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EFFECT OF SULFATE LOADING RATE AND ORGANIC LOADING RATE ON ANAEROBIC BAFFLED REACTORS USED FOR TREATMENT OF SANITARY LANDFILL LEACHATES

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Abstract - This study investigated the effect of organic loading rate (OLR) and sulfate loading rate (SLR) on landfill leachate treatment by a lab-scale anaerobic baffled reactor (ABR). Landfill leachate contained a concentration of organic matter between 3966 and 5090 mg COD.L^{-1} and no detectable amounts of sulfate. Reactors were started-up by feeding them with iron-sulfate at a SLR of 0.05 g SO_4^{2-}.L^{-1}.day^{-1} (4 weeks). Factorial design and response surface techniques were used to evaluate and optimize the effects of these operating variables on COD removal. ABRs were operated at OLRs ranging from 0.30 up to 6.84 g COD.L^{-1}.day^{-1} by changes in influent volumetric flow. SO_4^{2-} was added to the influent at a SRL from 0.06 to 0.13 g SO_4^{2-}.L^{-1}.day^{-1}. The highest value of COD removal (66%) was reached at an OLR of 3.58 g COD.L^{-1}.day^{-1} and SLR of 0.09 g SO_4^{-2}.L^{-1}.day^{-1} with a COD/SO_4^{-2} ratio of 40. Under these conditions sulfate is mainly used for molecular hydrogen consumption while organic matter is preferentially degraded via methanogesis.

Keywords: Antanas sanitary landfill; Anaerobic baffled reactor; Response surface methodology; COD/sulfate ratio.

INTRODUCTION

In Colombia, sanitary landfills are the most common method for the disposal of municipal solid wastes (SSPD, 2008). More than half of all municipalities dispose their wastes in local or regional sanitary landfills and less than 10% use a solid waste integrated facility (SSPD, 2008; Noguera and Olivero, 2010). Leachate production is considered the most complex environmental issue related with sanitary landfills (Bashir *et al*., 2010; Kulikowska and Klimiuk, 2008; Ghafari *et al*., 2009). Landfill leachate contains significant amounts of organic matter and inorganic salts, especially heavy metals, which can contaminate groundwater and surface water far away from the original location (Tchobanoglous, 2002).

Leachates are treated by different technologies specific to each country, type of solid waste and cost. The most common technologies used for leachate treatment can be classified into three groups: i.) recycling and combined treatment with municipal domestic sewage, ii.) biological treatment under aerobic or anaerobic conditions or a mix of these, and iii) chemical/physical methods (Renou *et al*., 2008). In

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*To whom correspondence should be addressed addition to its simplicity and reliability, biological treatment is the best cost-effective strategy for the treatment of landfill leachate (Wiszniowski *et al*., 2006; Renou *et al*., 2008). Anaerobic biological processes have economic advantages resulting from lower energy consumption and solid production when compared with aerobic process. The major disadvantage of the anaerobic process is its low rate of reaction. Consequently it requires stable operating conditions and warm temperatures (35 °C) (Berrueta and Castrillón, 1992). Anaerobic reactors treating landfill leachates at temperatures lower than 35 °C require the use of high performance treatment technologies (Kettunen *et al*., 1996; García *et al*., 1996).

Antanas Sanitary Landfill (ASL) serves as a regional landfill for the central region of Nariño Province in the Southwest of Colombia. ASL is located at an elevation of 2750 masl (meters above sea level) with an average temperature of 12 °C. Anaerobic reactors used for ASL leachate treatment exhibit poor performance even when they are operated at low OLRs (less than 1 $g.L^{-1}.day^{-1}$) (Burbano-Figueroa, 2002). Anaerobic reactors require temperatures higher than 18 °C for optimal performance. At low reaction rates, molecular hydrogen accumulates, resulting in inhibition of methanogenesis and VFA degradation (García *et al*., 1996; Kettunen *et al*., 1996; Lettinga *et al*., 1999). High anaerobic reaction rates can be achieved if hydrogen is depleted by oxidation with a suitable electron acceptor. Sulfate can accomplish this role in a cost-effective way with a low environmental impact (JWH *et al*., 1994, Kalyuzhnyi *et al*., 1998; Dar *et al*., 2009; Zhao *et al*., 2010).

Sulfate-reducing bacteria (SRB) can remove molecular hydrogen, allowing optimal performance of methanogenic microorganisms (JWH *et al*., 1994; Kalyuzhnyi *et al*., 1998; Dar *et al*., 2009; Zhao *et al*., 2010). Under anaerobic conditions, SRB, alone or in consortia, use sulfate as the main electron acceptor, consuming hydrogen and VFAs. Syntrophic propionate oxidizers are outcompeted by SRB under non-limiting sulfate conditions. Butyrate is degraded at the same rate by syntrophic oxidizers and SRB. Additionally, SRB are more efficient hydrogen consumers than methanogenic archaea. SRB consume molecular hydrogen at higher rates in consideration of their superior scavenging capability (lower Ks facilitated by periplasmic location of the hydrogenase enzyme) (Kristjanson *et al*., 1992; Barber and Stuckey, 2000) and thermodynamics of sulfate reduction (Dries *et al*., 1998; Wang *et al*., 2008).

Accumulation of cells and optimal growth conditions are critical factors for successful operation of an anaerobic reactor. Microbial growth rates are constrained by low temperatures, substrate complexity, thermodynamical constraints and the need of physical separation of anaerobic catabolism phases (Barber and Stuckey, 1999). These limitations can be resolved using anaerobic baffled reactors (ABR). These reactors have additional advantages compared with other systems: they are cheap to build and operate, are tolerant to changes in hydraulic and organic shock loadings and have high biomass retention (Bachmann *et al*., 1985; Grobicki and Stuckey, 1991; Wang *et al*., 2004)). Few studies using ABRs in landfill leachate treatment have been reported. An ABR reached COD removal efficiencies of 80% for an OLR range of 1-7 $g\ COD.L^{-1}.day^{-1}$ (Reza *et al*., 2007). Wang and Shen (2000) reported an ABR used for the treatment of mixed wastewater of landfill leachate and municipal sewage.

We hypothesized that addition of sulfate to an ABR used for the treatment of landfill-leachate (a rich VFA substrate) could increase its organic matter removal efficiency by elimination of accumulated hydrogen. Effects of OLR and SLR over an ABR performance used on leachate treatment were studied using response surface methodology (RSM). A baffled reactor design was selected due to the following advantages: high retention and accumulation of biomass and its tolerance to volumetric loading providing a stable environment for microorganisms.

MATERIALS AND METHODS

Bioreactor Configuration

Lab-scale (2L) baffled reactors were used in this study (Figure 1). Reactors were built from polyethylene (PE) and rectangular in shape (length 25 cm, width 15 cm and height 6.5 cm), comprising five chambers. Reactors were seeded with anaerobic sludge (10% vol/vol), containing 15 $g\ VSS.L^{-1}$, from the Antanas Sanitary Landfill Wastewater Treatment (ASLWT) Facility. During the initial start-up period of four weeks, reactors were fed with iron-sulfate at a SLR of 0.05 $g\ SO_4^{2-}.L^{-1}.day^{-1}$ in order to promote growth of sulfidogenic bacteria. Fresh ASL leachate (COD concentration of 4000-5000 mg/L) (Table 1) was provided by using a macrodrip set for a daily dose (Nebot *et al.* 1995). Average room temperature during reactor operation was maintained at 15 ± 2 °C. OLRs variations were obtained by using different HRTs. A single batch of fresh leachate was used for each SSOP in all reactors. Different levels of SLR were obtained by iron-sulfate addition to the influent. Reactors were operated at OLRs from 0.30 to 6.84 g $COD.L^{-1}.day^{-1}$ and SLRs from 0.06 to 0.13 $g.L^{-1}.day^{-1}$.

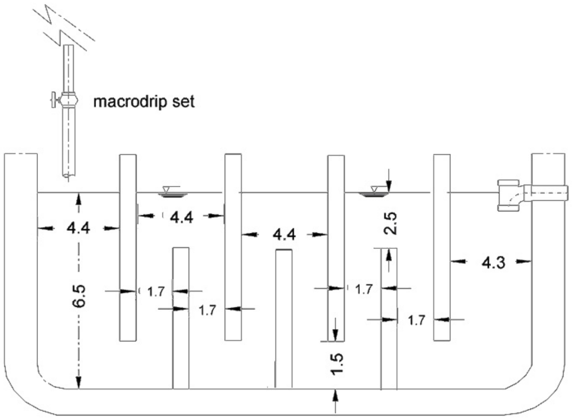


Figure 1: Scheme of the baffled reactor design used in this study. External dimensions are: length 25 cm, width 15 cm and height 6.5 cm. Internal dimensions are shown in the graph in cms. Effective reactor volume = 2L.

Table 1: Characteristics of landfill leachate taken from ASL in mg $TSS.L^{-1}$.

Parameter	Units
Chemical oxygen demand (COD) ($mg.L^{-1}$)	3966-5090
Volatile fatty acid (VFA) ($mg.L^{-1}$)	1678-2035
Total suspend solids (TSS) ($mg.L^{-1}$)	8.16-10.67
Volatile suspend solids (VSS) ($mg.L^{-1}$)	0.090-0.49
Sulfate ($mg.L^{-1}$)	Not detected
pH	6.52-7.98

Experimental Design and Optimization

The experimental design and data analysis were performed with the help of the Design Expert software (version 6.0.7, Stat Ease, Inc., Minneapolis, MN, USA) using the response surface model. This multivariate data analysis merges mathematical and statistical tools with the purpose of quantifying the influence of several variables on one or more response variables (Myers *et al.*, 1989; Khuri, 2006; Zinatizadeh *et al.*, 2006; Baş and Boyacı, 2007). Linear and quadratic models were used to predict optimal conditions. ANOVA analysis was used for testing the interaction between independent and dependent variables (response). Fitting of the polynomial model was tested by the correlation coefficient and statistically validated by the F-test. Model terms were only considered useful when their probability (P-value) offered a 95% confidence level.

Seven reactors were used in this study. Each experimental run was defined as reactors working at the steady-state operating point (SSOP). A SSOP is defined as a reactor operating during at least three times its hydraulic retention time (HRT) and a variation of organic matter removal lower than 10%.

Three phases were performed to find appropriate conditions for COD removal: exploratory, path of steepest ascent (PSA) and optimal conditions (Table 2). During the exploratory phase, initial operational points for RSM were estimated from the conditions employed for the anaerobic reactor used by ASLWT (SSOPs representing central points are the actual operational conditions). During the PSA phase, the contour plot defined in the exploratory phase was used to estimate a first-order equation that drives to the optimal point, the highest COD removal. Five operational points were used at step-size of 400 g $COD.L^{-1}.day^{-1}$ and 0.05 g $SO_4^{2-}.L^{-1}.day^{-1}$. The highest COD removal point obtained in the PSA phase was used as a central point for the optimization experiment. The loading rates used on this study ranged from 0.30 to 6.84 g $COD.L^{-1}.day^{-1}$ and from 0.06 to 0.13 g $SO_4^{2-}.L^{-1}.day^{-1}$.

Table 2: Experimental design describing variables in coded levels for exploratory, path of steepest ascent and optimization phases.

Experiment (run-SSOP)	Coded levels					
	Exploratory		Path of steepest ascent		Optimization phase	
	OLR	SLR	OLR	SLR	OLR	SLR
1	+1	+1	+1	+1	+1.4	0
2	+1	-1	+2	+2	+1	+1
3	-1	+1	+3	+3	0	+1.4
4	-1	-1	+4	+4	-1	+1
5	0	0	+5	+5	-1.4	0
6	0	0	+6	+6	-1	-1
7	0	0			0	-1.4
8					+1	-1
9					0	0
10					0	0
11					0	0

Analytical Methods

400 mL were taken from each reactor effluent and analyzed for the next parameters following the Standard Methods (APHA 1992): COD (5220 D. Closed Reflux, Colorimetric Method), Sulphate (4500 E. Turbidimetric Method), VFA (5560 C. Distillation Method), TSS (2540 D. Total Suspended Solids Dried at 103-105 °C) and VSS (2540 E. Fixed and Volatile Solids Ignited at 550 °C). pH was measured immediately after sampling with a Metrohm 744 pH meter. Samples were stored at 4 °C for no more than 6 hours before being analyzed.

RESULTS

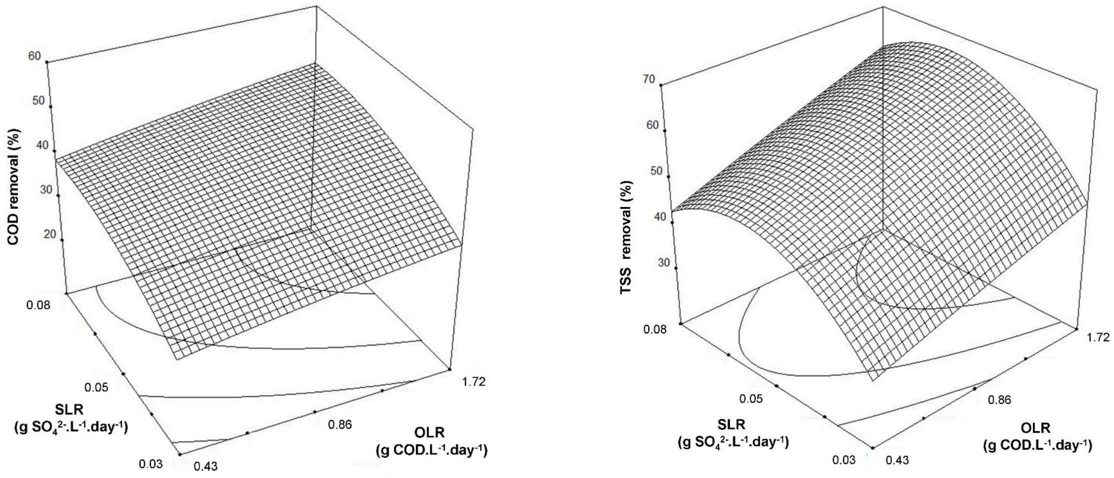
The data listed in Tables 3 and 4 show wide variations in COD removal (CODr), VFA removal (VFAr), TSS removal (TSSr) and VSS removal (VSSr) during the screening and optimization phase. An optimal response point for CODr was found along the path of steepest ascent (Table 4). This point was chosen for further optimization. The ANOVA results for statistical significant models of the exploratory and optimization phase are summarized in Table 6. The quality of the fit polynomial model was expressed by correlation coefficient ($r^2 > 0.94$). No significant effect of OLR and SLR on VFA removal or pH value was observed. Effluent pH values compared with the influent pH ones were less than 1 pH unit lower. During the optimization phase, no significant models explained the variation of VSS removal. Adequate precision of the signal-to-noise ratio for the selected models was greater than 6. This ratio indicated adequate signals for these models to be used to navigate the design space.

Effect of OLR and SLR on Reactor Performance and Calculation of the Path of Steepest Ascent

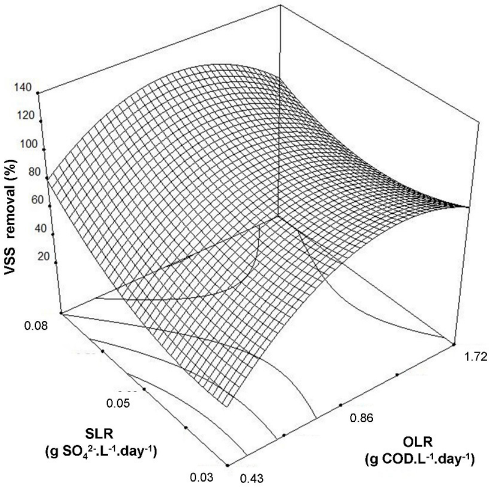
The RSM approach requires performing several experiments in a predetermined range of step changes for each selected factor. These changes are large enough to have a significant change in the evaluated response and obscure noise associated with the other non-evaluated factors. OLR and SLR ranges for exploratory screening were estimated from the operational conditions used in an ABR treating ASL leachates. A three-level partial factorial design was used to estimate the OLR and SLR effects on CODr, VFAr, TSSr and VSSr (Table 3). Adequate response surface models were obtained for CODr, TSSr, and VSSr (Figure 2). In this exploratory screening, the highest removal of organic matter was reached for SSOP 9, in which the reactor was performing at the highest levels possible for OLR and SLR (OLR of 1.72 g COD.L^{-1}.day^{-1} and SLR of 0.08 g.L^{-1}.day^{-1}).

Table 3: Exploratory screening of the OLR and SLR levels effect on CODr, VFAr, TSSr and VSSr.

	Variables				Response values			
Run	g.L^{-1}.day^{-1}		Coded Levels		Removal %			
SSOP	OLR	SLR	OLR	SLR	CODr	VFAr	TSSr	VSSr
1	0.43	0.025	-1	-1	27.06 ± 1.64	59.58 ± 1.78	30.25 ± 0.29	20.94± 6.30
2	0.43	0.050	-1	0	39.82± 0.81	52.97 ± 1.77	51.82 ± 0.68	42.99 ± 12.33
3	0.43	0.075	-1	1	37.47± 0.98	40.23 ± 1.09	41.52 ± 0.34	77.00 ± 8.77
4	0.86	0.050	0	0	41.42± 0.17	52.87 ± 1.14	57.51 ± 0.36	91.78 ± 7.81
5	0.86	0.050	0	0	41.60± 0.42	53.64 ± 2.06	57.17 ± 0.17	89.08 ± 12.55
6	0.86	0.050	0	0	41.43± 0.38	47.89 ± 2.83	56.97 ± 1.64	81.65 ± 21.28
7	1.72	0.025	1	-1	37.13± 0.65	39.39 ± 1.88	47.45 ± 0.37	87.02 ± 23.73
8	1.72	0.050	1	0	42.16± 0.79	50.96 ± 2.80	61.95 ± 0.31	59.97 ± 11.25
9	1.72	0.075	1	1	48.66± 3.63	60.15 ± 1.23	62.61 ± 0.29	92.19 ± 8.13



(a) (b)



(c)

Figure 2: Exploratory screening. Response surface plot showing the effect of SLR and OLR on COD removal (panel a), TSS removal (panel b), and VSS removal (panel c).

Organic matter removal (measured as COD) was significantly influenced by OLR and SLR (P>0.05). These are the equations describing organic removal, TSSr and VSSr:

$$\text{CODr\%} = 41.48 + 3.93\text{A} + 5.49\text{B} + 0.28\text{AB} - 0.49\text{A}^2 - 3.41\text{B}^2 \quad (1)$$

$$\text{TSSr\%} = 57.22 + 8.07\text{A} + 6.61\text{B} + 0.97\text{AB} - 0.33\text{A}^2 - 11.43\text{B}^2 \quad (2)$$

$$\text{VSSr\%} = 87.50 + 16.37\text{A} + 15.31\text{B} - 12.72\text{AB} - 36.02\text{A}^2 + 17.81\text{B}^2 \quad (3)$$

where A and B represent OLR and SLR, respectively.

The CODr equation was used to define the steepest ascent path. New SSOPs were performed along the steepest ascent path until the CODr showed no further increase. This experiment was conducted in steps of 0.86 gCOD.L^{-1}.day^{-1} for OLR and 0.014 gSO$_4^{2-}$.L^{-1}.day^{-1} for SLR (Figure 3). Tukey analysis revealed a significant difference between SSOP 4, the highest CODr value, and additional tested SSOPs. The highest CODr (66%) value was recorded at an OLR of 3.58 g COD. L^{-1}.day^{-1} and SLR of 0.09 g SO$_4^{2-}$.L^{-1}.day^{-1} (Table 4). This combination was used as the middle point for CODr optimization.

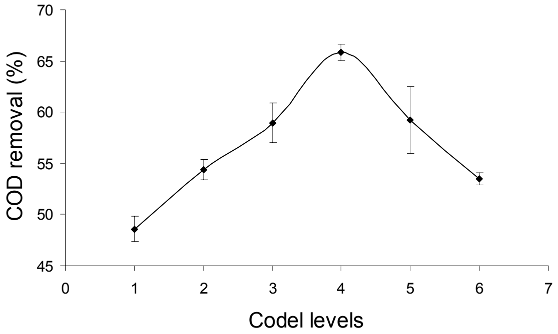


Figure 3: COD removal for each SSOP along the path of steepest ascent.

Table 4: COD removal during path of steepest ascent experiments.

Run	Variables				Response values % of removal
	g.L^{-1}.day^{-1}		Coded Levels		
SOOP	OLR	SLR	OLR	SLR	CODr
1	0.99	0.050	1	1	48.58 ± 1.73
2	1.23	0.063	2	2	54.43 ± 1.41
3	1.93	0.076	3	3	58.97 ± 2.74
4	3.58	0.089	4	4	65.75 ± 2.41
5	4.84	0.102	5	5	59.19 ± 4.62
6	5.19	0.115	6	6	53.50 ± 0.79

Optimization of COD Removal

The optimization of CODr was performed by CCD with the fixed middle point of OLR of 3.58 g COD. L^{-1}.day^{-1} and SLR of 0.09 g SO$_4^{2-}$.L^{-1}.day^{-1} and with an α value of ± 1.4 to produce design rotability.

The design matrix, the corresponding SSOPs and the CODr (experimental responses) are shown in Table 5. The ANOVA results indicated that the quadratic regression to produce the second-order model was significant for CODr and VSSr (P value < 0.01) (Table 6). Only 1% of the total variation of COD removal was not explained by the model. This suggested that the proposed model is an accurate representation of the data in the experimental region. The response surface was generated (Figure 4) based on the following second-order equations for CODr and VSSr:

$$\text{CODr }\% = 65.23 + 0.16\text{A} - 0.093\text{B} - 0.47\text{AB} - 5.25\text{A}^2 - 5.56\text{B}^2 \tag{4}$$

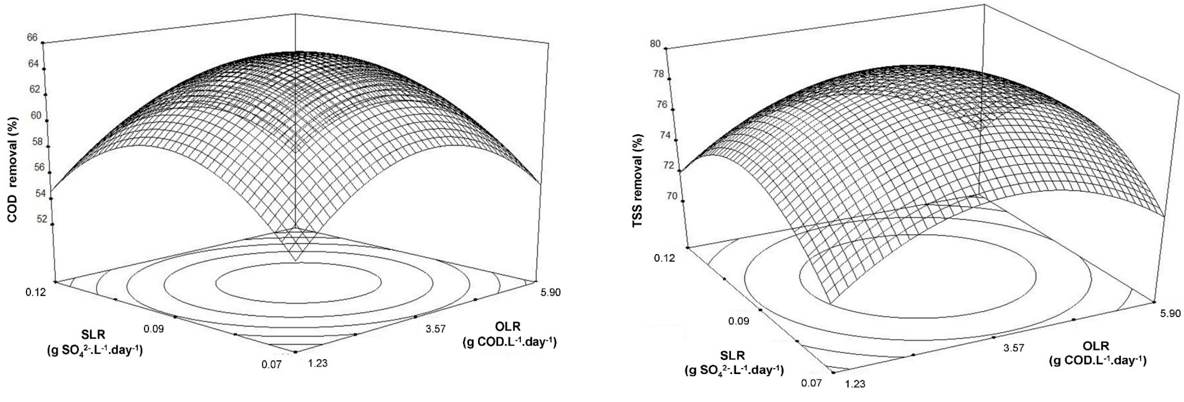
$$\text{VSSr }\% = 79.75 + 0.16\text{A} - 0.091\text{B} \quad \text{V} \quad - 0.46\text{AB} - 3.85\text{A}^2 - 4.15\text{B}^2 \tag{5}$$

Table 5: Optimization of COD removal. The COD/SO$_4^{-2}$ ratio and hydraulic retention time (HRT) for each SSOP was included.

Run	Variables				Response values				COD/SO$_4^{-2}$ Ratio (g.g^{-1})	HRT
	g.L^{-1}.day^{-1}		Coded Levels		% of removal					
SSOP	OLR	SLR	OLR	SLR	CODr	VFAr	TSSr	VSSr		days
1	0.30	0.090	-1.4	0	54.42 ± 0.10	42.33 ± 1.64	71.76 ± 1.32	75.60 ± 12.89	3.33	1.39
2	1.23	0.065	-1	-1	53.86 ± 2.59	55.00 ± 1.78	71.19 ± 0.98	87.60 ± 9.88	17.57	1.20
3	1.23	0.115	-1	1	54.82 ± 0.45	54.90 ± 2.06	72.15 ± 0.78	88.90 ± 23.99	10.25	1.20
4	3.57	0.055	0	-1.4	54.25 ± 0.99	59.63 ± 1.98	71.59 ± 0.18	77.00 ± 12.90	59.50	0.73
5	3.57	0.090	0	0	65.69 ± 1.70	63.40 ± 2.54	80.18 ± 0.23	86.70 ± 19.2	39.67	0.73
6	3.57	0.090	0	0	62.04 ± 0.45	59.80 ± 2.32	78.04 ± 0.76	80.90 ± 20.98	39.67	0.73
7	3.57	0.090	0	0	63.36 ± 0.34	61.70 ± 1.43	78.88 ± 0.56	83.50 ± 23.45	39.67	0.73
8	3.57	0.090	0	0	69.82 ± 2.09	62.64 ± 1.09	81.91 ± 0.45	84.50 ±19.77	39.67	0.73
9	3.57	0.125	0	1.4	53.69 ± 0.23	63.40 ± 2.65	71.02 ± 0.32	76.00 ± 9.56	27.46	0.73
10	5.90	0.065	1	-1	55.23 ± 1.38	63.70 ± 1.14	72.54 ± 0.98	75.60 ± 8.76	84.29	0.25
11	5.90	0.115	1	1	54.32 ± 1.17	64.00 ± 2.98	71.65 ± 1.09	90.50 ± 9.87	49.17	0.25
12	6.84	0.090	1.4	0	54.74 ± 0.31	59.80 ± 2.34	72.07 ± 1.87	88.80 ± 23.45	76.00	0.06

Table 6: Analysis of variance (ANOVA) of the predicted response surface quadratic models for reactor performance.

	Source	Sum of squares	Degree of Freedom	Mean Square	F value	P>F
SCREENING						
COD removal (%)	Model	244.29	5	48.86	6.39	0.0788
	Residual	22.93	3	7.64		
	Lack of Fit	22.91	1	22.91	2238.57	0.0004
	Pure Error	0.02	2	0.01		
	SD = 2.76, CV = 6.97, PRESS = 1237.08, R-Squared = 0.9142, Adeq Precision = 8.345					
TSS removal (%)	Model	869.69	5	173.94	19.16	0.0175
	Residual	27.24	3	9.08		
	Lack of Fit	27.09	1	27.09	363.46	0.0027
	Pure Error	0.15	2	0.075		
	SD = 3.01, CV = 5.80, PRESS = 1463.20, R-Squared = 0.9696, Adeq Precision = 13.495					
VSS removal (%)	Model	4782.99	5	956.6	11.88	0.0343
	Residual	241.56	3	80.52		
	Lack of Fit	186.52	1	186.52	6.78	0.1213
	Pure Error	55.04	2	27.52		
	SD = 8.97, CV = 12.57, PRESS = 10195.00, R-Squared = 0.9519, Adeq Precision = 8.649					
OPTIMIZATION						
COD removal (%)	Model	313.32	5	62.66	10.67	0.006
	Residual	35.24	6	5.87		
	Lack of Fit	0.27	3	0.089	7.65E-03	0.9989
	Pure Error	34.97	3	11.66		
	Cor Total	348.56				
	SD = 2.42, CV = 4.18, PRESS = 64.07, R-Squared = 0.8989, Adeq Precision = 6.625					
TSS removal (%)	Model	172.32	5	34.46	23.45	0.0007
	Residual	8.82	6	1.47		
	Lack of Fit	0.26	3	0.088	0.031	0.9913
	Pure Error	8.55	3	2.85		
	SD = 1.21, CV = 1.63, PRESS = 17.09, R-Squared = 0.9513, Adeq Precision = 9.954					



(a) (b)

Figure 4: COD removal optimization. Three-dimensional contour plots showing the effect of SLR and OLR on COD removal (panel a) and TSS removal (panel b)

DISCUSSION

We hypothesized that sulfate addition should improve ABR performance used in leachate treatment. The results of the present study support that statement. An optimum point for CODr (66%) was observed with a SLR of 0.09 g $SO_4^{-2}.L^{-1}.day^{-1}$ and HRT of 0.73 days, a quarter of the HRT used in the ABR located in ASL. A further increase in the volumetric loading rate decreased the reactor performance by bacterial washout.

The COD/SO_4^{2-} ratio has been used as a criterion to predict the dominance of SRB or MPB in the anaerobic environment. The theoretical feed COD/SO_4^{2-} ratio of 0.67 is the critical stoichiometric value required for complete removal of OM by sulfate reduction (Lens *et al*., 1998). At lower COD/SO_4^{2-} ratios, SRB tends to dominate the reactor microbial community, whereas MPB dominates at higher ratios (De Smul *et al*., 1999; Vallero *et al*., 2003; O'Reilly and Colleran, 2006). In consideration of the thermodynamic properties of sulfate as an electron acceptor, microbial communities dominated by SRB have a higher growth rate that results in increased reactor performance. However, greater reactor performance has been observed at COD/SO_4^{2-} ratios over 0.67. In other cases, little, if any effect of sulfate concentration on anaerobic reactor performance was observed (Choi and Rim, 1991; Henry and Prasad, 2000).

This work analyzed the performance of an anaerobic reactor at COD/SO_4^{2-} ratios ranging from 3.33 to 84.29. Previous studies had reported COD/SO_4^{2-} ratios ranging from 6.6 to 1.7 as optimal for CODr (Choi and Rim, 1991; Friedl *et al*., 2009; Mockaitis *et al*., 2010; Silva *et al*., 2011; Camiloti *et al*., 2013). The highest CODr observed in this study was obtained when the COD/ SO_4^{2-} ratio was 40. This value fairly exceeds any previous ratio reported as being optimal for CODr. At this ratio, sulfate was not responsible for significant removal of organic matter but increased the overall performance of the reactor. OM was mainly consumed via methanogenesis.

Improved performance of ABRs at high COD/SO_4^{2-} ratios can be explained by the following two assumptions: a) Landfill leachate was mainly composed of acetate. Under methanogenic conditions inside the landfill, acetate accumulates two or three times faster than propionate or butyrate (Schink, 1997; Mormile *et al*., 1996). b) Previous researches have revealed a differential degradation of VFA under sulfidogenic conditions. Acetate is poorly consumed at high sulfate loading rates. Propionate is preferentially degraded by BRS, while the butyrate degradation rate is not affected by sulfate concentration (O'Reilly and Colleran, 2006; Bharati and Kumar, 2012). Based on this scenario, the acetate degradation rate is affected by sulfate reduction, provoking its inhibition at low COD/SO_4^{2-} ratio (Omil *et al.* 1998; Barber and Stuckey, 2000). At high COD/SO_4^{2-} ratio, acetogenesis is not inhibited by sulfate reduction, while the overall reactor performance is improved by molecular hydrogen removal (JWH *et al*., 1994; Kalyuzhnyi *et al*., 1998; Dar *et al*., 2009; Zhao *et al*., 2010). If SO_4^{2-} is present, SRB consumes molecular hydrogen at higher rates compared with methanogenic archeas because of its superior scavenging capability (Kristjansson *et al*., 1982). Poor reactor performance at COD/SO_4^{-2} ratios higher than 40 is explained by the scarcity of sulfate for significant H_2 removal.

A complementary explanation for improved ABR performance at such COD/SO_4^{2-} ratio is the spatial distribution of microorganisms and tolerance to changing COD/SO_4^{2-} ratios of baffled reactors (Vossoughi *et al*., 2003). ABRs exhibit a plug flow behavior that, in combination with compartmentalization, provokes staging of VFA degradation (Vallero *et al*., 2003; Vossoughi *et al*., 2003; Krishna *et al*., 2009). Previous reports have indicated that, when an ABR is fed with sulfate, more than a half of the effluent OM and sulfate is removed in the first compartment. Propionate and butyrate are mainly degraded in the first compartment, resulting in acetate accumulation. Accumulated acetate is degraded in the subsequent compartments where sulfate is almost nonexistent or abandons the reactor as residual acetate in the effluent (Vallero *et al*., 2003). At higher SLR, sulfidogenic conditions are imposed on the whole reactor, slowing or inhibiting acetate degradation. The highest sulfate reduction rates do not occur in the first compartment, but in the subsequent ones (Vossoughi *et al*., 2003). ABRs used in this study were exposed to a range of COD/SO_4^{-2} ratios from 3.3 to 84.29, exhibiting stable operation at low ratios. At a COD/SO_4^{-2} ratio of 40, sulfidogenic conditions can only prevail in the first compartment. A previous research showed that COD/SO_4^{-2} ratios from 30 to 3 had a slight effect on COD removal (Borghei and Poorhashem, 2008).

A similar statistical approach for assessing the effect of OLR and SLR over CODr was previously reported. An anaerobic sequencing batch biofilm reactor was optimized using the Taguchi experimental design. Improved conditions for CODr (50% increase) were observed at an OLR of 3.5 $g.L^{-1}.day^{-1}$, neutral pH, BOD/COD ratio of 0.5, and low sulfate concentration (0.7 g/L) (Venkata Mohan *et al*., 2005). That work reached similar conclusions to those presented here: optimal reactor performance is reached at high OLR and low sulfate concentrations. Coincidentally, both studies reported a similar optimal OLR value (3.5 $g.L^{-1}.day^{-1}$) for CODr.

CONCLUSION

The effect of OLR and SLR on the performance of an ABR treating landfill leachate was studied. The results revealed that, with appropriate sulfate feeding, OLR can be increased without affecting reactor performance. A quadratic effect of OLR and SLR on CODr was observed. The highest COD removal (65%) was reached at a HRT of 18 hours (0.73 days), an OLR of 3.57 g $COD.L^{-1}.day^{-1}$, a SLR of 0.09 g $SO_4^{2-}.L^{-1}.day^{-1}$, and a COD/SO_4^{2} ratio of 40. An acceptable CODr (54%) was maintained even at a HRT 12 times lower (1.5 hours). A similar CODr for treatment of landfill leachates with low organic matter concentration (<10000 $mgCOD.L^{-1}$) has previously reported. However, the ABR described by this research is operated at an OLR three times higher than those previously been reported (Burbano-Figueroa, 2002; Castrillon *et al*., 2010; Yilmaz *et al*., 2012). Similar CODr performance at OLRs near to 4 g $COD.L^{-1}.day^{-1}$ were achieved by mixing leachate with municipal sewage (Wang and Shen, 2000) or feeding leachates with high concentrations of organic matter (>10000 mg $COD.L^{-1}$) to sequential sulfidogenic and methanogenic reactors (Nedwell and Reynolds, 1996) or up-flow anaerobic sludge blanket (UASB) reactors (Kettunen and Rintala, 1998).

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NOMENCLATURE

ASL	Antanas Sanitary Landfill
ASLWT	Antanas Sanitary Landfill Wastewater
COD	Chemical Demand of Oxigen ($mg\ O_2.L^{-1}$ or $g\ O_2.L^{-1}$)
CODr	COD removal efficiency (%)
HRT	Hydraulic Retention Time (days)
HS	Hydrogen Sulphide
OLR	Organic Loading Rate ($g\ COD.L^{-1}.day^{-1}$)
PSA	Path of Steepest Ascent
PE	Polyethylene
RSM	Response Surface Methodology
ABR	Anaerobic Baffled Reactor
SLR	Sulfate Loading Rate ($g\ SO_4^{2-}.L^{-1}.day^{-1}$)
SRB	Sulfate-Reducing Bacteria
SSOP	Steady State Operation Point
TSS	Total Suspend Solid ($mg\ TSS.L^{-1}$)
TSSr	TSS removal efficiency (%)
VFA	Volatile Fatty Acid ($mg\ CH_3COO^-.L^{-1}$)
VFAr	VFA removal efficiency (%)
VSS	Volatile Suspended Solids ($mg\ VSS.L^{-1}$)
VSSr	VSS removal efficiency (%)

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