Powdered activated carbon augmented activated sludge process for treatment of semi-aerobic landfill leachate using response surface methodology

Nasrin Aghamohammadi a, Hamidi bin Abdul Aziz b,*, Mohamed Hasnain Isa b, Ali Akbar Zinatizadeh c

a Graduate Faculty of Environment, University of Tehran, Iran
b School of Civil Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia
c Water and Environment Division, Water and Power Industry Institute for Applied and Scientific Higher Education, Kermanshah, Iran

Received 4 August 2006; received in revised form 13 November 2006; accepted 14 November 2006
Available online 5 February 2007

Abstract

This study was conducted to investigate aerobic biodegradation of semi-aerobic leachate with and without powdered activated carbon (PAC) addition. The experiment involved operating two 16 L laboratory-scale activated sludge reactors in parallel at room temperature and adjusted to pH 6.5 ± 0.5. One of the reactors was supplemented with PAC of 75–150 μm size to observe its effect on semi-aerobic leachate biodegradation. Three hydraulic retention times (0.92, 1.57 and 2.22 d) and influent COD concentrations (750, 1800 and 2850 mg/L) were applied in a factorial design for this study. The results showed enhanced reactor performance due to PAC addition with higher COD, colour and ammoniacal nitrogen removals. The PAC augmented reactor also had higher concentrations of NO₂-N and NO₃-N consequent of greater degree of nitrification.

Keywords: Semi-aerobic landfill leachate; Powdered activated carbon; Activated sludge process

1. Introduction

Sanitary landfill leachate is usually considered to be a very high strength wastewater containing many organic and inorganic components. A combined landfill leachate and domestic wastewater treatment study demonstrated that these could be treated at suitable mixing ratios. However, an increase in leachate ratio caused reduction in the overall organic substrate removal rate in batch reactors (Aktas and Çeçen, 2001). Besides, severe nitrification inhibition may be observed with high-strength leachates due to the high levels of free ammonia and presence of other inhibitors. Addition of powdered activated carbon (PAC) is known for its ability to enhance biological treatment efficiency, to remove refractory organic compounds and to enhance nitrification (US EPA Manual, 1995; Kang et al., 1990). Çeçen and Aktas (2001) concluded that nitrification inhibition could be completely prevented by PAC addition. The addition of PAC to activated sludge has also been found to improve sludge dewaterability (Çeçen et al., 2003). Activated carbon in conjunction with activated sludge increases the removal efficiency by adsorbing non-biodegradable, toxic and/or inhibitory organics and also some metals (Metcalf and Eddy, 2004). A synergy is thought to exist between activated carbon and microorganisms. Thus, the powdered activated carbon treatment (PACT) system could remove organic compounds more efficiently than would be expected from either biodegradation or adsorption alone. Activated carbon provides an attachment surface for micro-organisms to bioregenerate...
the activated carbon (Sublette et al., 1982; Orhansky and Narkis, 1997). This study was conducted to determine the effectiveness of PAC supplementation to Activated Sludge Process (ASP) for the improvement of COD, colour and ammoniacal nitrogen (NH₄-N) removal in semi-aerobic landfill leachate treatment. It also aimed at determining appropriate reactor operating conditions using response surface methodology (RSM).

RSM is a practical approach to reactor modeling as it arises from experimentation which includes interactive effects of the variables in the overall prediction of reactor performance. In recent years, RSM has been applied to various chemical and biochemical processes such as fermentation of starch to lactic acid (Altaf et al., 2007), acidogenesis of cattail (Hu et al., 2006), advanced treatment of olive oil processing wastewater using Fenton’s peroxidation (Ahmadi et al., 2005) and, acidogenesis of cheese-whey wastewater to acetic and butyric acids (Yang et al., 2003).

2. Methods

2.1. Leachate sampling and characterization

Leachate samples were collected from a municipal waste semi-aerobic landfill (Pulau Burung Landfill Site, PBL), situated within Byram Forest Reserve in Penang, Malaysia. The total area of the landfill is 23.7 ha and it is equipped with a leachate collection pond. This site has a natural marine clay liner. The site was developed semi-aerobically and is one of the only three sites of its kind in Malaysia. The leachate characteristics are presented in Table 1. The collected samples were stored at 4°C and taken for use in experiments when needed. The low BOD₅/COD ratio (0.17) and high ammoniacal nitrogen concentration (1225 mg/L) indicated low biodegradability and high degree of stabilization of the leachate within the landfill (Kurg and Ham, 1997).

2.2. Activated sludge characteristics

The activated sludge (AS) used in this study was obtained from a textile industry in Penang, Malaysia. The characteristics of the AS were (mg/L) TCOD 13,800–13,879, SCOD 224–232, MLSS 9740–9760, MLVSS 8050–8070, and SVI 98.5 mL/g and pH 7–7.66.

2.3. Preliminary study: determination of optimum dose of PAC

A batch preliminary experiment was conducted to determine the optimum dose of PAC for the continuous flow experiments. Powdered activated carbon of size 75–150 μm was used for this purpose. PAC was pre-dried at 103°C before use. The study was carried out in six 1-L beakers with 600 ml leachate and 200 ml activated sludge. Different amounts (0–4 g/L) of PAC were then added to the beakers and the contents were aerated for two days after which the COD removal in each of the beakers was determined. The results showed an increase in COD removal with PAC dosage and suggested the use of 3 g/L PAC in the continuous flow study (as the increase in COD removal beyond 3 g/L PAC was only marginal).

2.4. Sludge acclimatization

The sludge was acclimated by starting with an initial sludge-leachate mixture of 0.5 L each. The mixture was aerated for one day and 0.5 L of supernatant was withdrawn and replaced by 1 L of leachate. Thereafter, the procedure was continued with 0.5 L supernatant withdrawal daily and leachate was fed in increments of 0.5 L, i.e. 1, 1.5, 2, 2.5 L, etc. This was continued till the reactor contents reached 16 L. COD removal and pH were monitored. The acclimatization period was continued for another week. The COD removal was observed to be stable (33%). The acclimated sludge was used as seed in the reactors for further studies.

2.5. Experiments with continuous flow (CF) activated sludge units

The study involved operating two 16 L semi-aerobic leachate fed laboratory-scale continuous flow activated sludge reactors in parallel at room temperature and adjusted to pH = 6.5 ± 0.5. One reactor was operated as such,
without PAC addition (NPAC reactor) while the other (PAC reactor) was supplemented with PAC of 75–150 μm size to observe its effect on semi-aerobic leachate treatment. The feed container was placed over a magnetic stirrer to maintain uniformity of feed characteristics. Peristaltic pumps were used to adjust the desired flow rates to the reactors.

### 2.6. Statistical design of the experiments

The statistical analyses were performed using Design-Expert software (version 7.0). A central composite face-centered design (CCFD) was applied with two design factors viz., hydraulic retention time, HRT \((A)\) and influent chemical oxygen demand concentration, COD\(_{in}\) \((B)\). 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 was employed to fit the second-order polynomial models and to obtain an experimental error for this study. The two operating variables were each considered at three levels viz., low \((-1)\), central \((0)\) and high \((1)\). RSM was then used to analyze the data. In this study, HRT \((0.92, 1.57\) and \(2.22\) d) and COD\(_{in}\) \((750, 1800\) and \(2850\) mg/L) were chosen as independent variables (operating factors) in order to study the effect of organic loading rate and feed flow rate on reactor performance.

In order to carry out a comprehensive analysis of the aerobic process, six dependent parameters were measured as responses. These parameters were COD removal, colour removal, effluent pH, NH\(_4\)-N removal, NO\(_2\)-N concentration and NO\(_3\)-N concentration. After conducting the experiments, the coefficients of the following polynomial model were calculated:

\[
Y = \beta_0 + \sum_{i=1}^{k} \beta_i \cdot X_i + \sum_{i=1}^{k} \beta_{ij} \cdot X_i^2 + \sum_{i<j}^{k} \beta_{ij} \cdot X_i \cdot X_j + \cdots + \epsilon
\]

### Table 2
Experimental conditions and results for the NPAC reactor

<table>
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<th>Run</th>
<th>Factor 1 (A): HRT (d)</th>
<th>Factor 2 (B): COD(_{in}) (mg/L)</th>
<th>COD removal (%)</th>
<th>Colour removal (%)</th>
<th>Effluent pH</th>
<th>NH(_4)-N removal (%)</th>
<th>NO(_2)-N concentration (mg/L)</th>
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### Table 3
Experimental conditions and results for the PAC reactor

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<th>Factor 1 (A): HRT (d)</th>
<th>Factor 2 (B): COD(_{in}) (mg/L)</th>
<th>COD removal (%)</th>
<th>Colour removal (%)</th>
<th>Effluent pH</th>
<th>NH(_4)-N removal (%)</th>
<th>NO(_2)-N concentration (mg/L)</th>
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where \( i \) and \( j \) are the linear and quadratic coefficients, respectively, \( \beta \) is the regression coefficient, \( k \) is the number of factors studied and optimized in the experiment and \( \epsilon \) is the random error. Model terms were selected or rejected based on the \( P \) value with 95% confidence level. The results were completely analyzed using analysis of variance (ANOVA) by the Design-Expert software. Three dimensional plots and their respective contour plots were obtained based on the results of the experiments. From the three-dimensional plots, effects of interaction of the two factors on the responses were studied. The optimum region was also identified based on the main parameters in the overlay plot.

### 2.7. Analytical methods

Analyses were carried out in accordance with Standard Methods for the Examination of Water and Wastewater (APHA, 1992). COD analyses were performed by the dichromate closed refluxed colorimetric method. Soluble COD (SCOD) was determined after filtering the samples through GFC 50 filter (Advantec). NH\(_4\)-N analyses were also identified based on the main parameters in the overlay plot.

### 3. Results and discussion

#### 3.1. Test for operational conditions

Various responses were investigated in this study and different degree polynomial models were used for data fitting. The experimental conditions and results for the NPAC and PAC reactors are shown in Tables 2 and 3, respectively. The regression equations obtained are presented in Table 4. In order to quantify the curvature effects, the data from the experimental results were fitted to higher degree polynomial equations, i.e. two factor interaction (2FI), quadratic and so on. In the Design-Expert software, the response data were analyzed by default. The ANOVA results for all responses are summarized in Table 4.

The model terms in the equations (Table 4) were obtained after the elimination of insignificant terms. Based on statistical analysis, the models were highly significant with very low probability values (from 0.01 to <0.0001). The square of correlation coefficient for each response was computed as the coefficient of determination (\( R^2 \)). It showed high significance at 95% confidence level. Model adequacy was tested through lack-of-fit \( F \)-tests (Montgomery, 1991). The lack of fit \( F \)-statistic was not statistically significant as the \( P \) values were greater than 0.05. Adequate precision is a measure of the range in predicted response relative to its associated error. Its desired value is 4 or more (Mason et al., 2003). Detail analysis of the models results
and comparative studies are presented in the following sections.

3.2. Analysis and comparison of reactor performance

3.2.1. COD removal

The effect of the variables on COD removal efficiencies are shown as 3D (Fig. 1a and b) and contour (Fig. 1c and d) plots for NPAC and PAC reactors. A stable COD removal efficiency of 49% was achieved at the highest HRT (2.22 d, corresponding to COD$_{\text{in}}$ of 2850 mg/L) (Fig. 1b) with the PAC reactor whereas for the NPAC reactor under the same conditions only 29% COD removal (Fig. 1a) was achieved. As the HRT and COD$_{\text{in}}$ were increased, the effect on COD removal efficiency was improved. It was found that at the same HRT of 1.57 d (center point, COD$_{\text{in}}$ 1800 mg/L), greater COD removal efficiency (23–31%) (Table 3) was achieved with the PAC reactor compared to the NPAC reactor (8.2–11%) (Table 2). This might be attributed to either possible inhibitory effect of the leachate constituents or COD contribution of the recalcitrant organic compounds which may not have degraded under the experimental conditions in the NPAC reactor.

3.2.2. Colour removal

The effect of variables on colour removal efficiencies are shown as 3D (Fig. 2a and b) and contour (Fig. 2c and d) plots for NPAC and PAC reactors. The trend of changes in colour removal efficiency was quite different for both reactors as reflected by different model terms that describe the variations in colour removal (Table 4). The maximum colour removal efficiency achieved was 50% at the highest HRT (2.2 d) and the lowest COD$_{\text{in}}$ (750 mg/L) for the PAC reactor; whereas it was only 21% for the NPAC reac-

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![Fig. 1. 3D and contour plots of COD removal showing the effect of HRT and COD$_{\text{in}}$.](image-url)
tor corresponding to the operational conditions of highest HRT (2.2 d) and highest COD in (2850 mg/L). The low level of colour removal with the NPAC reactor was probably due to inhibition resulting from high concentration of leachate in the system in addition to colour adsorption by activated carbon in the PAC reactor.

3.2.3. Effluent pH

Fig. 3 presents variation of pH as a function of the operating variables for the NPAC and PAC reactors. HRT ($A$), $\text{COD}_{\text{in}}$ ($B$) and $A^2$ are the significant model terms for both reactors (Table 4). As can be noted in Fig. 3, increase in HRT had a reverse effect on pH at different values of HRT. At low range of HRT, an increase in HRT caused an increase in pH due to increase in alkalinity as no chemical was used to adjust pH or to provide buffering capacity to the feed. Whereas, at higher values, increase in HRT resulted in a decrease in pH due to possible production of acidic intermediates as well as nitrification; high organic loading at long retention time provided a favourable environment for nitrification. pH of the PAC reactor was generally lower than that of the NPAC reactor within the design region. It was attributed to higher degree of nitrification (Fig. 4) as well as adsorption of $\text{NH}_4^+$ by PAC.

3.2.4. $\text{NH}_4^-$N removal

Fig. 4 shows interactive effects of HRT and COD in on $\text{NH}_4^-$N removal. HRT ($A$) and $A^2$ are the significant model terms for both conditions. As noted in the figure, COD in did not affect $\text{NH}_4^-$N removal within the limits of variables tested. The $\text{NH}_4^-$N removal response surface followed a parabolic profile in both cases. For the NPAC reactor, the $\text{NH}_4^-$N removal dropped from 43% (HRT = 0.92 d) to a minimum value of 25.2% (HRT = 1.44 d) and then rose to a maximum value of 65% (HRT = 2.22 d). The corresponding values for the PAC reactor were 55%...
(HRT = 0.92 d), 28.8% (HRT = 1.52 d) and 69% (HRT = 2.22 d). At low range of HRT, decrease in HRT caused an increase in removal due to increased influent to the reactors. Whereas, at the higher HRT range, increase in HRT showed an increase in NH₄-N removal as explained in Section 3.2.3. NH₄-N removal was higher in the PAC reactor compared to the NPAC reactor within the design region. Higher removal of NH₄-N in the PAC reactor was also reflected in its lower pH (Fig. 3).

3.2.5. Effluent NO₂-N concentration

An increase in the variables caused an increase in the NO₂-N concentration of both reactors. It was found that the effluent NO₂-N concentrations of the PAC reactor were greater than those for the NPAC reactor owing to more nitrification in the former. The highest concentrations of NO₂-N obtained in the PAC and NPAC reactors were 2060 and 1666 mg/L, respectively, at HRT = 2.22 d and CODᵣᵣᵣ = 2850 mg/L.

3.2.6. Effluent NO₃-N concentration

It was understood that NO₃-N was produced through biological reactions as no chemical was added to supply NO₃-N. PAC addition improved this reaction because it provided media for nitrifiers. From the quadratic models in Table 4, the main effects of the three factors viz., B, A², and AB are significant model terms for both reactors. Effluent NO₃-N concentrations for the PAC reactor were greater than those for the NPAC reactor within the tested ranges of the two variables. Results from the experiments showed that over 600 mg/L NO₃-N was produced in both reactors. The maximum NO₃-N concentration was

Fig. 3. 3D and contour plots of effluent pH showing the effect of HRT and CODᵣᵣᵣ.
638 mg/L (corresponding to HRT = 1.76 d and COD$_{in}$ = 2847 mg/L) for the NPAC reactor and 693 mg/L (corresponding to HRT = 1.69 d and COD$_{in}$ = 2782 mg/L) for the PAC reactor.

4. Conclusions

RSM was successfully applied to compare the differences in the process responses using NPAC and PAC reactors for the treatment of semi-aerobic landfill leachate. A stable COD removal efficiency was achieved with the PAC reactor, whereas for the NPAC reactor under the same conditions lower COD removal was achieved. Similar pattern was observed for colour removal efficiency. Higher nitrification in the PAC reactor resulted in higher NH$_4$-N removal and higher effluent NO$_2$-N and NO$_3$-N concentrations. The results showed model predictions and experimental findings to be in close agreement. It was noted that despite an almost twofold higher COD removal efficiency of the PAC reactor over the NPAC reactor, the PAC reactor alone was not able to produce a treated effluent that would meet the local discharge standards. Other treatment units would, therefore, be required as part of the overall treatment scheme.

Acknowledgements

The authors acknowledge the Ministry of Science, Technology and Environment, Malaysia for the IRPA research grant that has resulted in this article. The authors also thank the Majlis Perbandaran Seberang Perai, Penang and the contractor Idaman Bersih Sdn. Bhd., Penang for their cooperation during the study.
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