



Treatment of landfill leachate in sequencing batch reactor supplemented with activated rice husk as adsorbent

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ARTICLE INFO

Article history:

Received 14 January 2010

Received in revised form 26 February 2010

Accepted 26 February 2010

Keywords:

Landfill leachate
Sequencing batch reactor
Treatment
Activated rice husk
Adsorbent

ABSTRACT

The objective of this study is to evaluate the performance of ethylenediamine-modified rice husk (MRH)-supplemented sequencing batch reactor (SBR) as compared to powdered activated carbon (PAC)-supplemented SBR in the removal of COD and nitrogen from a combined landfill leachate and domestic wastewater. The SBRs were operated with the FILL, REACT, SETTLE, DRAW and IDLE periods in the ratio of 2:12:2:1:7 for a cycle time of 24 h. The performance of the reactors was evaluated by monitoring the effluent quality as well as the concentration profiles of COD, ammonia nitrogen (AN), nitrite nitrogen and nitrate nitrogen during the REACT period of an operating cycle at various mixing ratios of the wastewaters. The results showed that equivalent performance of the MRH- and PAC-supplemented SBRs in terms of the efficiency and rate of COD and AN removal was achieved at a lower loading rate of MRH compared to that of PAC. The better performance of the MRH-supplemented SBR was postulated to be due to the presence of attached-growth biomass which is less inhibited by toxic constituents in leachate than suspended-growth biomass. Overall, MRH shows a good potential of being used as an alternative adsorbent to PAC in leachate treatment.

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1. Introduction

The sanitary landfill approach for the disposal of municipal solid wastes is widely used in areas where land is not a constraint. Despite the economic advantages, there are a number of environmental problems associated with the operation of a sanitary landfill, one of which is the generation of landfill leachate. Generally, leachate has relatively high COD as well as ammonia nitrogen (AN) concentrations and may contain many other chemicals such as pesticides, organics and heavy metals. As such, leachate must be properly treated before it is allowed to be discharged into receiving water courses. Conventional treatment of landfill leachate including physical, chemical and biological processes has been extensively reviewed [1]. As landfill leachate has a high degree of variability in quality and quantity, the sequencing batch reactor (SBR), which possesses greater process flexibility among biological treatment systems, is therefore well suited for leachate treatment [2–6]. However, the toxicity of the leachate often causes nitrification inhibition resulting in the unsatisfactory removal of AN. In this case, the effectiveness of powdered activated carbon (PAC) addition in reducing nitrification inhibition is well documented [7–10].

Owing to the relatively high cost of PAC, the potential of rice husk, which is an agricultural by-product, as an alternative adsorbent to PAC in the removal of dyes, heavy metals and organics has been investigated by researchers [11–14]. In those studies, rice husk was activated either thermally or chemically before use. Despite the reported success of the activated rice husk as an adsorbent, little has been reported on the application of the activated rice husk supplemented sequencing batch reactor (SBR) in the treatment of landfill leachate. The objective of this study is to evaluate the performance of ethylenediamine-modified rice husk (MRH) as compared to PAC in the removal of COD and nitrogen in landfill leachate under the adsorbent-supplemented SBR operation. Ethylenediamine activation which is in the alkaline pH range was used so that nitrification and denitrification processes in the SBR would not be affected as nitrification is inhibited at pH below 6.5. In addition, ethylenediamine is a chelating agent with a bidentate ligand containing two amino groups. The bidentate ligand is crucial for chelation with metals and organic compounds [15] and will be useful for leachate treatment.

2. Materials and methods

2.1. Preparation of adsorbents

Raw rice husk obtained from a rice mill was washed and soaked in tap water for 3 days. It was subsequently washed with tap water

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until odourless and dried in the oven at 60 °C. The dried rice husk was ground to pass through a 425 µm sieve. The sieved rice husk was then chemically modified in the following manner: 100 g of rice husk was mixed with 121.41 g of ethylenediamine in a beaker and kept in a water bath at 80 °C for 2 h with frequent stirring. After that, the mixture was washed with distilled water until neutral pH and filtered. The ethylenediamine-modified rice husk (MRH) which has a size range of 150–425 µm was dried in the oven at 60 °C.

The PAC used was Malbon S4 which was obtained commercially. The properties of the PAC were as follows: moisture: max. 10%, pH: 6–7, ash content: max. 8%, iodine number: min. 930 mg/g, caramel decolourising power: min. 93%, size: <75 µm.

2.2. Treatment studies

Two identical laboratory-scale plexiglass SBRs, each with the dimensions of 30 × 25 × 20 cm (Length × Width × Height) and a working volume of 10 L, were operated with the FILL, REACT (aerobic), REACT (anoxic), SETTLE, DRAW, IDLE periods in the ratio of 2:9:3:2:1:7 for a cycle time of 24 h. The reactors were initially fed with a synthetic wastewater (base mix) with the following composition representative of that of domestic wastewater (concentration in mg/L): bacto-peptone (100), glucose (280), CH₃COONa (600), (NH₄)₂SO₄ (250), KH₂PO₄ (100), K₂HPO₄ (100), MgSO₄·7H₂O (100), CaCl₂·2H₂O (30) and FeCl₃·6H₂O (10) giving a COD concentration of 750–850 mg/L and AN concentration of about 50 mg/L. The activated sludge was collected from a local municipal sewage treatment plant and acclimatized to the base mix for 1 month. During each cycle, 7 L of feed solution was introduced into the reactor and the same volume of treated effluent was removed during the DRAW period. Just before the termination of the REACT (anoxic) period during each cycle, 500 mL of mixed liquor was wasted to yield a sludge age of 20 days. Ethanol solution (≈4.6%, v/v) with a theoretical COD of 75.8 mg O₂/mL of this solution was added as a carbon source at the beginning of the REACT (anoxic) period. Landfill leachate samples were collected from a municipal sanitary landfill site in Penang and was found to have the following characteristics: pH (8.4–8.7), soluble COD (1040–4870 mg/L), AN (905–1650 mg/L). The feed solution was prepared by mixing the leachate with the synthetic domestic wastewater in certain ratio and the strength of the feed was changed by varying the mixing ratio of the two wastewaters. In view of the larger variation in the soluble COD as compared to the AN concentration of the leachate, it was more practical to quantify the strength of the combined wastewater in terms of the AN concentration. Thus, an increase in the ratio of the leachate with the synthetic wastewater is reflected in the increase of the AN concentration.

The various operational phases of the reactors are shown in Table 1. During phase I of the treatment study, the reactors were fed with the base mix at the AN concentration of 50 mg/L. For phases II and III of the treatment study, the reactors were fed with increasing AN concentrations in the combined wastewater. In phase IV, the AN concentration was reduced to 115 from 170 mg/L due to the observation of incomplete AN removal in the reactors. From phase V onwards, the reactors were added with MRH (designated as R-MRH) and PAC (designated as R-PAC), respectively, in increasing AN concentration and, in the case of R-PAC, in increasing PAC dosages (Table 1). The organic carbon source added at the beginning of the REACT (anoxic) period amounted to 609 mg COD in phase I (when only base mix was treated) and 1220 mg COD in subsequent phases. Treated effluents collected from the DRAW period in each cycle of the two SBRs were analysed immediately for the COD and AN concentrations whereas the mixed liquors were analysed for the mixed liquor suspended solids (MLSS) concentrations and the sludge volume index (SVI) following the Standard Methods [16]. The COD, AN, nitrite nitrogen (NO₂⁻-N), nitrate nitrogen (NO₃⁻-N) and dissolved

Table 1
Operation phases and mean COD removal efficiency for reactors R-MRH and R-PAC.

Concentration of AN (mg/L)	Adsorbent dosage (g/cycle)		Reactor R-MRH				Reactor R-PAC			
	Base mix	Combined wastewater	Phase	Mean influent COD concentration (mg/L)	COD removal (%)	Duration (days)	Phase	Mean influent COD concentration (mg/L)	COD removal (%)	Duration (days)
50			I	793	90	37	I	770	90	164
115			II	1116	79	52	II	782	72	39
170			III	1107	61	55	III	1063	61	29
115			IV	831	70	82	IV	993	72	76
115		0.5	V	852	81	57	V	884	79	21
115		1.0					VI	880	81	60
170		0.5	VI	989	73	55	VII	1176	66	135
170		1.0					VIII	982	75	255
215		0.5	VII	1138	72	32				

oxygen (DO) concentration profiles during the REACT (aerobic) and REACT (anoxic) periods were also determined at various phases of operation. The pH was found to vary within the range of 7.5–9.3 during a typical REACT period with higher pH values during the anoxic period.

2.3. Adsorption studies

Equilibrium adsorption studies on the removal of COD from landfill leachates using MRH and PAC as adsorbents, respectively, were conducted. The landfill leachate was diluted 10 times to achieve a COD in the range of 150–250 mg/L depending on the batch of landfill leachate used. The adsorbent was shaken in 50.0 mL diluted leachate for a period sufficiently long for the equilibrium to be established based on the results of the contact time study. The weights of MRH and PAC employed in the studies varied from 0.1 to 1.0 g and from 0.01 to 0.1 g, respectively. The adsorption data were fitted to the Langmuir and Freundlich models.

3. Results and discussion

3.1. General reactor performance

Determination of the SVI value, MLSS and effluent COD concentrations were performed regularly to assess the performance of reactor R-MRH. Fig. 1 shows the trends of SVI values and MLSS concentrations during the operational period of the reactor. It was observed that there was good sludge settleability before the addition of leachate in phase I as the SVI values were maintained below 100 mL/g. The introduction of the combined wastewater with the consequent increase of AN concentration to 115 mg/L in phase II resulted in a drastic increase of the SVI values at the initial stage. However, the SVI values improved to below 100 mL/g again at the later stage of phase II mainly due to acclimation of the biomass to the presence of leachate. Further increase of the AN concentration to 170 mg/L (indicating higher ratio of leachate to synthetic domestic wastewater) in phase III led to the increase of the SVI value to above 150 mL/g. Reduction of the AN concentration to 115 mg/L in phase IV saw the SVI values improved to below 100 mL/g. On the addition of 0.5 g MRH/cycle, the mean SVI value decreased to 58 mL/g in phase V and increased to only 88 mL/g in phase VI despite the fact that the AN concentration had been increased to 170 mg/L. In phase VII, the mean SVI value was above 150 mL/g indicating undesirable sludge settling characteristics when the AN concentration was further increased to 215 mg/L without the concomitant increase of the MRH dosage. The trend of the MLSS concentration during the operational period generally reflects the trend of

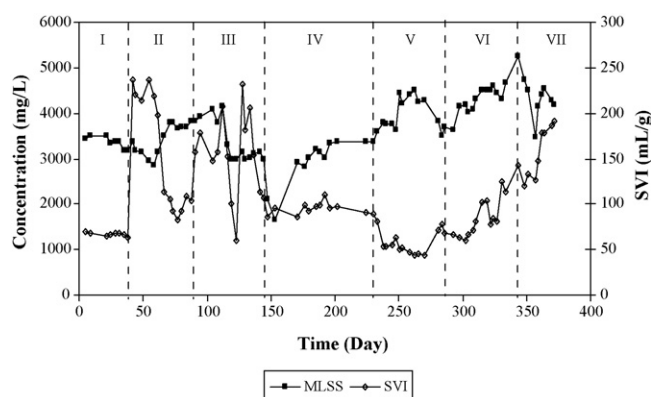


Fig. 1. The MLSS concentrations and SVI values in reactor R-MRH during the operational period.

the SVI value (Fig. 1). Thus, deterioration in the sludge settleability and compressibility (increasing SVI values) always results in decreasing MLSS concentration. Researchers [17,18] have shown that high SVI values (bulking sludge) and low biomass concentrations are indications of inhibitory effects of some toxic substances on microorganisms. This means that the presence of MRH was able to mitigate the inhibitory effect on the microorganisms due to the toxic components in the leachate. Similar beneficial effect was also exhibited by PAC in reactor R-PAC (not shown).

The mean COD removal efficiencies for both reactors in various operational phases are shown in Table 1. For the removal of COD in both reactors, the removal efficiency of COD was reduced from 90 to 61% when the leachate loading rate was increased before adsorbent addition in phases I–III. For reactor R-MRH, in the presence of 0.5 g MRH/cycle, the mean COD removal efficiency decreased by only 8%, i.e. from 81% in phase V to 73% in phase VI despite an increase in the AN concentration from 115 to 170 mg/L (an increase of 48%). In the case of reactor R-PAC, the mean COD removal efficiency was reduced from 81% in phase VI to 66% in phase VII for the corresponding increase in AN concentration despite the addition of 1 g PAC/cycle. Thus, lower dosage of MRH was needed as compared to that of PAC in achieving the equivalent performance in COD removal.

3.2. Concentration profile studies during the REACT period

Concentration profile studies are essential as the pollutant concentrations determined during the REACT period provide important information on the rate of removal of the pollutant in an operating cycle.

3.2.1. Removal of nitrogen species

For AN removal, the concentration profiles of the various nitrogen species determined during the REACT period provides information on their relative rates of production and removal in the nitrification/denitrification processes. Fig. 2a–d shows the DO, AN, NO_2^- -N and NO_3^- -N concentration profiles during the REACT (aerobic) and REACT (anoxic) periods in phases IV, V, VI and VII, respectively, for reactor R-MRH whereas Fig. 3a–e depicts those concentration profiles during the REACT (aerobic) and REACT (anoxic) periods in phases IV, V, VI, VII and VIII, respectively, for reactor R-PAC. These profiles were determined when the reactors were at the steady state. For both reactors, it was observed that some AN removal occurred during the initial REACT period before nitrification was observed. This may be explained by the occurrence of the simultaneous nitrification and denitrification (SND) process which has been reported by a number of researchers [19–21]. The relatively low (<1 mg/L) DO concentration found at the initial stage of the REACT period provided an ideal condition for this SND process to occur. The removal of AN via assimilation into new biomass and stripping was probably minor. Using the AN concentration profiles, the data for the period when the formation of oxidized nitrogen was observed were fitted to both the zeroth- and first-order kinetic models. It was found that the experimental data were better described by the zeroth-order kinetic model and the mean pseudo-zeroth-order rate constants, k_{AN} , for AN removal during nitrification are shown in Table 2.

Comparison of the concentration profiles in Fig. 2a with those in Fig. 2b–d clearly shows that there was an effective inhibition on the second step of nitrification, namely the oxidation of NO_2^- -N to NO_3^- -N, despite the addition of MRH. Nonetheless, the merits of MRH addition can be seen in the following observations: (i) almost complete AN removal was achieved within the REACT period for AN concentration up to 215 mg/L (an increase of 87%) even though the dosage of MRH was kept constant at 0.5 g/cycle and (ii) the rate of AN removal increased despite the increase of influent AN

Table 2
Mean values of pseudo-zeroth-order rate constants for AN removal, k_{AN} (mg/L min) and pseudo-first-order rate constants for COD removal, k_{COD} (1/min) for various operational phases in reactors R-MRH and R-PAC.

Phase	R-MRH				R-PAC			
	$k_{AN} (\times 10)$	R^2	$k_{COD} (\times 10^2)$	R^2	$k_{AN} (\times 10)$	R^2	$k_{COD} (\times 10^2)$	R^2
IV	2.5 ± 0.0	0.987	2.3 ± 0.3	0.976	2.3 ± 0.4	0.997	1.7 ± 0.8	0.816
V	2.9 ± 0.5	0.986	0.9 ± 0.8	0.893	2.1 ± 0.2	0.992	1.8 ± 0.5	0.914
VI	3.9 ± 0.5	0.988	1.0 ± 0.2	0.944	3.6 ± 0.5	0.961	1.7 ± 0.6	0.800
VII	4.6 ± 0.8	0.994	0.8 ± 0.1	0.983	4.4 ± 0.5	0.995	1.8 ± 0.3	0.890
VIII					3.6 ± 0.8	0.990	2.4 ± 0.5	0.972

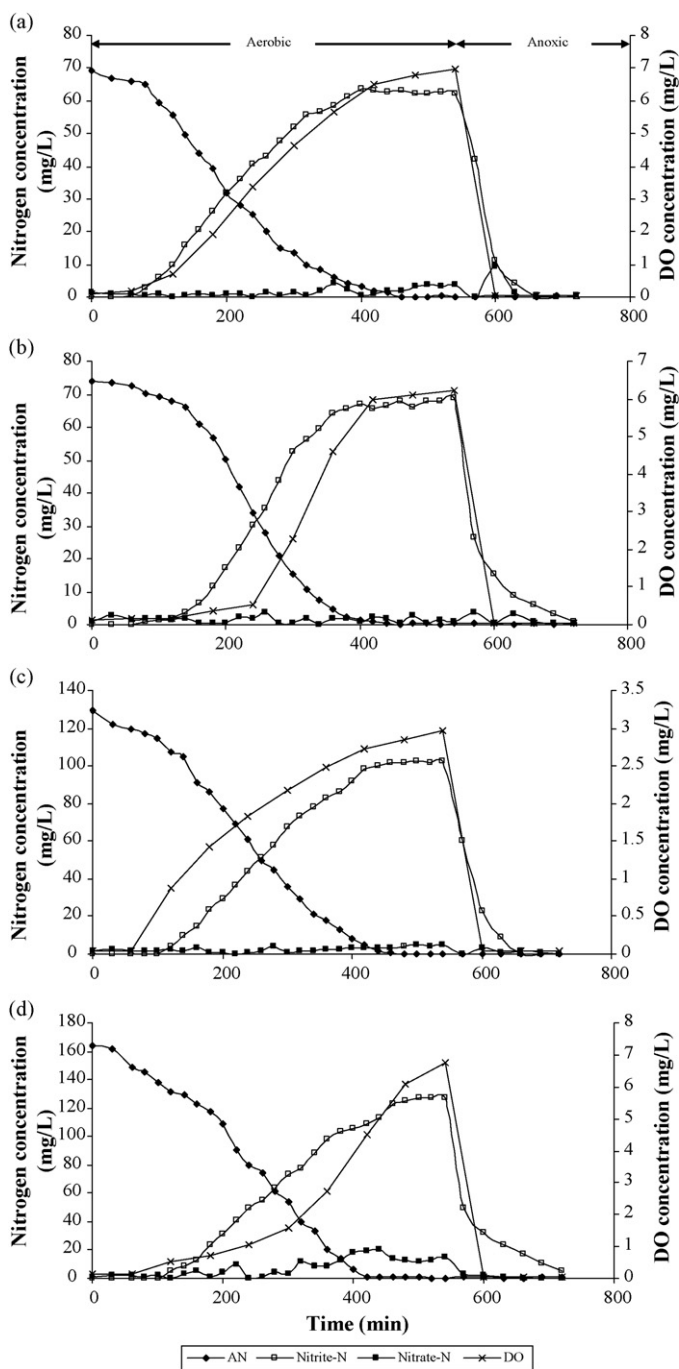


Fig. 2. The concentration profiles of AN, NO_2^- -N, NO_3^- -N and DO in reactor R-MRH during the REACT period of phases (a) IV, (b) V, (c) VI and (d) VII.

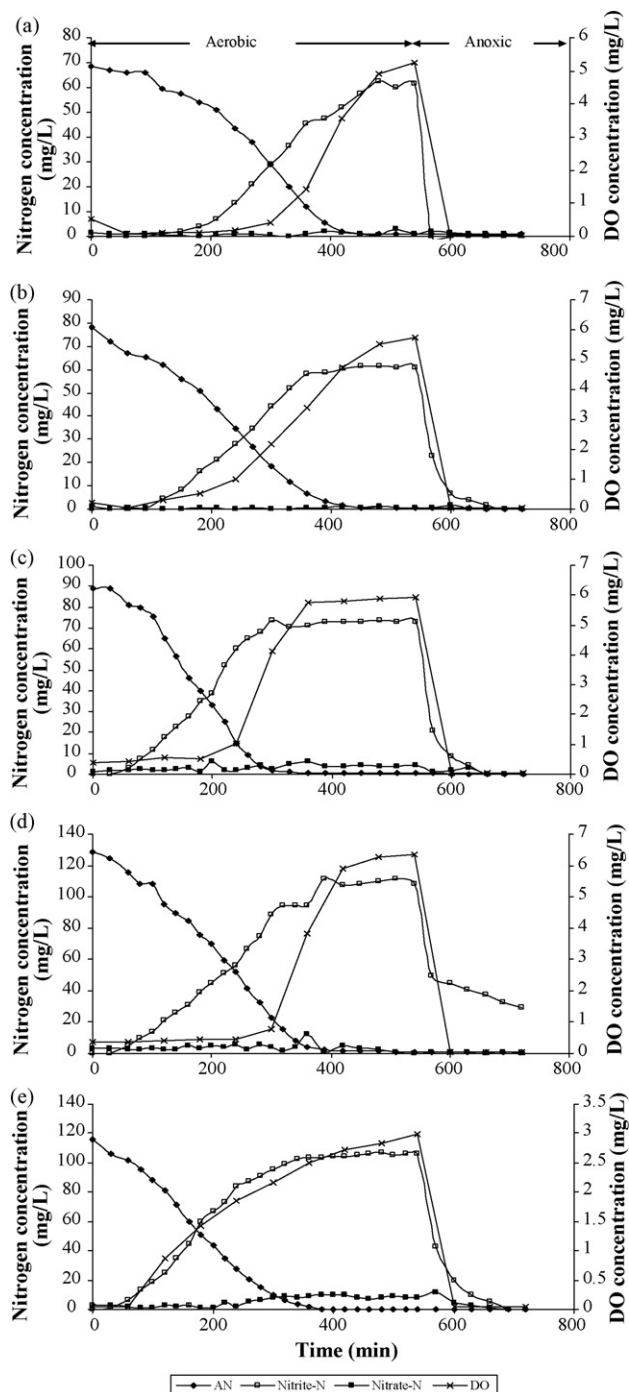


Fig. 3. The concentration profiles of AN, NO_2^- -N, NO_3^- -N and DO in reactor R-PAC during the REACT period of phases (a) IV, (b) V, (c) VI (d) VII and (e) VIII.

concentration from 115 mg/L in phase V to 170 mg/L in phase VI and to 215 mg/L in phase VII without the corresponding increase in the MRH dosage (Table 2).

Comparison of Fig. 3a–c, corresponding to phases IV, V and VI in reactor R-PAC, shows that PAC addition up to 1.0 g/cycle was unable to mitigate the inhibition of leachate on the second step of nitrification. On the other hand, given the same influent AN concentration in the three phases, complete AN removal was achieved within 300 min of the REACT period at 1.0 g PAC/cycle (Fig. 3c) as compared to around 400 min when PAC was not added (Fig. 3a). This is reflected in a larger rate constant value for phase VI (Table 2). Increase of the PAC dosage to 1.5 g/cycle enables the rate of AN removal in phase VIII to be maintained as that of phase VI despite the increase of influent AN to 170 mg/L.

3.2.2. Removal of COD

The results of the equilibrium adsorption study had shown that no observable COD removal was achieved by using MRH as the adsorbent. In the case of PAC, the adsorption data were found to be able to fit only the Freundlich model described by

$$q = K_f C^{1/n} \quad (1)$$

where q is the mass of adsorbate per unit mass of adsorbent (mg COD/g PAC), C is the equilibrium adsorbate concentration (mg/L) and K_f as well as $1/n$ are the Freundlich parameters. The values of K_f and $1/n$ were found to be 0.0027 and 2.17, respectively. The relatively small K_f value indicates a low adsorption capacity for COD which is in agreement with the findings of Aktas and Cecen [9]. This is due to the fact that leachate consists of various constituents with different adsorption affinity. The adsorption sites will be filled first with those constituents of higher adsorption affinity leaving those with lower adsorption affinity poorly adsorbed. In this case, the value of $1/n$ was greater than 1 indicating unfavourable adsorption. Thus, it can be concluded that COD removal during the REACT period for both reactors was primarily caused by biodegradation. This means that the efficiency and rate of COD removal in the reactor would depend on the measures adopted to reduce the toxicity of the combined wastewater. In this case, the presence of MRH and PAC, respectively, helps to remove the inhibitory organic matter and heavy metals through adsorption and thus reduces the toxic effect of the combined wastewater on biodegradation. More discussion on the roles of the adsorbents is presented in Section 3.3.

The time courses of the mean filtered COD removal efficiency during the REACT period in phases IV, V, VI and VII for reactor R-MRH and in phases IV, V, VI, VII and VIII for reactor R-PAC are shown in Fig. 4a and b, respectively. The COD concentration data during the aerobic REACT period were fitted to the first-order kinetic model and the pseudo-first-order rate constants are shown in Table 2. It is observed that the addition of MRH at 0.5 g/cycle in reactor R-MRH has enabled the COD removal efficiency to be maintained at around 70% and the COD removal rate to remain fairly constant (Table 2) in increasing leachate strength. In reactor R-PAC, comparison of the COD removal efficiency profiles in phase IV (during which no PAC was added) with those in subsequent phases (Fig. 4b) and of the calculated COD removal rate constant values in all the five phases (Table 2) indicate that increasing PAC dosage was able to mitigate the toxic effect of leachate in increasing strength as the COD removal efficiencies in phases V, VI and VIII as well as the rates in all the phases were fairly constant.

3.3. Role of adsorbents in leachate treatment under SBR operation

The positive effects of MRH and PAC addition, respectively, in enhancing the biological treatability of leachate have been shown in this study. In fact, the latter has been well documented [7–9].

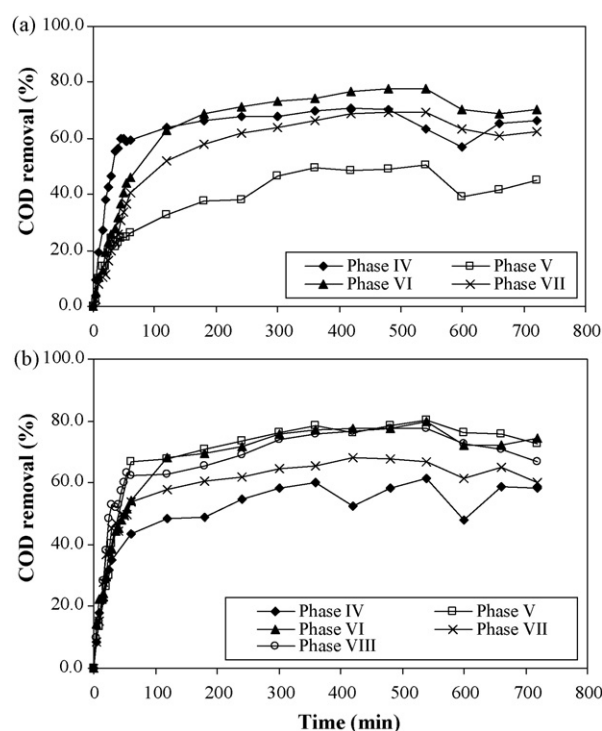


Fig. 4. Time courses of mean COD removal efficiency during the REACT period in reactors (a) R-MRH and (b) R-PAC.

A plausible reason to explain the positive effects of both adsorbents is that inhibitory substances among leachate constituents and also those formed as intermediates were adsorbed during the process thus reducing the negative impact. The MRH contains primary, secondary, tertiary and quaternary amines as well as carboxylate functional groups which help to bind the metals and organic compounds effectively [22,23]. On a per weight basis, it is evident that MRH was more effective than PAC in mitigating the inhibition of leachate as illustrated by similar performance of both reactors despite a lower MRH dosage used in reactor R-MRH. A plausible explanation for this observation lies in the particle size difference of MRH and PAC. According to the findings of Barragan et al. [24], bacterial colonization was found only on PAC with 0.490 mm particle size and not on those with 0.125 mm and smaller than 0.100 mm. In this study, the MRH used was of 0.150–0.425 mm particle size range as opposed to PAC with particle size smaller than 0.075 mm. This assures biofilms attachment on MRH and allows MRH to function like a carrier material in a sequencing batch biofilm reactor (SBBR). The better performance of SBBR is due to the bioactivity of attached-growth biomass being less inhibited by toxic constituents than the suspended-growth biomass [25]. In this study, the presence of attached biofilm on the surface of the MRH could not be confirmed experimentally due to interference caused by the overwhelming presence of the suspended biomass.

4. Conclusions

This study has shown that the ethylenediamine-modified rice husk (MRH) can be used as an alternative adsorbent to PAC in an adsorbent-supplemented SBR system for the removal of COD and AN from a combined leachate and domestic wastewater. Complete removal of AN up to 215 mg/L (loading rate 0.15 kg/m³ day) was achieved with the addition of 0.5 g MRH/cycle (loading rate 0.05 kg/m³ day). However, the addition of MRH was unable to alleviate the inhibition of the oxidation of NO₂⁻-N to NO₃⁻-N in the nitrification process due to the toxic constituents in leachate. The

better performance of MRH compared to PAC on a per weight basis in COD and AN removal was explained by the presence of attached-growth biomass on MRH due to the use of much larger sizes of MRH as compared to those of PAC.

Acknowledgement

Financial support from the Universiti Sains Malaysia under the Research University (RU) Grant No. 1001/PKIMIA/814020 is gratefully acknowledged.

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