent, (d) TN concentration of aeration tanks, (e) $\text{PO}_4\text{-P}$ concentration of effluent, and (f) TP concentration of aeration tanks.

COD, in other words, COD removal efficiency was not significantly decreased after ozonation as shown in Fig. 4(a).

Ozonation does not affect the nitrification. It was proved by the study of Huysmans et al. [39]. The ammonium efficiencies of ozone and control reactor were closed during the operation time of 50 days similar to the present study. The study by Dytczak et al. [37] showed that although additional ammonia released from recycled sludge after ozonation was approximately 5.9% more in an SBR, the ammonium in the effluent was always below the detection limit of 0.3 mg/L [29]. Nitrite was not detected, indicating complete nitrification. It can be seen from the Fig. 4 (b), similarly, in this study, the ammonium removal efficiency was not significantly affected by ozonation.

When compared with effluent, approximately 85–93% of the $\text{NH}_4\text{-N}$ was removed from two reactors. It can be easily realized from the Fig. 4(c), as a result of high level of nitrification capacity, the effluent $\text{NO}_3\text{-N}$ concentration in OR was higher than CR.

When the ozonated sludge was recirculated to the bioreactor, the nitrogen loading increased and the TN effluent concentrations were slightly higher compared to the control run [16]. It was also confirmed in this study with the higher TN concentration in OR during operation period compared to CR as presented in Fig. 4(d).

Effluent $\text{PO}_4\text{-P}$ concentration (Fig. 4(e)) and TP concentration of aeration tank in OR (Fig. 4(f)) were increased gradually during the operation period and

were always higher than CR due to the cell lysis. Most of the phosphorus released by sludge ozonation was discharged as part of the soluble component in the effluent due to the reduced sludge discharge.

3.6. Sludge settling properties and dewatering conditions

The settling properties of the sludge can also be improved by ozonation [25,33,40,41]. Improvement in sludge settling can be achieved by the recirculation of the ozonated sludge to aeration tank [23]. It can be attributed to rounder and more compact shape of floc

after ozonation [30]. An improvement in the settling properties of the sludge was reported by several researchers [25,28,30,41,42]. Sludge volume index (SVI) can be used to evaluate the sludge settleability. In this study, the SVI reduced from about 110 to 82 mL/mgMLSS by the partial ozonation of the returned sludge with doses of 0.05 g O₃/g TS. It can be seen from Fig. 5(a). SVI values of OR was lower than CR after fifteenth day of the operation period. It can be said that sludge settling properties can be improved for long-term operation by ozonation. It was concluded from previous studies that dewatering

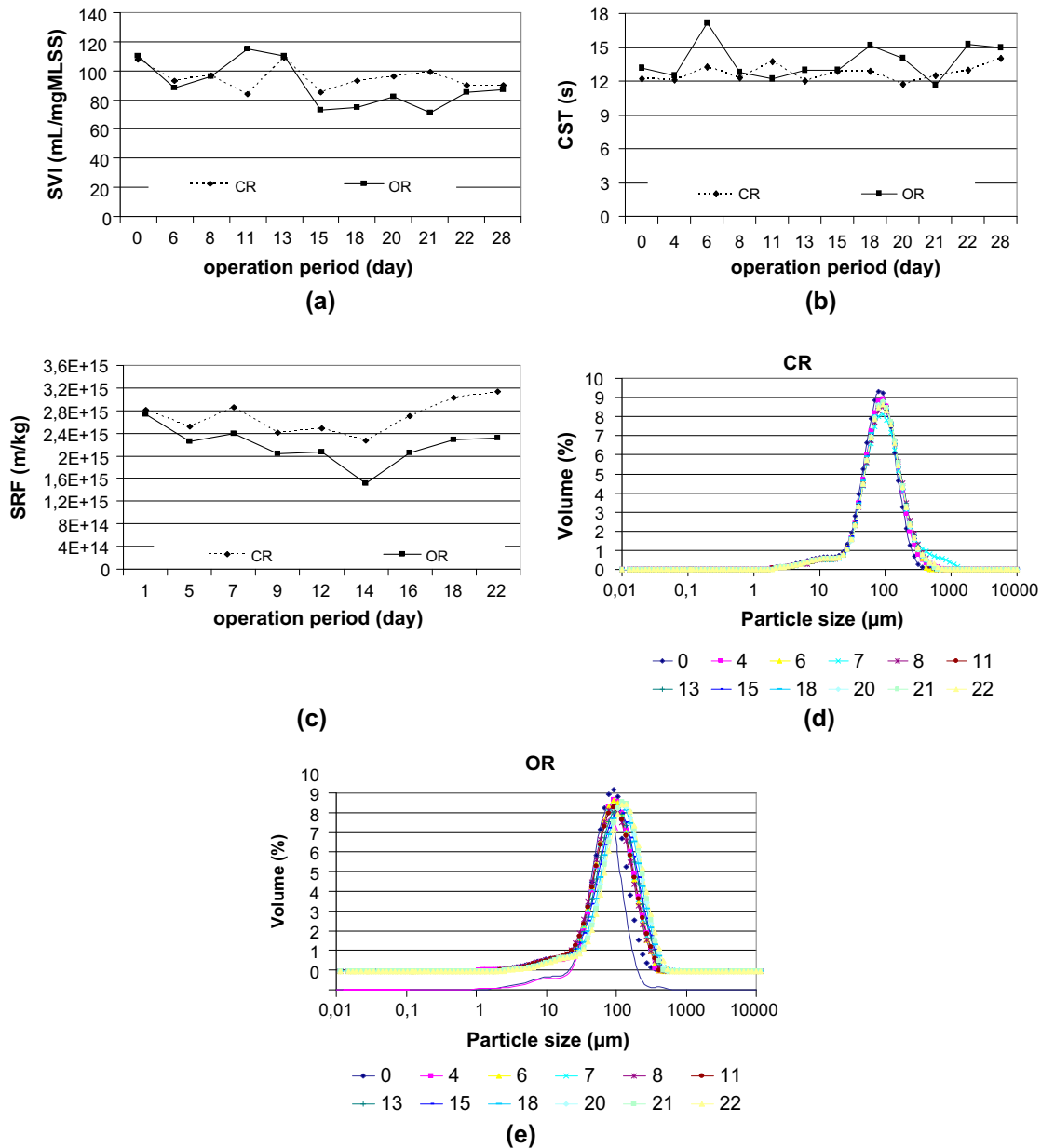


Fig. 5. Changes of (a) SVI, (b) CST, (c) SRF, (d) particle size (CR), and (e) particle size (OR).

and filterability of ozonated sludge was low compared with raw activated sludge due to the negative effect of surface charge of proteins released by cell lysis. Moreover, the microparticles may have also a negative effect on sludge filtration. The CST value increases from 151 to 382 s after ozonation with a dose of $0.1 \text{ g O}_3/\text{g TSS}$ [35]. In this study, lower dewatering capacity of OR was proved slightly higher CST values in OR as seen in Fig. 5(b). However, the CST value difference between OR and CR can be negligible. It can be concluded from these results that in continuous operation, the dewatering capacity of OR was not significantly affected.

In present study, SRF values in OR were always lower than CR (Fig. 5(c)) in continuous operation. However, in batch optimization study, SRF values of ozonated sludge was increased up to $0.02 \text{ g O}_3/\text{g TS}$, then decreased dramatically. In this continuous operation, the filterability of ozonated sludge was not badly affected in contrast to Bougrier et al. [35]. Lower SRF value is an indicator of improved filterability characteristics.

Particle size can be changed by ozonation. Lower ozone doses have not significantly effect on particle size [32]. Bougrier et al. [35] reported that the medium diameter of particles before and after ozonation ($0.16 \text{ g O}_3/\text{g TS}$) was 36.3 and $32.6 \mu\text{m}$, respectively. Zhao et al. [43] reported that the medium diameter of sludge particles reduced from 6 to $4 \mu\text{m}$ at an ozone dose of $0.04 \text{ g O}_3/\text{g TSS}$. Sludge destruction by ozonation leads to an increase of small particles at higher ozone doses. Sludge disintegration results in smaller flocs and a turbid supernatant. The changes of particle size distribution after ozonation are depicted in Fig. 5 (d) and (e). The two figures show the reduction of particle size as μm . During the operation period, the particle size of the sludge was reduced with the effect of the ozonated sludge. It can be realized from the figures, the ozonation changed the particle size. It is attributed to sludge disruption by ozonation resulted in smaller flocs formation.

4. Conclusion

In the present study, a comparison between extended aeration activated sludge process and activated sludge process coupled with ozonation system was investigated from the view points of sludge reduction and water treatment capacity. Moreover, changes of sludge characteristics during continuous operation were also considered in this comparison. In order to make such a comparison between two systems should be started with the same initial conditions. CODi/SRT/HRT ratio was determined as

optimum conditions of $400 \text{ mg/L}/25 \text{ d}/25 \text{ h}$ using Box–Behnken statistical design method. Optimum ozone dose of $0.05 \text{ g O}_3/\text{g TS}$ was determined considering DD prior to modification with ozonation. While 71% MLSS and 39% Yobs reduction were observed in OR during the operation period, 61% MLSS reduction and 40% Yobs reduction were obtained in OR compared to average MLSS concentration and Yobs value in CR.

The results of present study proved that there was no significant increase in effluent COD, in other words, the COD removal efficiency was not significantly decreased after ozonation. Ozonation did not also affect the nitrification capacity. The ammonium removal efficiency of the OR and the CR were similar. COD and $\text{NH}_4\text{-N}$ removal efficiencies were closed to CR with 92–100% and 85–96% in OR, respectively. $\text{NO}_3\text{-N}$ concentration of effluent and total nitrogen of aeration tank in OR were higher than CR due to release of cell contents as a result of cell lysis. Effluent $\text{PO}_4\text{-P}$ concentration and TP concentration of aeration tank in OR were increased gradually during the operation period and were always higher than CR due to the cell lysis as well as nitrogen. CST values of in OR were slightly higher than OR while SRF values in OR were always lower than the CR as an indicator of improved dewatering characteristics. Ozonation could change particle size and sludge destruction by ozonation led to an increase of small particles at higher ozone doses. It can be concluded that the ozonation is an effective method for sludge reduction as a result of cell lysis.

In the present study, the feasibility of the activated sludge system coupled with ozonation process was verified through the lab-scale plant operation without excess sludge production. Minimization of excess sludge production could be achieved by recirculating the ozone-treated sludge into a bioreactor.

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