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Landfill leachate treatment using powdered activated carbon augmented sequencing batch reactor (SBR) process: Optimization by response surface methodology

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ABSTRACT

In this study, landfill leachate was treated by using the sequencing batch reactor (SBR) process. Two types of the SBR, namely non-powdered activated carbon and powdered activated carbon (PAC-SBR) were used. The influence of aeration rate and contact time on SBR and PAC-SBR performances was investigated. Removal efficiencies of chemical oxygen demand (COD), colour, ammoniacal nitrogen (NH_3-N), total dissolved salts (TDS), and sludge volume index (SVI) were monitored throughout the experiments. Response surface methodology (RSM) was applied for experimental design, analysis and optimization. Based on the results, the PAC-SBR displayed superior performance in term of removal efficiencies when compared to SBR. At the optimum conditions of aeration rate of 1 L/min and contact time of 5.5 h the PAC-SBR achieved 64.1%, 71.2%, 81.4%, and 1.33% removal of COD, colour, NH_3-N, and TDS, respectively. The SVI value of PAC-SBR was 122.2 mL/g at optimum conditions.

1. Introduction

The disposal of municipal solid waste by sanitary landfilling is the most common method due to such advantages as simplicity, low price, and landscape-restoration of holes from mineral workings. However, its major weakness is the production of leachate in landfills [1–3]. Leachate is defined as the liquid formed by the percolation of precipitation through an open landfill or through the cap of a finished site. Leachates could contain huge amounts of pollutants such as organic substances (measured as chemical oxygen demand (COD) and biochemical oxygen demand (BOD_5)), ammonia, high concentrations of heavy metals, and inorganic salts [4–7]. Leachate is also rich in phenols, total dissolved salts (TDS), total alkalinity, total acidity, total hardness, chloride, sulfide and phosphorus [1,8]. Obviously, as landfill age increases, the biodegradable fraction of organic pollutants in leachate decreases due to anaerobic decomposition occurring in a landfill site. Thus, mature leachate contains much more refractory organics than young leachate. In this respect, young landfill leachate (age < 5 years) is typically characterized by high BOD_5 (4000–13,000 mg/L) and COD (30,000–60,000 mg/L) concentrations, fairly high amount of ammonia (<400 mg/L), high ratio of BOD_5/COD (0.4–0.7), and a pH value of <6.5. In contrast, stabilized landfill leachate (age > 10 years) normally contains high quantity of ammonia (>400 mg/L), moderately high strength of COD (<4000 mg/L), and a low BOD_5/COD ratio of less than 0.1 [9,10].

If not treated and disposed safely, landfill leachate could be a major source of water contamination because it could percolate through soil and subsoil, causing high pollution to receiving waters [11–13]. Thus, the treatment of hazardous leachate constituents before discharge has been made a legal requirement to prevent pollution of water resources and to avoid both acute and chronic toxicities.

To reduce the negative impacts of discharged leachate on the environment, several techniques of water and wastewater treatment have been used, including aerobic and anaerobic biological treatment [14–17], chemical and electrochemical oxidation processes [18,19], chemical precipitation [20], adsorption using various adsorbents [2,5], reverse osmosis [21], coagulation–flocculation [22,23], membrane processes [24], and ion exchange [25,26].

SBR is one of the biological processed applied to remove several pollutants. The SBR process varies from activated-sludge techniques, because SBR merges all treatment units and processes into a single basin or tank, whereas traditional systems rely on various tanks. Typically, SBR is divided into five stages: fill, react, settle, draw, and idle [27,28]. SBR has been used for the treatment of domestic, municipal, industrial, dairy, synthetic, toxic and slaughterhouse wastewaters, swine manure, and landfill leachates [7,24,27–40].

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Generally, due to low BOD_5/COD ratio, and high concentration of NH_3-N in landfill leachate, the capability of SBR in treating landfill leachate was lower in comparison to municipal and industrial wastes [7]. In literature, SBR has been used for the treatment of leachate with low BOD_5/COD ratio of 0.09–0.37 [9,36,41]. To enhance the capability of SBR for leachate treatment, landfill leachate was treated by powdered activated carbon augmented SBR (PAC) process.

Thus far, the effects of aeration rate and contact time on the removal of COD, colour, NH_3-N, and TDS in both SBR and PAC-SBR have not been reported in literature. Furthermore, the effects of combined parameters on sludge volume index (SVI) in both SBR and PAC-SBR have not been investigated previously. This paper aims to fill this knowledge gap in the SBR process.

2. Materials and methods

2.1. Leachate sampling and characterization

Leachate samples were collected from Kulim Sanitary Landfill situated in the town of Kulim, Kedah, Malaysia. Its geographical coordinates are 5°23′ N and 100°33′ E. It has an area of 56 ha and is bordered by palm oil plantation. This open dumping site started working in 1996. The landfill receives about 240 tons of municipal solid wastes daily. The depth of solid waste is around 20 m. This landfill is equipped with leachate collection facilities. Eight samples were collected from the Kulim Sanitary Landfill site. The samples were taken from May 2009 to March 2010, and instantaneously transported to the laboratory, and stored in a cold room at 4 °C prior to use in order to minimize biological and chemical reactions [42].

The characteristics of leachate samples are illustrated in Table 1. To identify the environmental risks of leachate, the obtained parameter values were compared with Malaysian Environmental Quality (Control of Pollution from Solid Waste Transfer Station and Landfill) Regulations 2009, under the Laws of Malaysia Environmental Quality Act 1974 [43].

Table 1
Leachate characteristics at Kulim landfill site.

No.	Parameter	Average value	Standard discharge limit[a]
1	Phenols (mg/L)	2.06	0.001
2	pH	7.87	6–9
3	Colour (Pt.Co)	3627	100
4	Electrical conductivity (m s/cm)	8.31	–
5	Temperature (°C)	33.6	40
6	Total solids (mg/L)	5640	–
7	Suspended solids (mg/L)	689	50
8	Acidity (mg/L $CaCO_3$)	2158	–
9	Alkalinity (mg/L $CaCO_3$)	15350	–
10	Total Hardness (mg/L $CaCO_3$)	1893	–
11	BOD (mg/L)	373	20
12	COD (mg/L)	1655	400
13	BOD_5/COD	0.218	0.05
15	Ammonia-N (mg/L NH_3-N Ness)	600	5
16	Nitrite-N (mg/L NO_2-N-HR)	53.6	–
17	Total phosphorus (mg/L PO_4^{3-}-TNT)	37	–
18	Magnesium (mg/L $CaCO_3$)	294	–
19	Calcium (mg/L $CaCO_3$)	1600	–
20	Chloride (mg/L)	324	–
21	Sulfide (mg/L S^{2-})	0.82	0.5
22	Total iron (mg/L Fe)	4.13	5
23	Zinc (mg/L Zn)	0.25	2
24	Salinity (g/L)	4	–
25	TDS (%)	5.07	
26	ORP (mV)	12.2	–

[a] Environmental Quality (Control of Pollution from Solid Waste Transfer Station and Landfill) Regulations 2009, under the Laws of Malaysia–Malaysia Environmental Quality Act 1974 [43].

Table 2
Characteristics of activated sludge sample.

Parameter	Average value
Temperature (°C)	26.95
Total solids (mg/L)	11540
Suspended solids (mg/L)	9893
MLVSS/MLSS	0.84
Electrical conductivity (m s/cm)	2.02
Total dissolved salts (%)	1.31
Salinity (g/L)	1.03
ORP (mV)	−139.6
NH_3-N (mg/L)	143
COD (mg/L)	4055
pH	6.75

2.2. Activated sludge characteristics

The activated sludge used in this study was obtained from Bayan Baru sewage treatment plant located in Penang, Malaysia. The characteristics of the activated sludge are shown in Table 2.

2.3. Operation of the reactors

The current study was carried out in six 2000 mL beakers each having a working volume of 1200 mL, an inner diameter of 113 mm, and a height of 200 mm. The beakers were filled with 1080 mL acclimated sludge and 120 mL of Kulim landfill leachate, using a mixing ratio of 10% (v/v). The acclimated sludge consisted of 90% returned activated sludge plus 10% landfill leachate. At the end of each run, 120 mL of supernatant was withdrawn and another 120 mL leachate was added for the new experiment. This procedure continued for at least 10 days to allow the system to adapt to new conditions (Fig. 1).

The reactors were divided into 2 groups comprising 3 for SBR and 3 for PAC-SBR. The PAC used for adsorption contaminants in the PAC-SBR pre-dried at 103–105 °C and sized 75–150 μm (passing sieve No. 100, retained on sieve No. 200). Table 3 depicts the characteristics of PAC.

Prior to aeration, 1.2 g of PAC (i.e. PAC dosage = 10 g/L) was added to each PAC-SBR. The experiments were conducted at room temperature, and air was supplied to the reactors by an air pump (YASUNAGA, Air pump INC. voltage: 240 V, Frequency: 50 Hz, Input power 61 W, Model: LP-60A, Pressure: 0.012 MPa, Air volume: 60 L/min, Serial No.: 08110014, Made in China). The air flow rate was manually regulated by an air flow meter (Dwyer Flow meter, Model: RMA-26-SSV).

Sequential operation of the reactor system comprised fill, react, settle, draw, and idle phases. In all experiments, the duration for

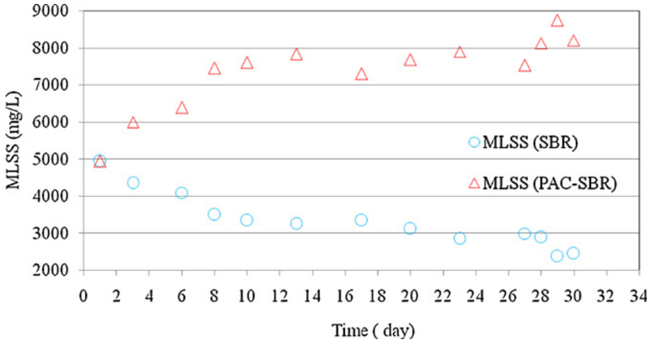


Fig. 1. Concentration of MLSS inside SBR and PAC-SBR.

Table 3
Characteristics of powdered activated carbon (PAC).

Parameter	Unit	Value
Bet surface area	sq. m/g	902
Langmuir surface area	sq. m/g	1214
Single point surface area at p/p_o 0.2027	sq. m/g	906
Micropore area	sq. m/g	448
Single point total pore volume of pores less than 1265.1476 *a* diameter at p/p_o 0.9845	cc/g	0.53
Micropore volume	cc/g	0.21
Average pore diameter (4 *v*/*a* by Langmuir)	A	17.5
BJH adsorption average pore diameter (4 *v*/*a*)	A	44.4

filling and mixing (20 min), settling (90 min), drawing, and idle (10 min) was fixed. Different aeration rates of 0.5, 4, and 7.5 L/min and contact times of 2, 12, and 22 h were applied to both SBR and PAC-SBR. Different contact times formed 3 cycles (4, 14, and 24 h). The sludge retention time was controlled by the daily manual discharge of a certain amount of mixed liquor from the reactor immediately before the start of the settle phase. SVI and removal efficiency of COD, colour, NH_3-N and TDS were monitored in the experiments. Removal efficiency was determined by measuring the target parameters before and after treatment. The following equation was used for calculating removal efficiency:

$$\text{Removal}\,(\%) = \frac{(C_i - C_f) * 100}{C_i} \qquad (1)$$

where C_i and C_f are the initial and final concentrations of the parameters, respectively.

2.4. Experimental design and data analysis

In this work, the central composite design (CCD) and response surface methodology (RSM) were used. CCD was established through Design Expert Software (6.0.7), and was used for the statistical design of experiments and data analysis. RSM was used to determine the optimum process parameter levels. RSM gathers mathematical and statistical techniques that are useful for the modeling and analysis of problems, in which responses of interest are influenced by some variables [44]. In addition, RSM is to optimize the responses.

The design consisted of k^2 factorial points augmented by $2k$ axial points and a center point, where k is the number of variables. Four replicates at the central points were employed to fit the second-order polynomial models and to obtain the experimental error for this study. Each of the 2 operating variables was considered at 3 levels, low (−1), central (0), and high (+1). In the present work, CCD and RSM were applied to appraise the association between the most important operating variables i.e. aeration rate (L/min) and contact time (h) [32,34,36] and their responses (dependent variables) in addition to optimizing the appropriate situation of operating variables to predict the best value of responses.

Aeration rates (0.5, 4, and 7.5 L/min) and contact times (2, 12, and 22 h) were used with SBR and PAC-SBR. To carry out an adequate analysis of the aerobic process, 5 dependent parameters (COD, colour, NH_3-N, TDS, and SVI) were measured as responses (Tables 4 and 5).

The quadratic equation model for forecasting the optimum conditions is explained by the following equation:

$$Y = \beta_0 + \sum_{i=1}^{k}\beta_i X_i + \sum_{i=1}^{k}\beta_{i_i} X_i^2 + \sum_{i_i<j}^{k}\sum_{j}^{k}\beta_{i_j} X_i X_j + \ldots + e, \qquad (2)$$

where Y is the response; X_i and X_j are the variables; β_0 is a constant coefficient; β_j, β_{jj}, and β_{ij} are the interaction coefficients of linear, quadratic and second-order terms, respectively; k is the number of studied factors; and e is the error. Here, the quality of the fit polynomial model was expressed by the coefficient of determination R^2, and the statistical significance was checked by Fisher's F-test in the same program. Model terms were evaluated by the P-value (probability) with 95% confidence level. The results were completely analyzed by analysis of variance (ANOVA) in the Design Expert Software. Three-dimensional plots with the respective contour plots were obtained from the results of the experiments. From these, the effects of interaction between the two factors on responses were studied.

2.5. Analytical methods

All tests were conducted in accordance with the Standard Methods for the Examination of Water and Wastewater [42]. A spectrophotometer (DR/2800 HACH) was used for measuring phenols (mg/L), colour (Pt.Co), total hardness (mg/L $CaCO_3$), NH_3-N (mg/L), nitrite-N (NO_2-N mg/L), total phosphorus (PO_4^{3-} mg/L), magnesium (mg/L), calcium (mg/L $CaCO_3$), chloride (mg/L), sulfide (mg/L S^{2-}), total iron (mg/L Fe), and zinc (mg/L Zn). COD concentration was determined using the closed reflux and colorimetric Method No. 5220D. YSI 556 MPS (YSI incorporated, USA) was used for recording the values of pH, electrical conductivity (m s/cm), temperature (°C), salinity (g/L), TDS (%), and oxidation reduction potential i.e. ORP (mV). Titration was performed for acidity (mg/L $CaCO_3$) and alkalinity (mg/L $CaCO_3$) determination.

SVI is an indication of the sludge settling ability in the final basin. It is a helpful test that indicates changes in sludge-settling characteristics and its quality. SVI is the volume of settled sludge (in mL) occupied by 1 g dry sludge solids after 30 min of settling in a 1000 mL graduated cylinder. One liter of mixed liquor sample was

Table 4
Experimental variables and results for the SBR.

Run	Variables		Responses				
	A: Aeration rate (L/min)	*B*: Contact time (h)	COD rem. (%)	Colour rem. (%)	NH_3-N rem. (%)	TDS rem. (%)	SVI mL/g
1	7.5	2	17	15.9	78.1	11.2	338.1
2	7.5	22	1.32	21	96.3	14.5	366.9
3	7.5	12	5.2	28.8	94.2	12.2	432.1
4	4	12	6.3	51.2	96.3	8.4	436.1
5	0.5	22	9.1	16.2	90.1	5.6	369.4
6	4	12	3.5	49.2	86.3	1.4	436.4
7	4	22	9.1	8.7	92.4	18.9	363.2
8	0.5	12	23.3	70.1	89.2	3	408.3
9	4	2	20.5	29.3	79.7	2.4	334.7
10	4	12	10.5	59.6	93.3	1.7	428.5
11	4	12	2.5	46.5	92.2	3.7	433.7
12	0.5	2	47.1	40.1	73.3	1.8	336.5
13	4	12	1.13	51.6	92	3.8	428.3

Table 5
Experimental variables and results for the PAC-SBR.

Run	Variables		Responses				
	A: Aeration rate (L/min)	*B*: Contact time (h)	COD rem. (%)	Colour rem. (%)	NH_3-N rem. (%)	TDS rem. (%)	SVI mL/g
1	7.5	2	52.1	38.5	82.9	13.2	130.1
2	7.5	22	38.1	50.2	97.6	17.8	86.9
3	7.5	12	44.5	44.6	95.9	14.8	112.1
4	4	12	48.8	68.5	96.2	4.2	108
5	0.5	22	69.8	75.5	78.1	4.3	98.8
6	4	12	50.2	72.2	85.5	6.7	112.5
7	4	22	49.5	63.2	93.7	16.4	93.3
8	0.5	12	69.3	82.3	87.3	4.6	112.1
9	4	2	57.1	45.7	81	7.8	130.1
10	4	12	45.8	73.7	92.1	4.9	108.8
11	4	12	43.8	72.5	90.3	6.5	109.3
12	0.5	2	66.1	62.8	74.6	0.8	128.8
13	4	12	45	66	91	5.6	109.6

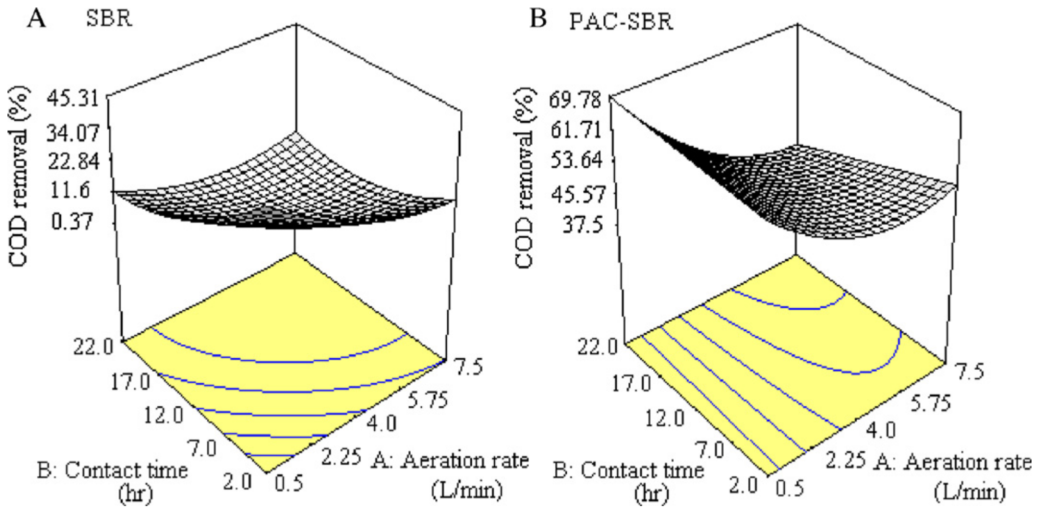


Fig. 2. Design-expert plot; response surface plot for COD removal (SBR and PAC-SBR).

taken from the aeration tank and was allowed to settle for 30 min in a 1 L graduated cylinder and sludge volume was reported in mL. SVI was calculated in mg/L by dividing the results of the settling test in mL by the mixed liquor suspended solids (MLSS) concentration in the reactor [42,45].

3. Results and discussion

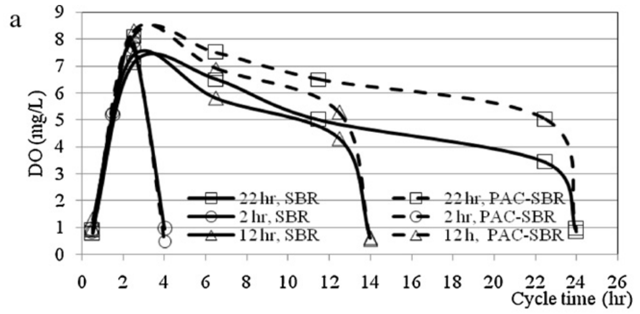
Table 1 shows that Kulim landfill leachate contained high concentration of COD (1655 mg/L) and high-intensity colour (3627 Pt.Co) caused by the presence of high molecular weight organic compounds. The concentration of NH_3-N was also high (600 mg/L). An average BOD_5 value of 373 mg/L was recorded (Table 1), which gave a low biodegradability ratio (BOD_5/COD) of 0.2 (age > 10 years). Moreover, the concentration of phenols, suspended solids, BOD_5, COD, BOD_5/COD, NH_3-N, and sulfide surpassed the allowable limits issued by the 1974 Environmental Quality Act of Malaysia [43]. In order to study the effects of aeration on leachate quality, Aziz et al. [1] compared the characteristics of leachate in unaerated and aerated ponds at the Pulau Burung Landfill site in Penang, Malaysia. They found that aeration had a significant effect on reducing the concentration of several contaminants in leachate [1]. In the current work, raw leachate of Kulim landfill was treated by PAC augmented SBR process in order to reduce the environmental risks from the Kulim landfill leachate.

3.1. *Reactor performance*

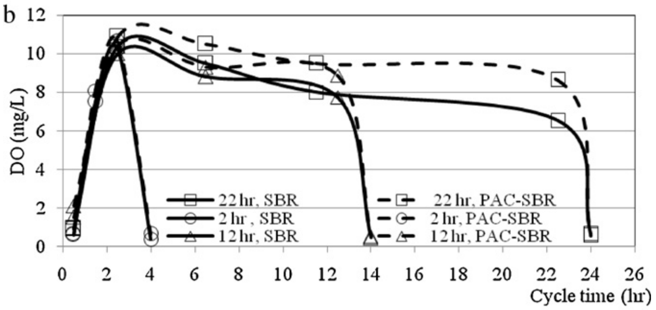
3.1.1. *COD removal*

The removal efficiency of SBR ranged from 1.32% (aeration rate = 7.5 L/min, contact time = 22 h) to 47.1% (aeration rate = 0.5 L/min, contact time = 2 h). However, a higher range of removal efficiency from 38.1% to 66.1% was obtained by PAC-SBR at same operation conditions (Tables 4 and 5). The present results agreed with those reported in literature [32]. Azimi et al. [32] reported that the increase in aeration rate from 25.2 to 90 L/h resulted in an increase in COD concentration of treated wastewater from 10.4 to 10.9 mg/L. In general, most of the organic substances, particularly soluble biodegradable part is eliminated at the beginning of reaction stage. Aeration rate has a complex influence on nitrification and denitrification processes. Some of the most vital valuable parameters on these processes are initial amount of nitrogen compounds inside the reactor, aeration rate, biological floc volume, quantity and characteristics of the existing organic substances [32].

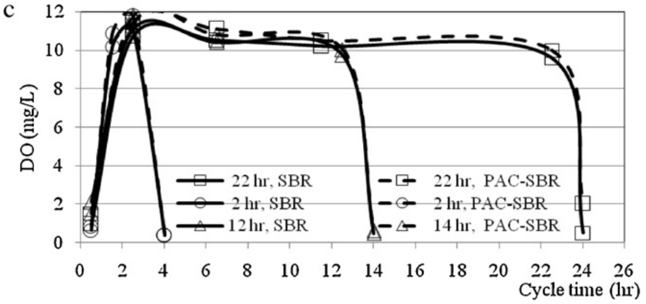
Using PAC with SBR clearly enhanced the COD removal efficiency in accordance with the results reported in literature [7]. Anaerobic SBR has been studied by Timur and Ozturk [46] for young landfill leachate (age 3.5 years) and the authors obtained COD removal rates within the range 64–85%. Spagni et al. [41] reported that low removal efficiency of COD (20%) confirmed the low biodegradability of leachate [39,41]. As demonstrated in Fig. 2, the best removal efficiency using PAC-SBR (69.8%) was obtained at



Aeration rate = 0.5 L/min



Aeration rate = 4 L/min



Aeration rate = 7.5 L/min

Fig. 3. DO variation inside SBR and PAC-SBR at different aeration rates.

0.5 L/min (aeration rate) and 22 h (contact time). Generally, increasing contact time in PAC-SBR caused increasing removal efficiency and the results agreed with Guo et al. [9] and Aghamohammadi et al. [17].

For both SBR and PAC-SBR, a relatively lower aeration rate (0.5 L/min) resulted in good COD removal efficiency. Fig. 3 illustrates the dissolved oxygen (DO) variation inside SBR and PAC-SBR at different aeration rates i.e. 0.5 L/min, 4 L/min, and 7.5 L/min. During react phase in all the experiments, the DO concentration was more than 3 mg/L (Fig. 3). It has been mentioned in literature that DO concentration inside the SBR should be more than 2 mg/L [7]. Minimum aeration rate of 0.5 L/min and contact time of 2 h provided sufficient DO inside the SBR and the PAC-SBR (>2 mg/L). It can be noticed from Fig. 3 that the increase in aeration rate did not influence the removal efficiency of COD. This was due to the adequate amount of DO (>2 mg/L) provided via minimum aeration rate (0.5 L/min). Thus, a great part of COD was removed at the beginning of the SBR process.

3.1.2. *Colour removal*

Minimum and maximum colour removal efficiency achieved by SBR reactors was 8.7% (aeration rate = 4 L/min, contact time = 22 h) and 71% (aeration rate = 0.5 L/min, contact time = 12 h), respectively. At the same operational conditions, PAC-SBR reactors offered higher removal efficiency of 82.3% which signifies the role of PAC in colour removal (Tables 4 and 5). In PAC-SBR, an optimum removal efficiency of 82.3% was achieved at a reaction time of 0.5 L/min and 12 h contact time. Higher removal efficiencies were generally obtained at low aeration rates (0.5 L/min). Increasing aeration rates caused a reduction in removal efficiencies (Fig. 4). Due to inconsistent trends of removal efficiency by both SBR and PAC-SBR, the influence of contact time on removal was not established, although 12 h contact time displayed the best behavior. The results obtained from SBR and SBR-PAC (Tables 4 and 5) demonstrated that the elimination of organic substances (indicated by COD and colour) was due to both biological and adsorption phenomenon. As illustrated in Table 5, treatment of low biodegradable leachate by SBR resulted in low removal of COD and colour. However, adding PAC to SBR considerably enhanced the removal efficiency. Activated carbon is the most effective adsorbent owing to its superior ability for removal of a wide variety of dissolved organic pollutants from wastewater [4,5]. The kinetic rate of adsorption was found to be affected not just by film diffusion, but also by the rate of adsorption and the internal surface diffusion on the solid surface of an adsorbent [10,45]. In general, high surface area, wide range of pore size distribution and hydrophobic surface helped activated carbon to adsorb organic pollutant from leachate [2,10].

3.1.3. *NH_3-N removal*

The existence of high levels of NH_3-N in landfill leachate over a long period of time is one of the most important problems faced by the landfill operators. This high quantity of unprocessed NH_3-N leads to reduced performance efficiency of biological treatment methods, accelerated eutrophication, and increased dissolved oxygen reduction. Consequently, NH_3-N is extremely toxic to aquatic organism [25]. As seen from Fig. 5, the increase in aeration rate and contact time caused an increase in the removal efficiency for both PAC-SBR and SBR. In SBR, biological removal of NH_3-N occurred via nitrification and denitrification processes [47]. Thus, the majority of NH_3-N was removed biologically as demonstrated in Fig. 5. However, according to Uygur and Kargi [7], the addition of PAC to activated sludge reactors enhanced nitrification efficiency in biological treatment of landfill leachate. Minimum removal for both SBR (74.35%) and PAC-SBR (76.23%) was recorded at an aeration rate of 0.5 L/min and a contact time of 2 h. On the other hand, the respective maximum removal of 96.90% and 99.66% was obtained at an aeration rate of 7.5 L/min and a contact time of 22 h. Both aeration rate and contact time affected removal efficiency (Table 6), and PAC-SBR achieved better NH_3-N removal than SBR alone. In this study, 3 different hydraulic retention times (HRTs) (1.67, 5.83, and 10 d) were used. Klimiuk and Kulikowska [36] and Laitinen et al. [48] studied the effect of HRT on SBR performance [36,48] and the results obtained in the current study agreed with their findings.

3.1.4. *TDS removal*

At the lowest aeration rate of 0.5 L/min and 2 h contact time, minimum removal efficiencies of 1.8% and 0.8% were recorded for the SBR and PAC-SBR, respectively. At the highest operational conditions i.e. 7.5 L/min aeration rate and 22 h contact time, the maximum removal efficiencies for SBR and PAC-SBR were 14.5% and 17.8%, respectively (Tables 4 and 5), which indicate the superior TDS removal efficiency of PAC-SBR compared with that of SBR. Furthermore, increasing both aeration rate and contact time had very obvious effect on TDS removal (Fig. 6). It could be noticed from the obtained results that a part of TDS removed biologically in SBR. On the other hand, the presence of PAC (as adsorbent) offered a better performance in removing TDS compared with SBR. The role of PAC obviously appeared in increasing TDS removal in PAC-SBR.

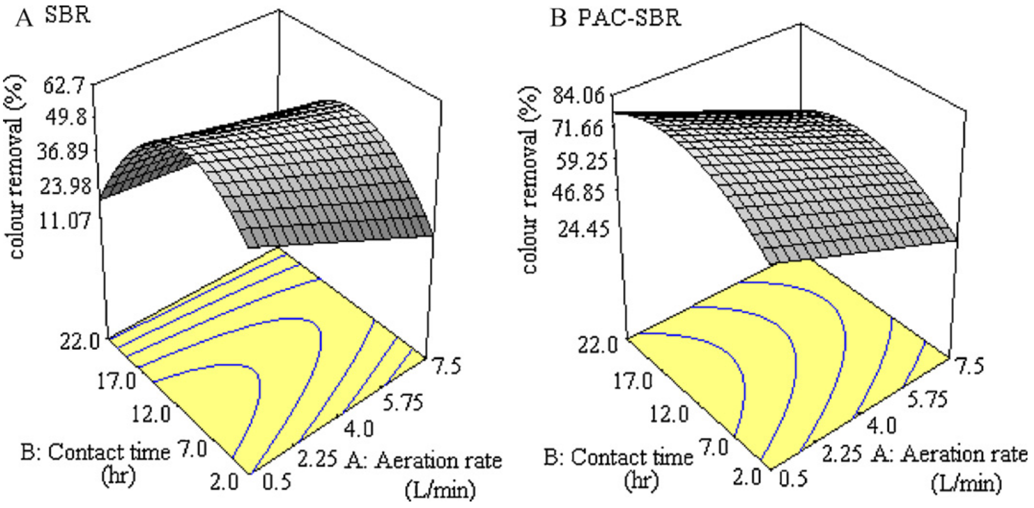


Fig. 4. Design-expert plot; response surface plot for colour removal (SBR and PAC-SBR).

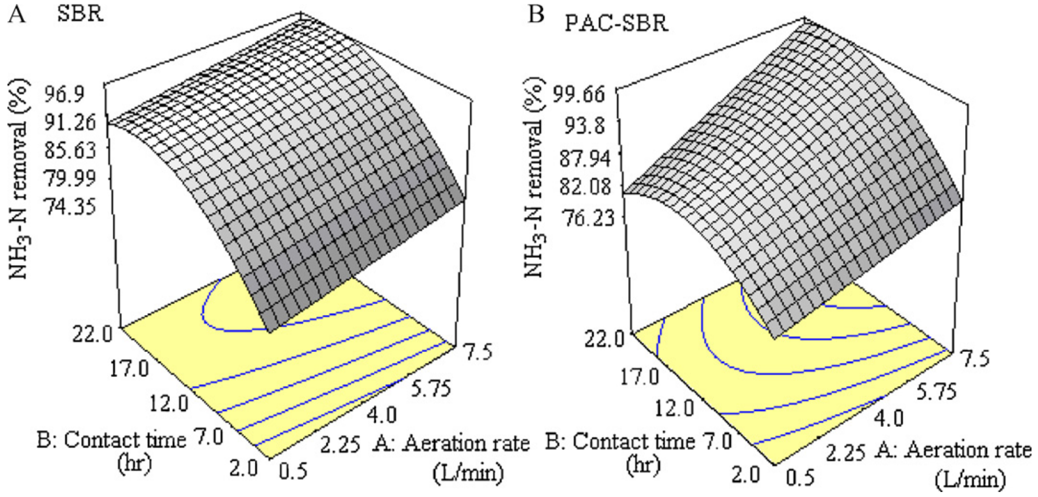


Fig. 5. Design-expert plot; response surface plot for NH_3-N removal (SBR and PAC-SBR).

Table 6
ANOVA results for response parameters.

SBR type	Response	Final equation in terms of actual factors	Prob.	R^2	Adj. R^2	Adec. P.	SD	CV	Press	Prob. LOF
hboxSBR	COD	$56.15-8.95A-3.47B+0.55A^2+0.07B^2+0.16AB$	0.001	0.9197	0.8624	13.495	4.72	39.24	1036.3	0.205
	Colour	$38.45-5.38A+5.50B-0.29B^2+0.21AB$	0.0008	0.884	0.8259	10.185	7.92	21.09	2834.4	0.096
	NH_3-N	$69.31+0.77A+2.47B-0.07B^2$	<0.0001	0.8898	0.865	14.24	2.69	3.03	106.6	0.17
	TDS	$-3.12+1.31A+0.39B$	0.0166	0.5597	0.4716	8.543	4.14	60.79	286.4	0.154
	SVI	$299.28+20.13B-0.78B^2$	<0.0001	0.9723	0.9667	25.018	7.71	1.96	831.5	0.058
PAC-SBR	COD	$70.01-7.09A+0.21B+0.66A^2-0.13AB$	0.0002	0.9247	0.887	15.113	3.44	6.59	181	0.221
	Colour	$58.73-4.16A+3.71B-0.13B^2$	<0.0001	0.9177	0.8903	19.296	4.55	7.24	391.4	0.175
	NH_3-N	$72.5+0.76A+1.77B-0.07B^2+0.08AB$	0.002	0.8533	0.78	10.521	3.44	3.9	320.1	0.682
	TDS	$-1.91+1.72A+0.28B$	0.0009	0.7526	7031	12.444	2.94	35.47	133.7	0.016
	SVI	$129.53+0.63A-1.36B-0.09AB$	<0.0001	0.9634	0.9512	26.534	2.81	2.52	157.5	0.102

A: first variable, aeration rate (L/min); *B*: second variable, contact time (h); prob.: probability of error; R^2: correlation coefficient; Adj. R^2: adjusted R^2; Adeq. P.: adequate precision; SD: standard deviation; CV: coefficient of variance; PRESS: predicted residual error sum of square; and Prob. LOF: probability of lack of fit.

3.1.5. SVI

The minimum SVI of 336.4 mL/g was obtained by SBR at operational conditions of 4 L/min and 2 h. For the same operational conditions by PAC-SBR, 130.1 mL/g SVI was reported. The maximum SVI value for SBR was 429.7 mL/g at aeration rate of 4 L/min and contact time of 12 h. Lowest SVI of 88.8 mL/g value was observed for PAC-SBR at operational conditions of 7.5 L/min (aeration rate) and 22 h (contact time) (Tables 4 and 5). Uygur and Kargi [7] have reported that PAC aids the formation of big microbial flocs, resulting in better settling properties and high biomass in the reactor [7]. In the current study, PAC-SBR showed good ability to improve sludge-settling characteristics compared with SBR as demonstrated in Fig. 7. The trend of MLSS concentration throughout the operational time commonly reflects the trend of the SVI value (Figs. 1 and 7). For instance, lower MLSS concentrations in SBR (Fig. 1) resulted in higher SVI values in the range of 336.4–429.7 mL/g (Fig. 7A). However, higher MLSS concentrations in PAC-SBR resulted in lower SVI values of 88.8–130.1 mL/g

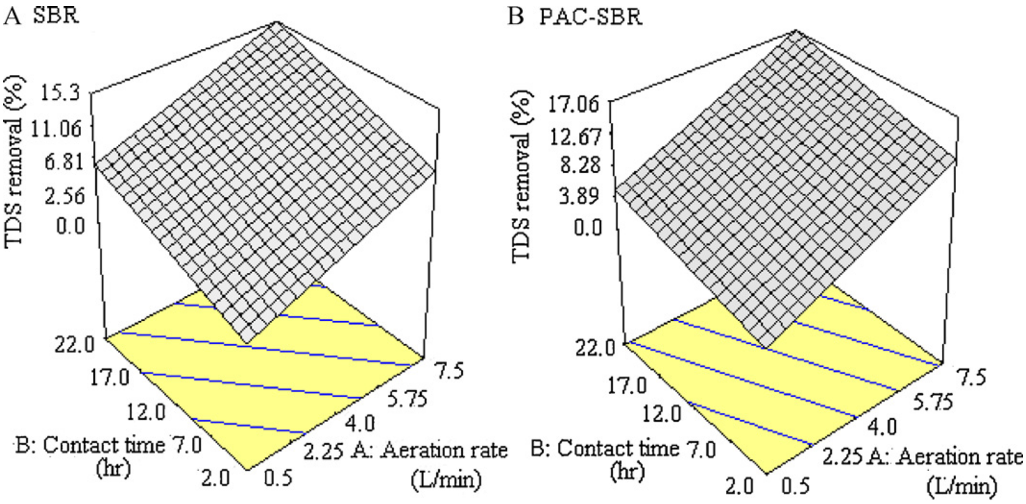


Fig. 6. Design-expert plot; response surface plot for TDS removal (SBR and PAC-SBR).

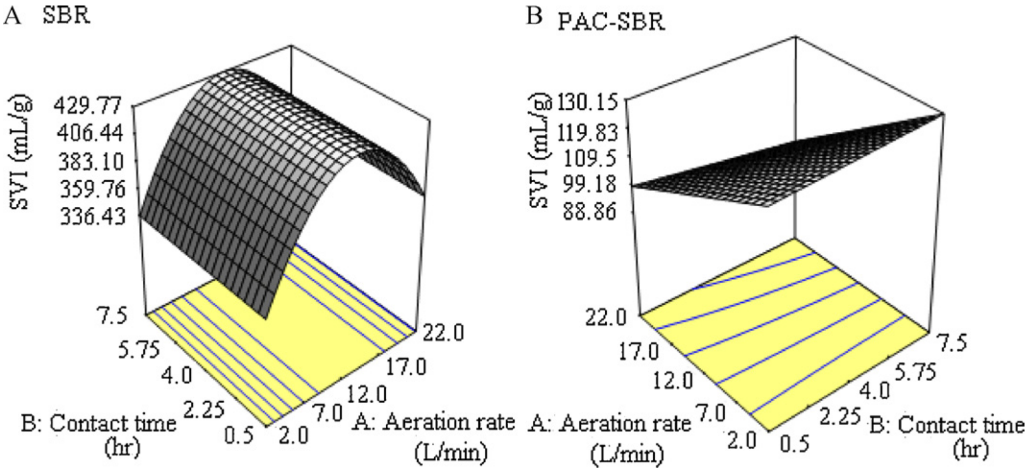


Fig. 7. Design-expert plot; response surface plot for SVI values (SBR and PAC-SBR).

as shown in Fig. 7B. Consequently, the deterioration of the sludge settling ability and compressibility (increasing SVI values) resulted in decreasing MLSS concentration. Previous study has shown that high SVI values (bulking sludge) and low biomass concentrations were indications of inhibitory effects of some hazardous substances on microorganisms [38].

3.2. Statistical analysis

RSM was used for analyzing the correlation between the variables (aeration rate and contact time) and the five important process responses (COD, colour, NH_3-N, TDS, and SVI) for both SBR and PAC-SBR. Considerable model terms were preferred to achieve the best fit in a particular model. CCD permitted the development of mathematical equations where predicted results (Y) were evaluated as a function of aeration rate (A) and contact time (B). The results were computed as the sum of a constant, two first-order effects (terms in A and B), one interaction effect (AB), and two second-order effects (A^2 and B^2), as shown in Eq. (1) and Tables 4 and 5. The results were analyzed by ANOVA to determine the accuracy of fit. Equations from the first ANOVA analysis were adapted by neglecting the terms found statistically irrelevant. Table 6 shows the reduced quadratic models in terms of actual factors. Table 6 also illustrates other statistical parameters. All models were significant at the 5% confidence level because probability values were less than 0.05. The lack of fit (LOF) F-test explains variation of the data around the modified model. LOF was significant, if the model did not fit the data well. Generally, large probability values for LOF (>0.05) (Table 6) explained that the F-statistic was insignificant, implying significant model relationship between variables and process responses. The correlation coefficient (R^2) gave the proportion of total variation in the response predicted by the model, indicating the ratio of sum of squares due to regression (SSR) to total sum of squares (SST). R^2 values close to 1 were desirable, and a high R^2 coefficient ensured acceptable modification of the quadratic model to the experimental data. Adequate precision compared the range of the predicted values at the design points to the mean prediction error. Adequate precision greater than 4 showed adequate model inequity [20]. All Adequate precision figures in Table 6 are greater than 4 and this confirmed that all the predicted models could be used to navigate the design space defined by the CCD. The suitability of the model could be judged by diagnostic plots i.e. predicted vs. actual values. Figs. 8–12 show the predicted vs. actual value plots of the response parameters for the SBR and PAC-SBR. These plots signified a sufficient agreement between the real data and the values achieved from the models. The coefficient of variance (CV) is the ratio of the standard error of estimate to the average value of the observed response defined by the reproducibility of the model. If the CV of the model is greater than 10%, then the model is reproducible [22,26]. In this work,

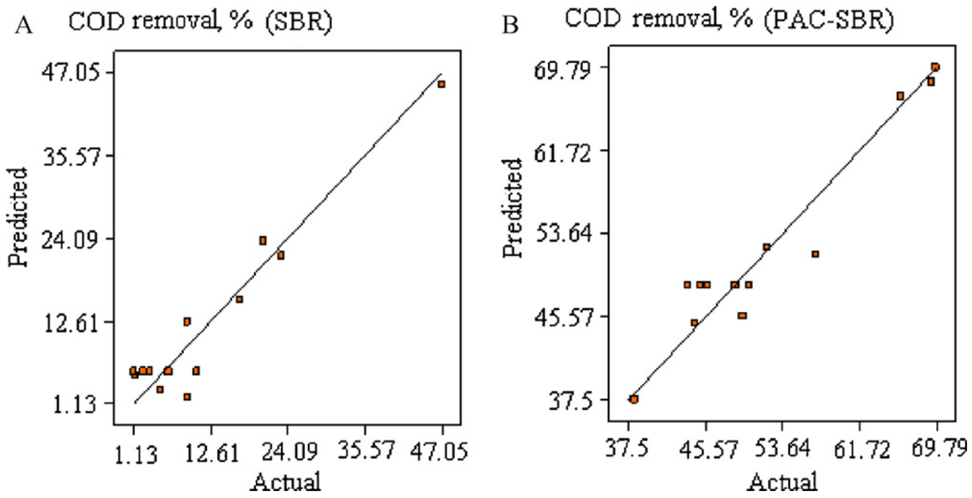


Fig. 8. Design-expert plot; predicted vs. actual values plot for COD removal.

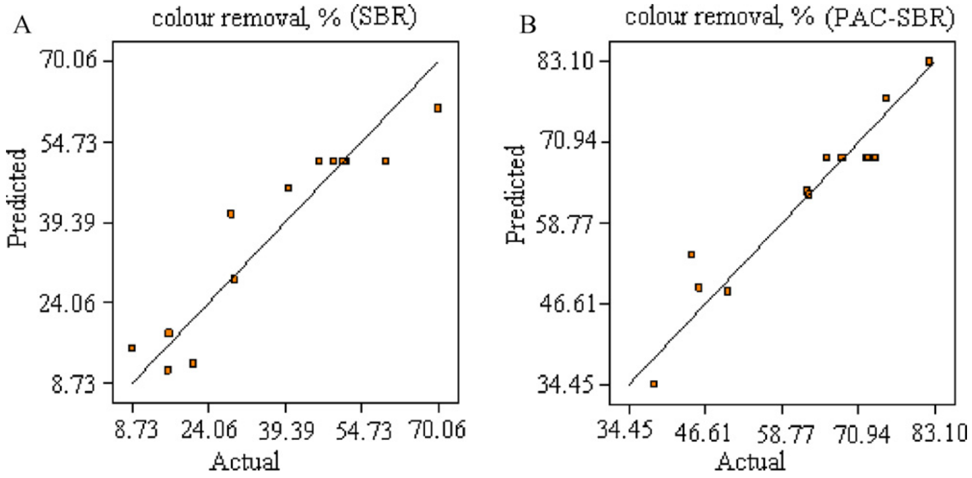


Fig. 9. Design-expert plot; predicted vs. actual values plot for colour removal.

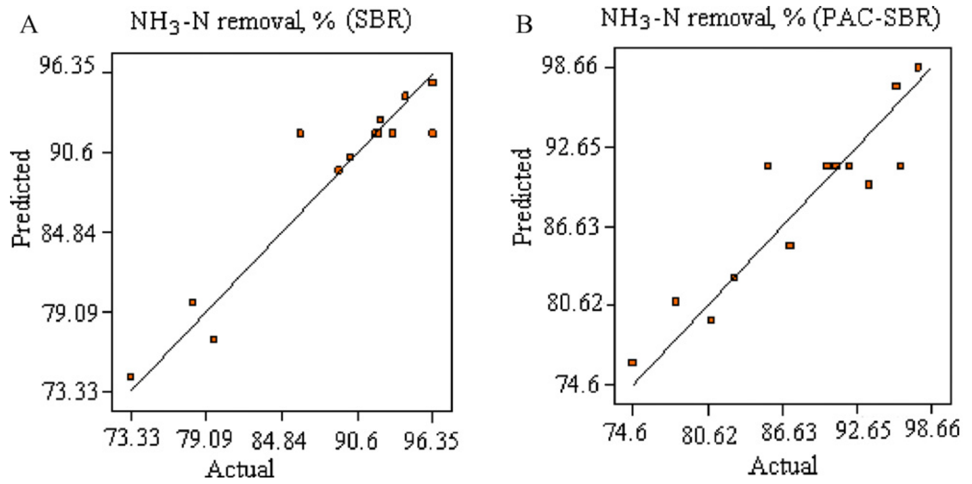


Fig. 10. Design-expert plot; predicted vs. actual values plot for NH_3-N removal.

Table 7
The value of response at optimum conditions.

Reactor	Responses				
	COD, rem (%)	Colour, rem (%)	NH_3-N, rem (%)	TDS, rem (%)	SVI (mL/g)
SBR	25.1	51.6	82.5	1.7	387.3
PAC-SBR	64.1	71.2	81.4	1.3	122.2

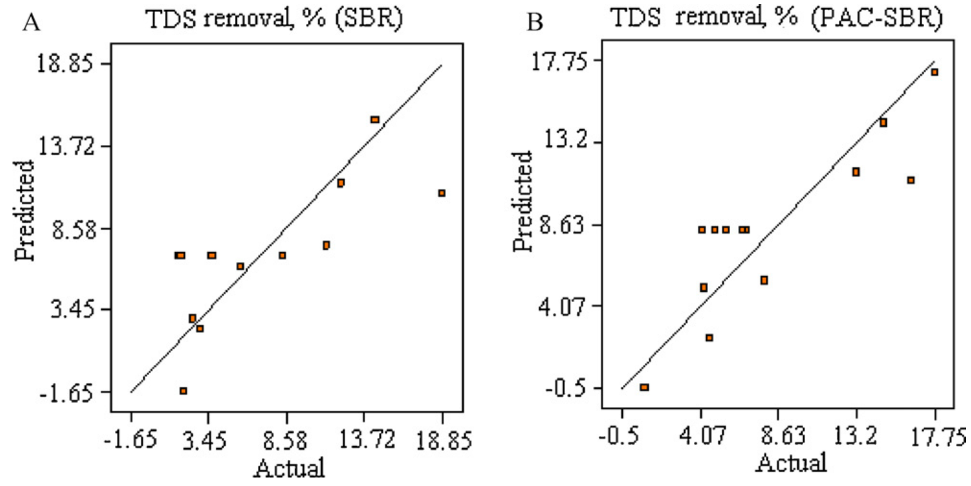


Fig. 11. Design-expert plot; predicted vs. actual values plot for TDS removal.

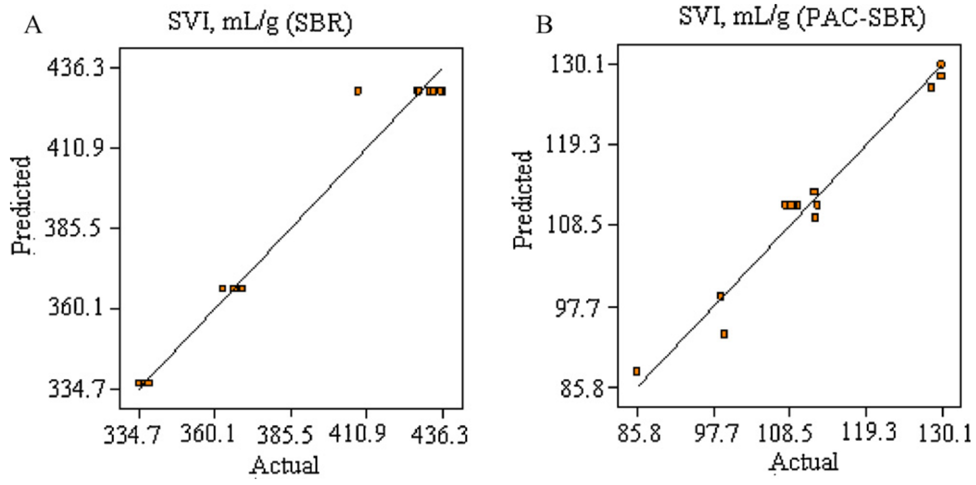


Fig. 12. Design-expert plot; predicted vs. actual values plot for SVI values.

PAC-SBR models had better reproducibility than SBR (Table 6). All PAC models (except in TDS removal) were thus considered reproducible.

3.3. Experimental condition optimization

RSM was used to recognize independent variables (aeration rate and contact time) that produced optimum values of the responses (COD, colour, NH_3-N, TDS, and SVI). Both independent variables were individually increased or decreased in an attempt to find the optimum practical responses. Subsequently, these optimum variables were selected as the conditions for obtaining the best results [26].

Table 7 shows the chosen response values for each parameter. These constraints were chosen relatively close to the acquired maximum removal and practicability standards of treatment plants.

The optimization of experimental conditions was identified by considering whether the rates of COD, colour, NH_3-N, and TDS removal, and SVI value were higher than the arbitrarily chosen constraint values. Two optimum conditions were predicted by the Design Expert Software. According to the model, the optimized conditions occurred for the SBR reactor at the aeration rate of 2 L/min and contact time of 5.56 h, which resulted in 25.1%, 51.6%, 82.5%, and 1.7% removal rates for COD, colour, NH_3-N, and TDS, respectively, and an SVI value of 387.3 mL/g. The second predicted optimum conditions for the PAC-SBR reactor occurred at the aeration rate of 1 L/min and contact time of 5.5 h, which resulted in 64.1%, 71.2%, 81.4%, and 1.3% removal rates for COD, colour, NH_3-N, and TDS, respectively, and an SVI value of 122.2 mL/g. The cycle time selected for both SBR and PAC-SBR was 8 h which included filling for 30 min for both the reactors, aeration for 5.56 h (334 min) for SBR and 5.5 h (330 min) for PAC-SBR, settling for 90 min for both the reactors, draw and idle for 26 min (SBR) and 30 min (PAC-SBR). The selected cycle times agreed with those used in previous studies [34,47,49,50].

4. Conclusions

The treatability of raw low biodegradable leachate (average BOD_5/COD ratio = 0.22) generated from Kulim landfill was studied by using SBR and PAC augmented SBR process. A number of contaminants in Kulim landfill leachate exceeded the permissible discharge limits including COD, colour, NH_3-N and TDS. The results indicated that low aeration rate of 0.5 L/min was sufficient and efficient for target parameters removal from stabilized landfill leachate. Furthermore, the results demonstrated that the operational parameters (i.e. aeration rate and contact time) had considerable influence on the removal efficiency. In the SBR treatment case, the achieved optimum removal levels of COD, colour, NH_3-N, and TDS were 25.1%, 51.6%, 82.5%, and 1.7%, respectively. On the other hand, the application of the PAC-SBR treatment resulted in 64.1%, 71.2%, 81.4%, and 1.3% removals, respectively. As a result, the application of the PAC-SBR for the treatment of low biodegradable landfill leachate was more effective than the employment of the traditional SBR.

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References

[1] S.Q. Aziz, H.A. Aziz, M.S. Yusoff, M.J.K. Bashir, M. Umar, Leachate characterization in semi-aerobic and anaerobic sanitary landfills: A comparative study, J. Environ. Manage. 91 (2010) 2608–2614.

[2] A.A. Halim, H.A. Aziz, M.A.M. Johari, K.S. Ariffin, Y.T. Hung, Removal of ammoniacal nitrogen and COD from semi-aerobic landfill leachate using low-cost activated carbon zeolite composite adsorbent, Int. J. Environ. Waste Manage. 4 (2009) 399–411.

[3] J. Wiszniowski, J. Surmacz-Gorska, D. Robert, J.V. Weber, The effect of landfill leachate composition on organics and nitrogen removal in an activated sludge system with bentonite additive, J. Environ. Manage. 85 (2007) 59–68.

[4] S. Renou, G.J. Givaudan, S. Poulain, F. Dirassouyan, P. Moulin, Landfill leachate treatment: review and opportunity, J. Hazard. Mater. 150 (2008) 468–493.

[5] A.A. Foul, H.A. Aziz, M.H. Isa, Y.T. Hung, Primary treatment of anaerobic landfill leachate using activated carbon and limestone: batch and column studies, Int. J. Environ. Waste Manage. 4 (2009) 282–298.

[6] H.A. Aziz, Z. Daud, M.N. Adlan, Y.T. Hung, The use of polyaluminium chloride for removing colour, COD and ammonia from semi-aerobic leachate, Int. J. Environ. Eng. 1 (2009) 20–35.

[7] A. Uygur, F. Kargi, Biologicaol nutrient removal from pre-treated landfill leachate in a sequencing batch reactor, J. Environ. Manage. 71 (2004) 9–14.

[8] H.A. Aziz, M.S. Yusoff, S.Q. Aziz, M. Umar, M.J.K. Bashir, A leachate quality at Pulau Burung Kuala Sepetang and Kulim landfills—a comparative study, in: Proceedings Civil Engineering Conference (AWAM 09), ISBN 978-983-42190-2-4 In "Meniti Pembanguna Lestari Dalam Kejuruteraan Awam", Corus Hotel, Kuala Lumpur, Malaysia, October, 2009.

[9] J.S. Guo, A.A. Abbas, Y.P. Chen, Z.P. Liu, P. Chen, Treatment of landfill leachate using a combined stripping, Fenton, SBR, and coagulation process, J. Hazard. Mater. 178 (2010) 699–705.

[10] K.Y. Foo, B.H. Hameed, An overview of landfill leachate treatment via activated carbon adsorption process, J. Hazard. Mater. 171 (2009) 54–60.

[11] B.C. Oman, C. Junestedt, Chemical characterization of landfill leachates–400 parameters and compounds, Waste Manage. 28 (2008) 1876–1891.

[12] A.A. Tatsi, A.I. Zouboulis, K.A. Matis, P. Samaras, Coagulation-flocculation pretreatment of sanitary landfill leachates, Chemosphere 53 (2003) 737–744.

[13] N. Sanphoti, S. Towprayoon, P. Chaiprasert, A. Nopharatana, The effects of leachate recirculation with supplemental water addition on methane production and waste decomposition in a simulated tropical landfill, J. Environ. Manage. 81 (2006) 27–35.

[14] J. Bohdziewicz, E. Neczaj, A. Kwarciak, Membrane bioreactor landfill leachate treatment by means of anaerobic, Desalination 221 (2008) 559–565.

[15] X.Z. Li, Q.L. Zhao, Efficiency of biological treatment affected by high strength of ammonium–nitrogen as pretreatment, Chemosphere 44 (2001) 37–43.

[16] J.P.Y. Jokela, R.H. Kettunenb, K.M. Sormunena, J.A. Rintala, Biological nitrogen removal from municipal landfill leachate: low-cost nitrification in biofilters and laboratory scale in-situ denitrification, Water Res. 36 (2002) 4079–4087.

[17] N. Aghamohammadi, H.A. Aziz, M.H. Isa, A.A. Zinatizadeh, Powdered activated carbon augmented activated sludge process for treatment of semi-aerobic landfill leachate using response surface methodology, Bioresour. Technol. 98 (2007) 3570–3578.

[18] M.J.K. Bashir, M.H. Isa, S.R.M. Kutty, Z.B. Awang, H.A. Aziz, S. Mohajeri, I.H. Farooqi, Landfill leachate treatment by electrochemical oxidation, Waste Manage. 29 (2009) 2534–2541.

[19] S. Mohajeri, H.A. Aziz, M.H. Isa, M.A. Zahed, M.J.K. Bashir, M.N. Adlan, Application of the central composite design for condition optimization for semi-aerobic landfill leachate treatment using electrochemical oxidation, Water Sci. Technol. 61 (2010) 1257–1266.

[20] D. Kima, H.D. Ryua, M.S. Kimb, J. Kima, S.I. Lee, Enhancing struvite precipitation potential for ammonia nitrogen removal in municipal landfill leachate, J. Hazard. Mater. 146 (2007) 81–85.

[21] A. Chianese, R. Ranauro, N. Verdone, Treatment of landfill leachate by reverse osmosis, Water Res. 33 (1999) 647–652.

[22] S. Ghafari, H.A. Aziz, M.H. Isa, A.A. Zinatizadeh, Application of response surface methodology (RSM) to optimize coagulation-flocculation treatment of leachate using poly-aluminum chloride (PAC) and alum, J. Hazard. Mater. 163 (2009) 650–656.

[23] F.J. Rivas, F. Beltran, F. Carvalho, B. Acedo, O. Gimeno, Stabilized leachate: sequential coagulation–flocculation + chemical oxidation process, J. Hazard. Mater. 116 (2004) 95–102.

[24] J. Tsilogeorgisa, A. Zouboulisa, P. Samarasb, D. Zamboulisa, Application of a membrane sequencing batch reactor for landfill leachate treatment, Desalination 221 (2008) 483–493.

[25] M.J.K. Bashir, H.A. Aziz, M.S. Yusoff, M.N. Adlan, Application of response surface methodology (RSM) for optimization of ammoniacal nitrogen removal from semi-aerobic landfill leachate using ion exchange resin, Desalination 254 (2010) 154–161.

[26] M.J.K. Bashir, H.A. Aziz, M.S. Yusoff, S.Q. Aziz, S. Mohajeri, Stabilized sanitary landfill leachate treatment using anionic resin: treatment optimization by response surface methodology, J. Hazard. Mater. 128 (2010) 115–122.

[27] W.S. Al-Rekabi, H. Qiang, W.W. Qiang, Review on sequencing batch reactors, Pak. J. Nutrition 6 (2007) 11–19.

[28] A.H. Mahvi, Sequencing batch reactor: a promising technology in wastewater treatment, Iran. J. Environ. Health Sci. Eng. 5 (2008) 79–90.

[29] M. Ros, J. Vrtovsek, Industrial and municipal wastewater treatment in the sequencing batch reactor, Kem. Ind. 57 (2008) 459–463.

[30] J. Keller, K. Subramaniam, J. Gosswein, P.F. Greenfield, Nutrient removal from industrial wastewater using single tank sequencing batch reactor, Water Sci. Technol. 35 (1997) 137–144.

[31] F. Neczaj, M. Kacprzak, T. Kamizela, J. Lach, F. Okoniewska, Sequencing batch reactor system for the co-treatment of landfill leachate and dairy wastewater, Desalination 222 (2008) 404–409.

[32] S.H.H. Azimi, G.N. Bidhendi, R. Mahmoodkhani, Aeration ratio effect on efficiency of organic materials removal in sequencing batch reactors, Pak. J. Biol. Sci. 8 (2005) 20–24.

[33] I.M. Al harazin, G.F. Nakhla, S. Farooq, Start-up of sequencing batch reactors for toxic wastewater treatment, J. Environ. Sci. Health Part A: Toxic/Hazard. Subst. Environ. Eng. 26 (1991) 673–687.

[34] J. Li, M.G. Healy, X. Zhan, D. Norton, M. Rodgers, Effect of aeration rate on nutrient removal from slaughterhouse wastewater in intermittently aerated sequencing batch reactors, Water Air Soil Pollut. 192 (2008) 251–261.

[35] Z.J. Zhang, J. Zhu, J. King, W.H. Li, A two-step fed SBR for treating swine manure, Process Biochem. 41 (2006) 892–900.

[36] E. Klimiuk, D. Kulikowska, The influence of hydraulic retention time and sludge age on the kinetics of nitrogen removal from leachate in SBR, Pol. J. Environ. Stud. 15 (2006) 283–289.

[37] H. Monclus, S. Puig, M. Coma, A. Bosch, M.D. Balaguer, J. Colprim, Nitrogen removal from landfill leachate using the SBR technology, Environ. Technol. 30 (2009) 283–290.

[38] P.E. Lim, S.P. Lim, C.E. Seng, A.M. Noor, Treatment of landfill leachate in sequencing batch reactor supplemented with activated rice husk as adsorbent, Chem. Eng. J. 159 (2010) 123–128.

[39] A. Spagni, S. Marsili-Libelli, Nitrogen removal via nitrite in a sequencing batch reactor treating sanitary landfill leachate, Bioresour. Technol. 100 (2009) 609–614.

[40] Q. Zhong, D. Li, Y. Tao, X. Wang, X. He, J. Zhang, J. Zhang, W. Guo, L. Wang, Nitrogen removal from landfill leachate via ex situ nitrification and sequential in situ denitrification, Waste Manage. 29 (2009) 1347–1353.

[41] A. Spagni, S. Marsili-Libelli, M.C. Lavagnolo, Optimisation of sanitary landfill leachate treatment in a sequencing batch reactor, J. Water Sci. Technol. 58. (2) (2008) 337–443.

[42] APHA Standard Methods for the Examination of Water and Wastewater, 21st ed., American public health association, Washington DC, 2005.

[43] Environmental Quality (Control of Pollution from Solid Waste Transfer Station and Landfill) Regulations 2009, under the Laws of Malaysia–Malaysia Environmental Quality Act, 1974.

[44] D. Bas, I.H. Boyaci, Modeling and optimization I: usability of response surface methodology, J. Food Eng. 78 (2007) 836–845.

[45] Metcalf & Eddy, INC., Wastewater Engineering-Treatment and Reuse, 4th ed., Mic Graw-Hill, Inc., 2003.

[46] H. Timur, I. Ozturk, Anaerobic sequencing batch reactor treatment of landfill leachate, Water Res. 33. (15) (1999) 3225–3230.

[47] R.Y. surampalli, R.D. Tyagi, O.K. Scheible, J.A. Heidman, Nitrification de nitrification and phosphorus removal in sequential batch reactors, Bioresour. Technol. (1997) 151–157.

[48] N. Laitinen, A. Luonsi, J. Vilen, Landfill leachate treatment with sequencing batch reactor and membrane bioreactor, Desalination 191 (2006) 86–91.

[49] K. Gorfelt, Nitrification and Denitrification of Leachate with SBR in Pilot Scale at Spillepeng Waste Deposition Site, Water and Environmental Engineering Department of Chemical Engineering, Lund University, Sweden, 2008.

[50] S. Morling, Nitrogen removal and heavy metals in leachate treatment using SBR technology, J. Hazard. Mater. 174 (2010) 679–686.