Effect of PAC addition in combined treatment of landfill leachate and domestic wastewater in semi-continuously fed batch and continuous-flow reactors

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Abstract

The combined biological treatability of landfill leachate and domestic wastewater was investigated in both semi-continuously fed batch (SCFB) and continuous-flow (CF) activated sludges with recycle. Powdered activated carbon (PAC) was added in order to investigate the improvement in organic carbon removal and nitrification. The results obtained in SCFB and CF operations were compared to each other. In both types of operations, COD and ammonia removal efficiencies decreased with an increase in the leachate ratio of the total wastewater. As the leachate ratio increased, the positive effect of PAC on COD removal and nitrification became more apparent. In SCFB-type operations, nitrification was more inhibited than in CF operations. Additionally, the enhancement of nitrification was more apparent in CF operations than in SCFB operations where there was PAC addition. In CF operations, sufficient PAC addition could completely prevent nitrification inhibition and nitrite accumulation was avoided. With regard to nitrification, the positive impact of PAC was observed after some time since inhibition of nitrifiers was more severe than heterotrophs.

Nomenclature

BOD_5	5-day biochemical oxygen demand ($mg\cdot\ell^{-1}$)
CF	continuous-flow reactor
COD	chemical oxygen demand ($mg\cdot\ell^{-1}$)
TCOD	total COD
SCOD	soluble COD
MLCOD	mixed liquor COD
NO_x-N	nitrite and nitrate nitrogen (mg $N0_2$-N+$N0_3$-N$\cdot\ell^{-1}$)
MLSS	mixed liquor suspended solid ($mg\cdot\ell^{-1}$)
MLVSS	mixed liquor volatile suspended solids ($mg\cdot\ell^{-1}$)
OUR	oxygen uptake rate ($mg\cdot\ell^{-1}\cdot h^{-1}$)
PAC	powdered activated carbon
PACT	powdered activated carbon treatment
SCFB	semi-continuously fed batch reactor
TKN	total Kjeldahl nitrogen ($mg\cdot\ell^{-1}$)

Introduction

Sanitary landfill leachate is usually a very high strength wastewater containing many organic and inorganic constituents. Due to the high strength of leachate, care should be given in combined treatment of leachate and domestic wastewater in an activated sludge system. A previous study on combined landfill leachate and domestic wastewater treatment demonstrated that these could be treated at suitable mixing ratios (Çeçen and Çakiroglu, 2001). However, in that study leachates were shown to contain non-biodegradable matter which could not be removed by biological treatment alone. Also an increase in leachate ratio caused a reduction in the overall organic substrate removal rate in batch reactors. In addition to this, a severe nitrification inhibition may be observed in high-strength leachates due to the high free ammonia levels and presence of other inhibitors. Activated carbon addition in the form of PAC is known for its ability to enhance biological treatment efficiency, remove refractory organic compounds and to enhance nitrification. Therefore, PAC addition to activated sludge could also be tested in leachate treatment systems (U.S. EPA, 1995; Kang et al., 1990).

Organic matter removal in a PACT system is a combination of adsorption and biodegradation. Activated carbon in conjunction with activated sludge increases the removal efficiency by adsorbing non-biodegradable, toxic and/or inhibitory organics and also some metals. Many researchers have suggested that a synergy exists between activated carbon and micro-organisms. Thus, the PACT system could remove an organic compound more efficiently than would be expected from either biodegradation or adsorption alone. The mechanism consists of the stimulation of biological activity by bioregeneration of PAC. Activated carbon provides an attachment surface for micro-organisms and protects them from shock loadings of toxic and inhibitory materials, whereas micro-organisms bioregenerate the activated carbon (Sublette et al., 1982, Marquez and Costa, 1996; Kim et al., 1997; Jonge et al., 1996; Orhansky and Narkis, 1997).

Many studies in literature also showed that nitrification was enhanced by the addition of PAC to activated sludge (Ng et al., 1987, Ng and Stenstrom, 1987; Specchia and Gianetto, 1984). The most probable reason was the removal of toxic and inhibitory organics and inorganics by PAC (Ng et al., 1987, Ng and Stenstrom, 1987). The majority of studies deal with nitrification enhancement in industrial wastewater treatment and there is a lack of information on nitrification in landfill leachate treatment in the case of PAC addition.

The objective of this study was the investigation of PAC addition in combined biological treatment of sanitary landfill leachate and domestic wastewater. In another study (Aktas and Çeçen, 2001), adsorption isotherms were shown and the effect of PAC in batch reactors was discussed in detail. On the other hand, this study addressed the impact of PAC under steady operating

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TABLE 1
Characterisation of landfill leachate

pH	8.2
TCOD ($mg\cdot\ell^{-1}$)	10750
SCOD ($mg\cdot\ell^{-1}$)	9070
BOD_5 ($mg\cdot\ell^{-1}$)	6380
TKN ($mg\cdot\ell^{-1}$)	2031
NH_4-N ($mg\cdot\ell^{-1}$)	2002
NO_x-N ($mg\cdot\ell^{-1}$)	128
Total P ($mg\cdot\ell^{-1}$)	6.8
Cl^- ($mg\cdot\ell^{-1}$)	4322
Alkalinity (mg $CaCO_3\cdot\ell^{-1}$)	10600
Total solids ($mg\cdot\ell^{-1}$)	17326
TSS ($mg\cdot\ell^{-1}$)	1013
VSS ($mg\cdot\ell^{-1}$)	786
Salinity (%)	18.2
Conductivity ($mS\cdot cm^{-1}$)	29.5

conditions and aimed at demonstrating the differences between semi-continuous and continuous-flow operations. Also investigated was whether PAC addition could relieve the negative impact of leachate when the ratio of leachate was increased. This impact was studied with regard to both organic carbon removal and nitrification.

Materials and methods

Wastewater characteristics

Leachate characteristics

Throughout the study, landfill leachate was mixed with domestic wastewater at certain volumetric ratios and its treatability was studied in activated sludge systems (Aktas,1999). The leachate sample was taken from the Kemerburgaz landfill in Istanbul which receives municipal solid wastes and was characterised as in Table 1. The concentrations reflected the average of multiple analyses during the storage period at 4°C.

Leachate quality indicated the degree of stabilisation within a landfill (Krug and Ham, 1997). As seen in Table 1, a relatively biodegradable wastewater was received based on the BOD_5/COD ratio (Quasim and Chiang, 1994). In all leachate samples TKN concentration was high and a major part of it consisted of ammonium nitrogen showing the hydrolysis of organic nitrogen into ammonia nitrogen.

Domestic wastewater

Domestic wastewater was prepared synthetically as a stock solution having a total COD of 10 000 $mg\cdot\ell^{-1}$, TKN of 1 060 $mg\cdot\ell^{-1}$, phosphorus of 812 $mg\cdot\ell^{-1}$ and pH 7.1. The solution comprised 6 000 $mg\cdot\ell^{-1}$ CH_3COONa, 5 600 $mg\cdot\ell^{-1}$ glucose, 2 000 $mg\cdot\ell^{-1}$ peptone, 5 000 $mg\cdot\ell^{-1}$ $(NH_4)_2SO_4$, 2 000 $mg\cdot\ell^{-1}$ KH_2PO_4, 2 000 $mg\cdot\ell^{-1}$ K_2HPO_4, 2 000 $mg\cdot\ell^{-1}$ $MgSO_4.7H_2O$, 600 $mg\cdot\ell^{-1}$ $CaCl_2.2\ H_2O$, 200 $mg\cdot\ell^{-1}$ $FeCl_3.6\ H_2O$. This solution was diluted to a typical domestic wastewater COD of 500 $mg\cdot\ell^{-1}$.

Although leachate constituted a small percentage of the total wastewater, it contributed much to the initial COD of the wastewater. For example, when leachate made up 6.7% of the mixture (1/15 of total wastewater) on a volumetric basis, its contribution to the initial COD was as high as 42%.

Experimental steps

In a previous study it was shown that in an aerated batch activated sludge reactor the adsorption onto PAC was much higher than that predicted by isotherms (Aktas and Çeçen,2000). In those batch experiments PAC did not considerably influence the biodegradation rate of organics. PAC was mainly effective in the adsorption of residual non-biodegradable matter. Although batch tests may clarify substrate removal kinetics, they do not provide sufficient information about treatability in continuous-flow systems since transient conditions are present in these batch reactors with respect to substrate and biomass composition.

Therefore, in this study the effect of PAC addition was first examined in semi-continuously fed batch reactors (SCFB) as outlined in (a) below. The activated carbon used throughout the study was Norit SA 4 in powdered form. PAC was dried at 103°C before use in experiments. In each case, the results obtained in activated sludge systems (AS) and in PAC-added activated sludge systems (AS+PAC) were compared to each other in terms of organics and nitrogen removal. The data were also subjected to statistical analysis and the differences were tested for significance at a level of 95% confidence using the paired t-test. In the next step, experiments were continued in a continuous-flow (CF) activated sludge reactor with sludge recycle as outlined in (b) below. Results for COD removal, ammonium nitrogen removal, NO_x-N production, nitrite build-up and OUR were interpreted along with data generated from previous batch experiments.

In each SCFB run and at the beginning of the CF operation a fresh sludge was taken for seeding purposes. This seed sludge was obtained from a batch activated sludge system fed with synthetic domestic wastewater at a loading rate of 500 mg $COD\cdot\ell^{-1}\cdot d^{-1}$. In that system the sludge age was adjusted to 20 d in order to enhance the activity of nitrifiers.

a) Experiments in SCFB activated sludge reactors

In SCFB operation, a batch reactor is fed and the effluent is withdrawn intermittently. At the end, steady-state conditions are reached and this operation simulates a continuous-flow operation. In the present study, this operation was applied since it allowed for better and easier control in simultaneous monitoring of AS and AS+PAC reactors.

For this purpose, two batch plexiglass reactors were used, each having a liquid volume of 2 ℓ. One of them was operated as an **AS** and to the other, PAC was also added (**AS+PAC**). The operational conditions in these runs can be followed from Table 2. In total, four runs (SCFB Runs 1-4) were conducted**.** The influent was composed of leachate and domestic wastewater mixed at certain ratios. This influent was discontinuously fed once a day and the effluent was withdrawn on the next day. The hydraulic residence time was adjusted to 32 h by discharging 1.5 l of the supernatant liquid daily. Mainly the reduction in organic matter and nitrogen was investigated. For this purpose, TCOD, SCOD, pH, MLSS, MLVSS, TKN, NH_4-N, NO_x-N, NO_2-N measurements were made. The response of activated sludge to substrate dosing was also monitored by daily OUR measurements from the mixed liquor. As seen in Table 2 a, the sludge age q_c, was adjusted to 20 d in SCFB Runs 2 and 4, and to 10 d in SCFB Run 3 which was fed with a high COD wastewater. When the sludge age was adjusted to 20 d, one twentieth of the total mixed liquor was wasted daily. Only in SCFB Run 1, which was regarded as a preliminary run, no sludge wastage was done. Since in all other runs PAC was wasted daily with the withdrawn sludge, a new PAC addition was made daily and the wasted amount was replaced.

TABLE 2 (a)
Evaluation of SCFB operation in terms of COD removal

Run	Reactor Configur.	Leachate ratio in the feed (Vol.%)	PAC conc. (mg·ℓ^{-1})	q (h)	q_c (d)	Basis	Influent COD, S_o (mg·ℓ^{-1})	Effluent COD, S (mg·ℓ^{-1})	Average MLVSS, X (mg·ℓ^{-1})	F/M (gCOD· g MLVSS^{-1}·d^{-1})	COD removal rate, q (gCOD· g MLVSS^{-1} ·d^{-1})
SCFB 1	AS	6.7	0	32	-	SCOD	1035	116	2003	0.388	0.344
	AS+PAC	6.7	1000	32	-	SCOD	1035	110		0.388	0.346
SCFB 2	AS	6.7	0	32	20	SCOD	1035	125±15	2082	0.373	0.328
	AS+PAC	6.7	1000	32	20	SCOD	1035	130±23		0.373	0.326
SCFB 3	AS	20	0	32	10	TCOD	2277	618±23	1738	0.983	0.716
						SCOD	2153	435±15		0.929	0.741
	AS+PAC	20	2000	32	10	TCOD	2277	519±73		0.983	0.759
						SCOD	2153	399±16		0.929	0.757
SCFB 4	AS	13.3	0	32	20	TCOD	1854	408±14	2083	0.668	0.521
						SCOD	1626	274±35		0.586	0.487
	AS+PAC	13.3	2000		20	TCOD	1854	325±37		0.668	0.551
						SCOD	1626	215±27		0.586	0.508

TABLE 2 (b)
Evaluation of SCFB operation in terms of ammonium nitrogen removal and nitrification

Run	Reactor configur.	Leachate ratio in the feed (Vol.%)	PAC conc. (mg·ℓ^{-1})	q (h)	q_c (d)	Influent NH_4-N (mg·ℓ^{-1})	Effluent NH_4-N (mg·ℓ^{-1})	Average MLVSS, X (mg·ℓ^{-1})	NH_4-N removal rate (g NH_4-N· g MLVSS)^{1}·d^{-1})	NO_x-N production rate (g NO_x-N· g MLVSS^{-1}·d^{-1})
SCFB 1	AS	6.7	0	32	-	197	72	2003	0.047	0.029
	AS+PAC	6.7	1000	32	-	197	70		0.048	0.028
SCFB 2	AS	6.7	0	32	20	197	75±17	2082	0.044	0.019
	AS+PAC	6.7	1000	32	20	197	81±9		0.042	0.020
(pH adjust.)	AS	6.7	0	32	20	197	25±8	2082	0.062	0.038
	AS+PAC	6.7	1000	32	20	197	24±6		0.062	0.040
SCFB 3	AS	20	0	32	10	484	222±22	1738	0.113	0.002
	AS+PAC	20	2000	32	10	484	247±26		0.102	0.002
SCFB 4	AS	13.3	0	32	20	345	144	2083	0.072	0
	AS+PAC	13.3	2000	32	20	345	61		0.102	0.072

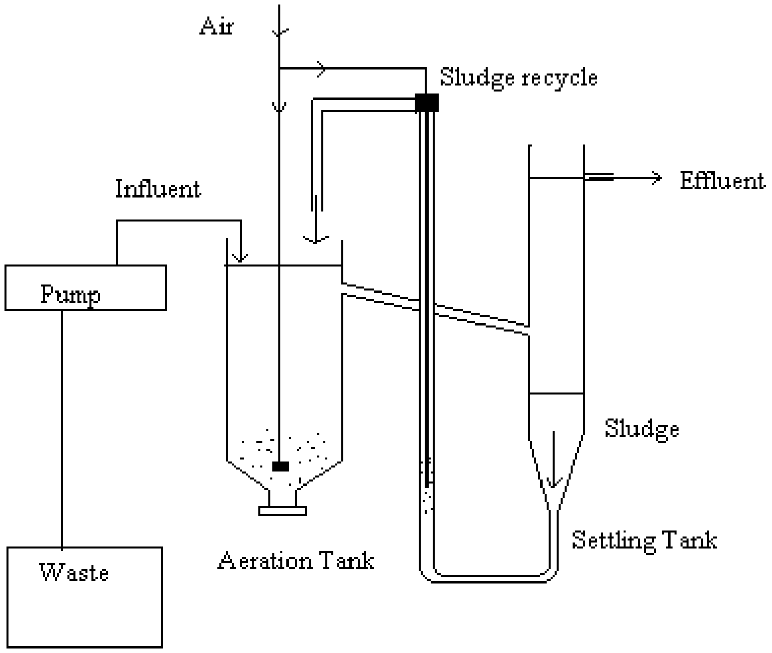

Figure 1
Set-up for the CF experiments

b) Experiments in the CF activated sludge unit

In order to simulate the impact of PAC in full-scale activated sludge operation, a lab-scale CF was employed (Fig.1). The aeration and the settling tanks had volumes of 3.6 l and 2.5 ℓ, respectively. The sludge was recycled to the aeration tank by means of an air lift.

A feed composed of leachate and domestic wastewater was continuously supplied to the system. The operational conditions may be seen in Table 3a and b. Influent and effluent TCOD, SCOD, pH, MLSS, MLVSS, TKN, NH_4-N, NO_x-N, NO_2-N were measured regularly. The response of activated sludge to substrate dosing was also monitored by daily OUR measurements from the mixed liquor. The operation was divided into two periods as follows:

Period 1: The operation was first started with a feed in which the volumetric leachate ratio was about 6.7% as in the previous SCFB Runs 1 and 2. This period lasted for 27 d. On the 19th day of normal operation, PAC was added to the aeration tank to yield 2 000 $mg \cdot \ell^{-1}$ and its influence on effluent quality was examined.

Period 2: On the 27th day of operation, the leachate ratio in the influent was increased to 13.3% in accordance with previous semi-continuous runs. When steady-state was achieved on the 36th day, a second PAC addition was made to the aeration tank to yield an additional PAC of 2 000 $mg \cdot \ell^{-1}$, thus the total PAC concentration was increased to 4 000 $mg \cdot \ell^{-1}$. The operation was stopped on the 44th day when the effect of this addition was no longer observed.

Analytical methods

Analyses were carried out in accordance with Standard Methods, 1989. COD analyses were performed by the dichromate closed reflux method. Nitrite accumulation interfered in COD analyses and therefore COD data were corrected (Aktas, 1999) by considering the nitrite nitrogen concentrations.

Total COD (TCOD) was defined as the COD of the unfiltered raw sample. Soluble COD (SCOD) was the COD of the supernatant filtered through 0.45 µm Millipore filter. SCOD was taken as the main organic parameter throughout the study.

NH_4-N analysis was carried out by the Gerhardt Vapodest 12 ammonia distillation apparatus and subsequent titration. TKN analysis was done by the same procedure after digestion of samples with Gerhardt Kjeldatherm. The NO_x-N (NO_2-N+NO_3-N**)** concentration was determined by the Devarda's Alloy Reduction Method and subsequently by the same procedure as for ammonia. NO_2-N concentrations in the samples were measured spectrophotometrically using Hach DR/3 Spectrophotometer and Nitriver 2 test kits.

MLSS analysis was carried out by drying the residue on filter paper (Millipore 0.45 µm) for one hour at 103°C. MLVSS analyses were carried out by igniting the MLSS analysis residue for 30 min at 600°C. Since PAC contributed to MLVSS measurements, the biomass-MLVSS in the PAC sludge of the continuous-flow reactor was determined separately according to a procedure proposed in the literature (Arbuckle and Griggs,1982). In accordance with this procedure tests for MLSS, MLVSS at 400°C and MLVSS at 550°C were performed on both the PAC sludge and the PAC used. By incorporating the volatile suspended solids due to PAC, the biomass-MLVSS was estimated.

For pH measurement the pH meter Orion SAS20 was used. BOD_5 analysis was performed by the dilution method. OUR in the activated sludge reactors was measured automatically by WTW Microprocessor Oximeter Oxi 3000. Details are outlined in a previous study (Aktas, 1999).

Results and discussion

SCFB activated sludge operation

The total period in each semi-continuously fed batch run was long enough to reach pseudo steady-state conditions. Steady state was defined as the condition when a constant COD level was reached in the effluent. Since MLVSS was a disputable parameter and was subject to errors, MLCOD was occasionally measured from the agitated activated sludge. MLCOD included both the total COD of the bulk liquid and the biomass-COD. Steady state condition was also checked with MLCOD measurements. Following the start of intermittent feeding, steady state was achieved after two or three hydraulic residence times (3 to 4 d) had passed.

In Tables 2a and b the operational conditions and results are summarised with respect to organics removal and nitrogen removal, respectively. The effluent COD values in Table 2a reflected the mean COD at pseudo steady-state conditions. The F/M value represented the food-to micro-organism ratio, the COD loading per amount of MLVSS. Also in the AS+PAC reactors the same MLVSS concentration was assumed to exist as in AS reactors. The substrate removal rate, q, was calculated as shown in Eq. (1). Correspondingly, in AS+PAC reactors the substrate removal rates were calculated for comparative purposes.

$$q = \frac{So - S}{q.X} \qquad (1)$$

where:

q substrate removal rate (g COD·gMLVSS^{-1}·.d^{-1})

TABLE 3 (a)
Evaluation of CF operation in terms of COD removal

	Reactor operation	Leachate ratio in the feed (Vol.%)	PAC conc. (mg·ℓ^{-1})	q (h)	Basis	Influent COD, S_o (mg·ℓ^{-1})	Effluent COD, S* (mg·ℓ^{-1})	Average MLVSS, X (mg·ℓ^{-1})	F/M (gCOD· g MLVSS^{-1}·d^{-1})	COD removal rate, q (gCOD· g MLVSS^{-1}·d^{-1})
PERIOD I	AS	6.7	-	34.1±3.9	TCOD	1255	161±28	2018	0.438	0.382
					SCOD	1020	124±15		0.356	0.312
	AS+PAC	6.7	2000	30.6±2.5	TCOD	1255	92±20	1080^a	0.911	0.845
					SCOD	1020	41±18		0.741	0.711
PERIOD II	AS+PAC	13.3	2000	33.3±3.9	TCOD	1854	340±39	1065^a	1.255	1.025
					SCOD	1626	221±5		1.100	0.951
	AS+PAC	13.3	4000	29.3±0.5	TCOD	1854	198±15	1200^a	1.266	1.130
					SCOD	1626	165±3		1.110	0.997

a: Superscript a denotes the biomass-MLVSS in the AS+PAC reactor determined according to a procedure described by Arbuckle and Griggs, 1982.
* Steady-state effluent values.

TABLE 3 (b)
Evaluation of CF operation in terms of ammonium nitrogen removal and nitrification

	Reactor operation	Leachate ratio in the feed (Vol.%)	PAC conc. (mg·ℓ^{-1})	q (h)	Influent NH_4-N (mg·ℓ^{-1})	Effluent NH_4-N* (mg·ℓ^{-1})	Average MLVSS, X (mg·ℓ^{-1})	NH_4-N removal rate (g NH_4-N· g MLVSS^{-1}·d^{-1})	NO_x-N production rate (g NO_x-N· g MLVSS^{-1}·d^{-1})
PERIOD I	AS	6.7	-	34.1±3.9	205	67±13	2018	0.048	0.032
	AS+PAC	6.7	2000	30.6±2.5	205	48±4	1080^a	0.114	0.089
PERIOD II	AS+PAC	13.3	2000	33.3±3.9	345	106±15	1065^a	0.162	0.136
	AS+PAC	13.3	4000	29.3±0.5	345	80	1200^a	0.181	0.160

a: Superscript a denotes the biomass-MLVSS in the AS+PAC reactor determined according to a procedure described by Arbuckle and Griggs, 1982.
* Steady-state effluent values.

S_o influent COD concentration ($\text{mg}\cdot\ell^{-1}$)
S effluent steady-state COD concentration ($\text{mg}\cdot\ell^{-1}$)
X average biomass concentration during a run ($\text{mg}\cdot\text{MLVSS}\ell^{-1}$)
q hydraulic retention time (h)

Evaluation of effluent SCOD data (Table 2 a) led to the conclusion that in the effluent mainly non-biodegradable COD was left over. As the ratio of leachate increased, a higher residual substrate concentration was observed. In previous batch studies it was shown that this leachate possessed an inert COD fraction of about 30% and that the rate of COD removal in a batch reactor could be described by a first-order model incorporating this fraction (Aktas and Çeçen, 2001). Within the scope of those experiments it was assumed that all of the residual SCOD seen in the effluent was of substrate origin (Aktas and Çeçen, 2001) since in our experiments no evidence was provided that soluble microbial products (SMP) were generated.

SCFB Run 1 was a preliminary run lasting for 5 d. At the beginning PAC was added to the AS+PAC reactor only to yield a constant concentration of 1 000 $\text{mg}\cdot\ell^{-1}$ in the aeration tank. Although a slight improvement in COD removal was observed on the next day, in the succeeding days the differences between the AS and AS+PAC reactors diminished and finally the same levels were reached with respect to COD (Table 2a) and NH_4-N and NO_x-N (Table 2b).

The semi-continuous operation lasted for 35 d in SCFB Run 2, for 18 d in SCFB Run 3 and for 11 d in SCFB Run 4. Figures 2, 3 and 4 illustrate the profiles in these runs.

In SCFB Run 2 the ratio of leachate was the same as in SCFB Run 1 (Figs. 2 a, b, c). PAC was added in small amounts to the AS+PAC reactor daily in order to compensate for the PAC loss with the daily wasted sludge. The effluent SCOD decreased to about 125±15 $\text{mg}\cdot\ell^{-1}$ and 130±23 $\text{mg}\cdot\ell^{-1}$ in the reactors AS and AS+PAC, respectively, as followed from Table 2a. These differences were statistically not significant. As seen in Fig. 2b, the OUR profiles in both reactors were also close to each other. The only considerable difference arose after the shock PAC addition of 1 000 $\text{mg}\cdot\ell^{-1}$on the 15th day, but it did not last long.

In addition to this, at this leachate ratio of 6.7%, PAC addition to the AS+PAC reactor (Table 2b) neither improved NH_4-N removal nor enhanced the production of NO_x-N (Figs. 2c and d). Analyses by the paired t-test indicated no significant differences between the AS and AS+PAC reactors with respect to both NH_4-N and NO_x-N. In SCFB Runs 1 and 2 the feed pH was brought near neutrality in order to prevent free ammonia inhibition seen in batch operation (Aktas and Çeçen,2000). But in this case, pH decreased below 5 and a serious nitrite build-up of up to 80 to 100 mg NO_2-$\text{N}\cdot\ell^{-1}$ took place in the reactors. Correspondingly, the free nitrous acid (FNA) concentrations rose to 3.25 $\text{mg}\cdot\ell^{-1}$ which could be inhibitory to both *Nitrosomonas* and *Nitrobacter* (Anthonisen et al.,1976). Therefore on the 23rd day,

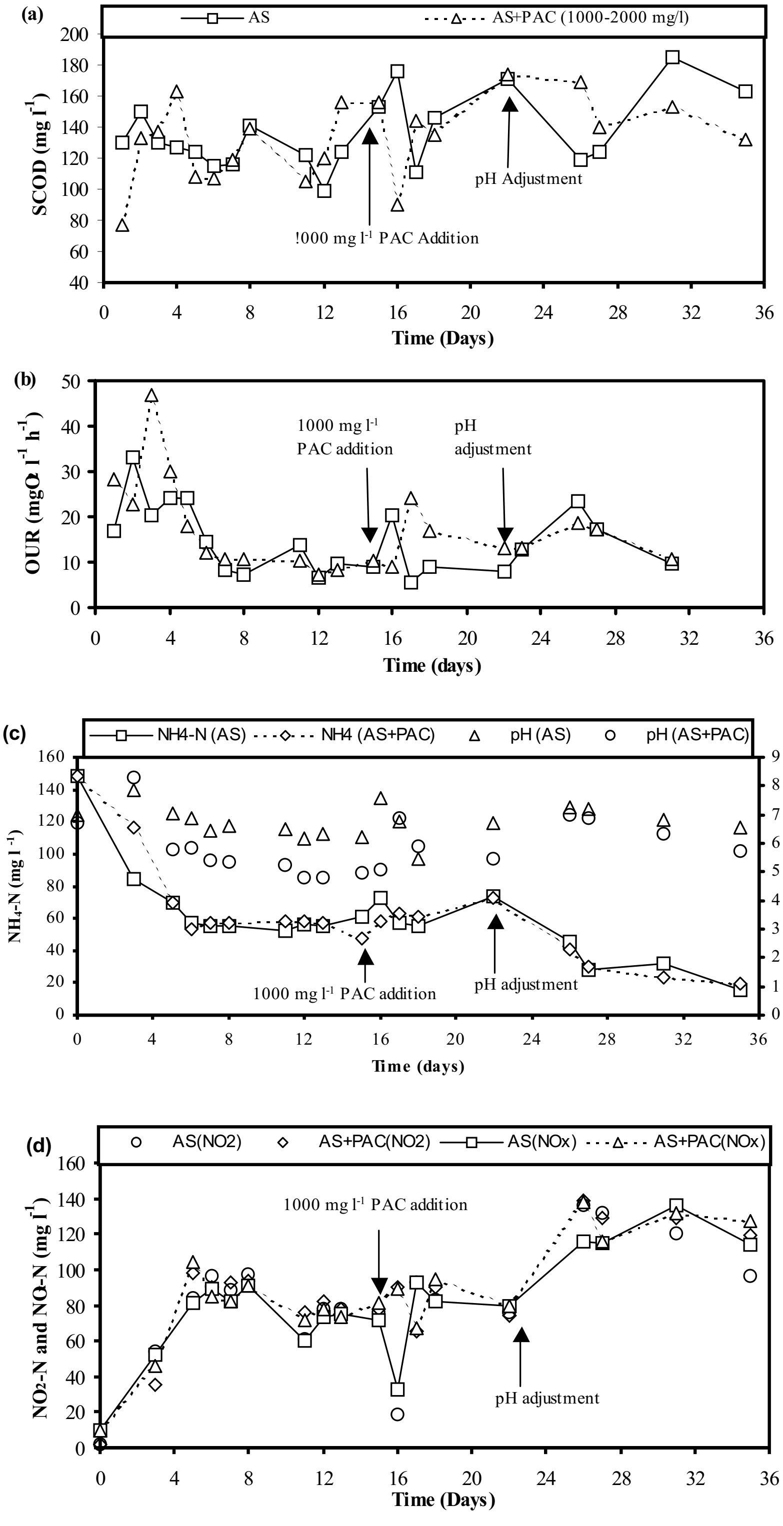

Figure 2

Profiles after the start-up of SCFB Run 2 in AS and AS+PAC reactors (with initial PAC conc. of 1 000 $\text{mg}\cdot\ell^{-1}$ in AS+PAC reactor and feed concentrations of TCOD 1 338 $\text{mg}\cdot\ell^{-1}$, SCOD 1 035 $\text{mg}\cdot\ell^{-1}$, TKN 265 $\text{mg}\cdot\ell^{-1}$, NH_4-N 197 $\text{mg}\cdot\ell^{-1}$, NO_x-N 15 $\text{mg}\cdot\ell^{-1}$and feed pH of 7.17).

(a) Final soluble COD (SCOD) concentrations
(b) OURs in the reactors
(c) Final NH_4-N concentrations and pH in the reactors
(d) Final NO_x-N and NO_2-N concentrations

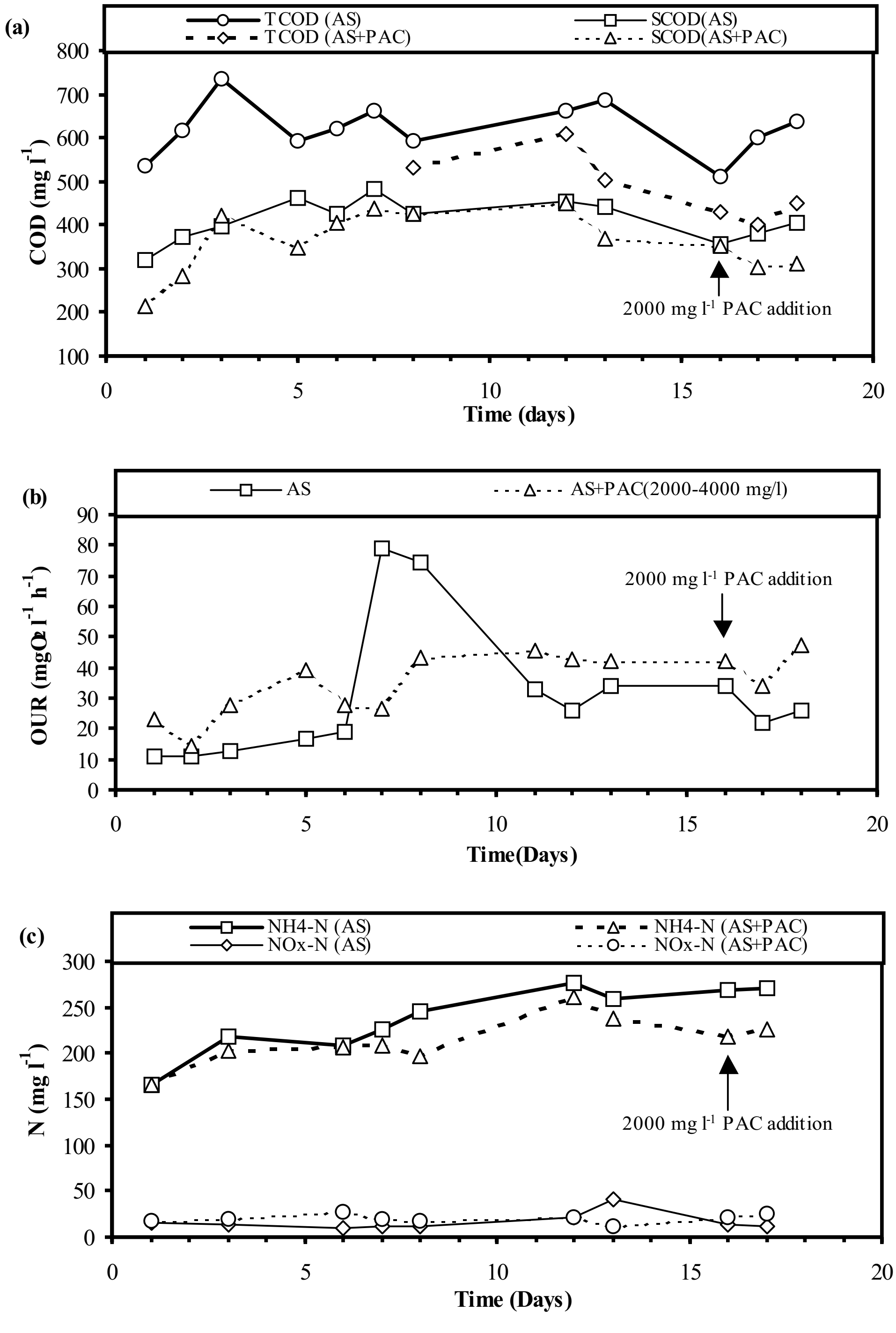

Figure 3

Profiles after the start-up of SCFB Run 3 in AS and AS+PAC reactors (with initial PAC conc. of 2 000 mg·ℓ$^{-1}$ *in AS+PAC reactor and feed concentrations of TCOD 2 277 mg·ℓ*$^{-1}$*, SCOD 2 153 mg·ℓ*$^{-1}$*, TKN 542 mg·ℓ*$^{-1}$*,* NH_4*-N 484 mg·ℓ*$^{-1}$*,* NO_x*-N 12 mg·ℓ*$^{-1}$ *and feed pH of 7.62)*

(a) Final total COD (TCOD) and soluble COD (SCOD) concentrations
(b) OURs in the reactors
(c) Final NH_4*-N and* NO_x*-N concentrations*

pH adjustments were made and nitrification improved obviously (Figs. 2c and d). NH_4-N concentrations decreased from about 80 to about 25 mg·ℓ$^{-1}$ in both the AS and AS+PAC reactors (Fig. 2c). FNA concentrations were decreased to 0.6 mg·ℓ$^{-1}$ which was not inhibitory to *Nitrosomonas* but may be inhibitory to *Nitrobacter*. Therefore, nitrification was seen to proceed to the stage of NO_2-N only and the major portion of NO_x-N consisted of nitrite. All these observations indicated the sensitivity of nitrifiers to pH changes. On the other hand, COD removal did not change with such pH decreases since heterotrophs were much more resistant.

In SCFB Run 3 the ratio of leachate was increased to 20% and 72% of the initial COD originated from leachate. This did not only increase the organic and nitrogenous strength of the feed, but also caused a higher level of inhibitory or toxic substances. As seen in Table 2a, in the effluent of the AS reactor the residual TCOD and SCOD amounted to 618±23 and 435±15 mg·ℓ$^{-1}$, respectively. These high values suggested that additional treatment techniques would be required if the leachate ratio was increased. As seen in Fig. 3a and Table 2a, a considerable reduction was observed in the final TCOD and SCOD concentrations in the case of PAC addition to the AS+PAC reactor. During the period from 0 to 16 d and after the slug PAC dose on the 16th day, the effluent SCOD concentrations reached relatively lower values in the AS+PAC reactor compared to the AS reactor. These differences were also statistically significant. Generally, when the leachate ratio in the feed increased, the effect of PAC became more apparent. Also, the differences were more apparent in terms of effluent TCOD than SCOD since PAC improved sludge settleability and decreased the concentration of particulate matter contributing to TCOD. In all former batch runs (Aktas and Çeçen, 2001) and these SCFB runs a clearer effluent was observed in PAC sludges.

In each case, OUR usually proceeded at higher values in the AS+PAC reactor than in the AS reactor and followed COD profiles (Fig. 3b). This was also observed in previous batch studies (Aktas and Çeçen, 2001).

In SCFB Run 3, no recordable nitrification was observed both in the AS and AS+PAC reactors as evidenced from poor NO_x-N production (Fig. 3c). The final NH_4-N concentrations were as high as 222±22 and 247±26 $mg \cdot \ell^{-1}$ in the AS and AS+PAC reactors, respectively. These differences in final ammonium nitrogen concentrations were significant at 95% confidence level (Table 2b, Fig. 3c). Although the feed pH was about 7.46 in the AS reactor, as a result of aeration and CO_2 stripping, pH increased to values exceeding 9. In the AS+PAC reactor this increase was slightly less, resulting in less ammonia stripping. Correspondingly, in both reactors the free ammonia (FA) level was as high as 55 to 75 $mg \cdot \ell^{-1}$ at high pH, resulting in inhibition of *Nitrosomonas*. Thus, an increase in leachate ratio also caused a severe nitrification inhibition. At this leachate ratio of 20% even PAC addition could not relieve this inhibition as seen from the results belonging to the AS+PAC reactor.

In SCFB Run 4 the leachate ratio was 13.3% as seen in Table 2a and b and 59% of the initial COD originated from leachate. In the AS+PAC reactor a constant PAC concentration of 2 000 $mg \cdot \ell^{-1}$ was maintained during the first 9 d of operation (Fig. 4a). The biggest differences between the AS and AS+PAC reactors were observed in this run. The statistical analysis of effluent TCOD and SCOD shown in Fig. 4a indicated a significant difference between these two reactors. On the 9th day a shock PAC addition was made to the AS+PAC reactor yielding an additional 2 000 $mg \cdot \ell^{-1}$. The final TCOD in the AS+PAC reactor could be decreased further to 100 $mg \cdot \ell^{-1}$ by this addition, whereas this was at about 400 $mg \cdot \ell^{-1}$ in the parallel AS reactor. The SCOD in the AS+PAC reactor decreased to 27 $mg \cdot \ell^{-1}$ whereas in the AS reactor this was at about 300 $mg \cdot \ell^{-1}$. PAC obviously adsorbed a great portion of the non-biodegradable COD.

As in other runs, in the AS+PAC reactor, OUR profiles remained at a considerably higher level than in the AS reactor (Fig. 4b).

As seen in Fig. 4c after the start of intermittent feeding, in the first 5 d of operation, no nitrification was observed in both reactors as evidenced from NO_x-N profiles. In this period, free ammonia

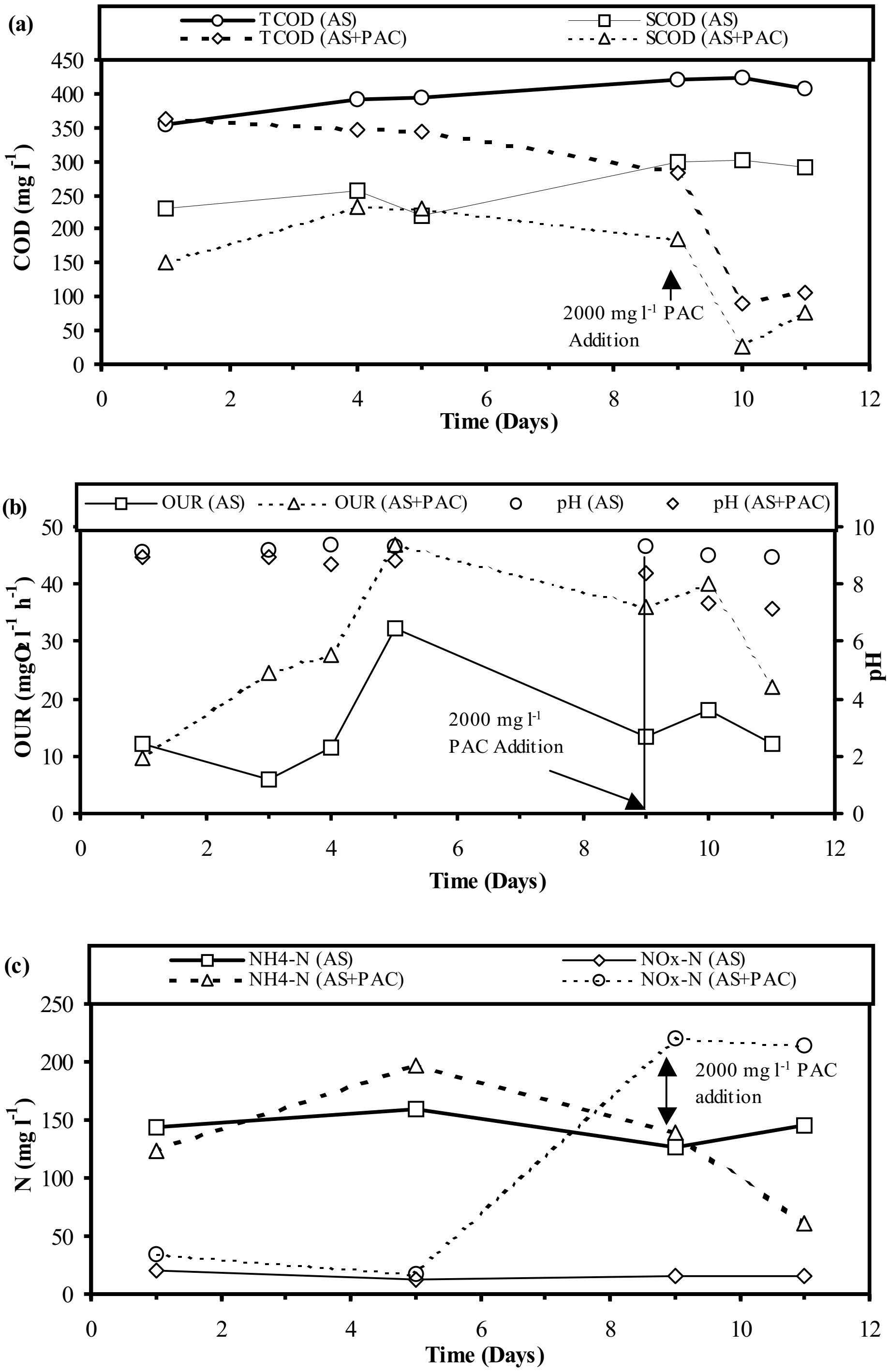

Figure 4

Profiles after the start-up of SCFB Run 4 in AS and AS+PAC reactors (with initial PAC conc. of 2 000 $mg \cdot \ell^{-1}$ in AS+PAC reactor and feed concentrations of TCOD 1 854 $mg \cdot \ell^{-1}$, SCOD 1 626 $mg \cdot \ell^{-1}$, TKN 406 $mg \cdot \ell^{-1}$, NH_4-N 345 $mg \cdot \ell^{-1}$, NO_x-N 15 $mg \cdot \ell^{-1}$, and feed pH of 7.46)

(a) Final total COD (TCOD) and soluble COD (SCOD) concentrations
(b) OURs and pH in the reactors
(c) Final NH_4-N and NO_x-N concentrations

(FA) concentrations in the AS reactor (38 to 69 $mg \cdot \ell^{-1}$) and in the AS+PAC reactor (32 to 42 $mg \cdot \ell^{-1}$) were high and contributed to inhibition of *Nitrosomonas*. On the other hand, with PAC addition to the AS+PAC reactor not only was NH_4-N removal improved, but also the NO_x-N production rate was raised to 0.072 g NO_x-N·g $MLVSS^{-1} \cdot d^{1}$. This increased nitrification was accompanied by a decrease in pH and free ammonia after the 9th day. Increased COD and ammonium removals were the causes of higher OUR levels measured in the mixed liquor of the AS+PAC reactor (Fig. 4b). The positive effect of PAC on COD removal was immediately observed from the start-up. The later improvement in nitrification indicated that nitrifiers were much more sensitive to toxic and inhibitory shocks than heterotrophs. However, also in this run the major portion of NO_x-N in the AS+PAC reactor consisted of NO_2-N. In spite of PAC addition, NO_2-N concentrations exceeded even 200 $mg \cdot \ell^{-1}$ as seen in Fig. 4c. Also previous batch studies had revealed that nitrite build-up was considerable in leachate treatment (Aktas and Çeçen, 2001).

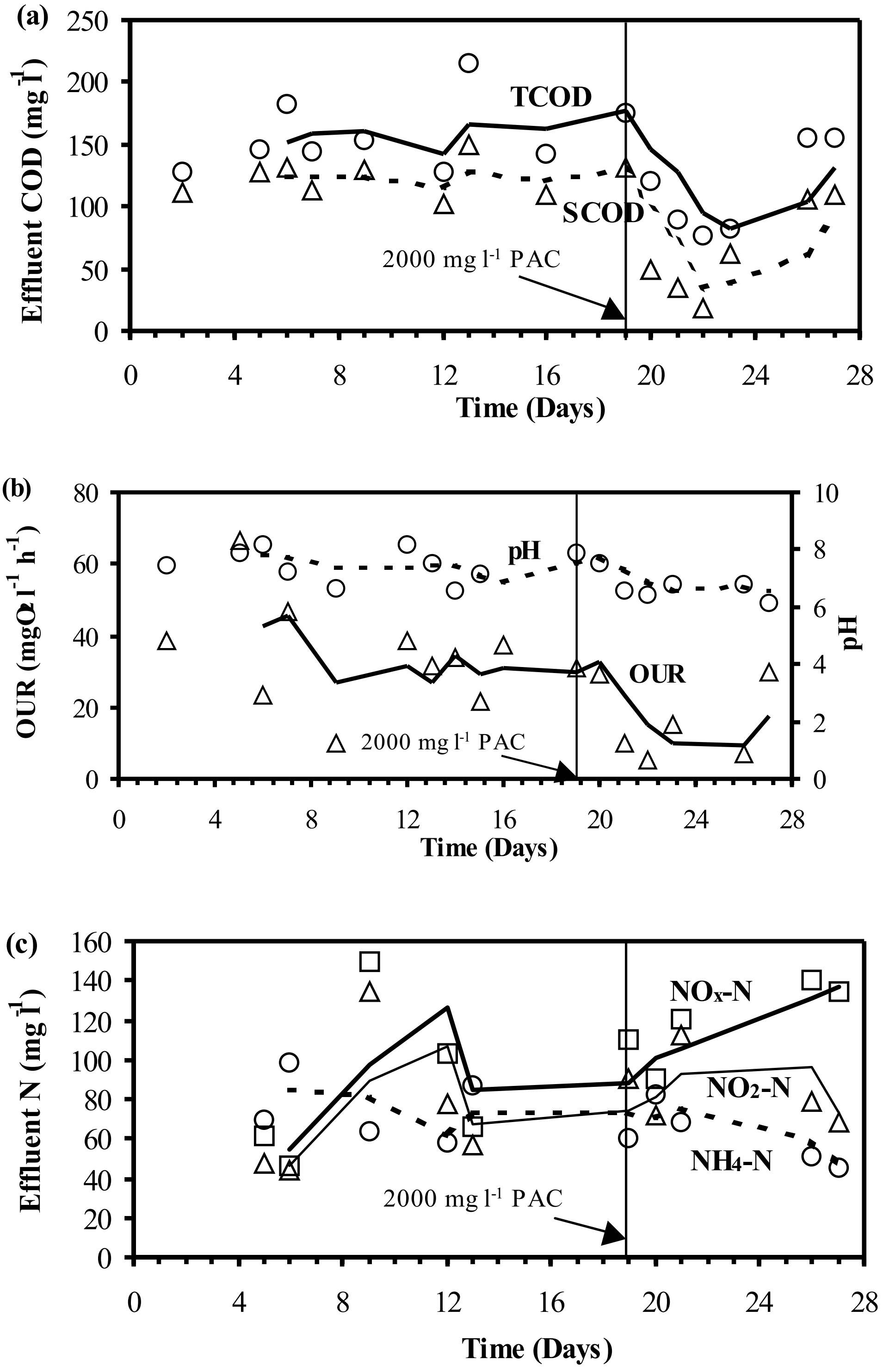

Figure 5

Profiles in PERIOD I of CF operation (with feed concentrations of TCOD 1 255 $mg \cdot \ell^{1}$, SCOD 1 020 $mg \cdot \ell^{1}$, TKN 215 $mg \cdot \ell^{1}$, NH_4-N 205 $mg \cdot \ell^{1}$, NO_x-N 15 $mg \cdot \ell^{1}$, and feed pH of 7.38)

(a) Effluent total COD (TCOD) and soluble COD (SCOD) concentrations
(b) OURs and pH in the reactor
(c) Effluent NH_4-N, NO_x-N and NO_2-N concentrations

Continuous-flow (CF) activated sludge operation

In Table 3 a the results about COD removal are presented. A relatively low standard deviation was obtained in steady-state values and substrate removal rate was calculated using these values as shown in Eq. (1). Similarly, Table 3b summarises the results achieved in terms of nitrogen.

Period I

In this period between 0 to 27 d, the feed concentrations were: TCOD: 1 255 $mg \cdot \ell^{-1}$, SCOD: 1 020 $mg \cdot \ell^{-1}$, TKN: 215 $mg \cdot \ell^{-1}$, NH_4-N: 205 $mg \cdot \ell^{-1}$ and NO_x-N :15 $mg \cdot \ell^{-1}$. The loading rate was as 0.44 gTCOD·gMLVSS-1·d^{1}. The effluent TCOD and SCOD concentrations are shown in Fig. 5a. The steady-state TCOD and SCOD concentrations in this period were about 161±28 $mg \cdot \ell^{-1}$ and 124±15 $mg \cdot \ell^{-1}$, respectively.

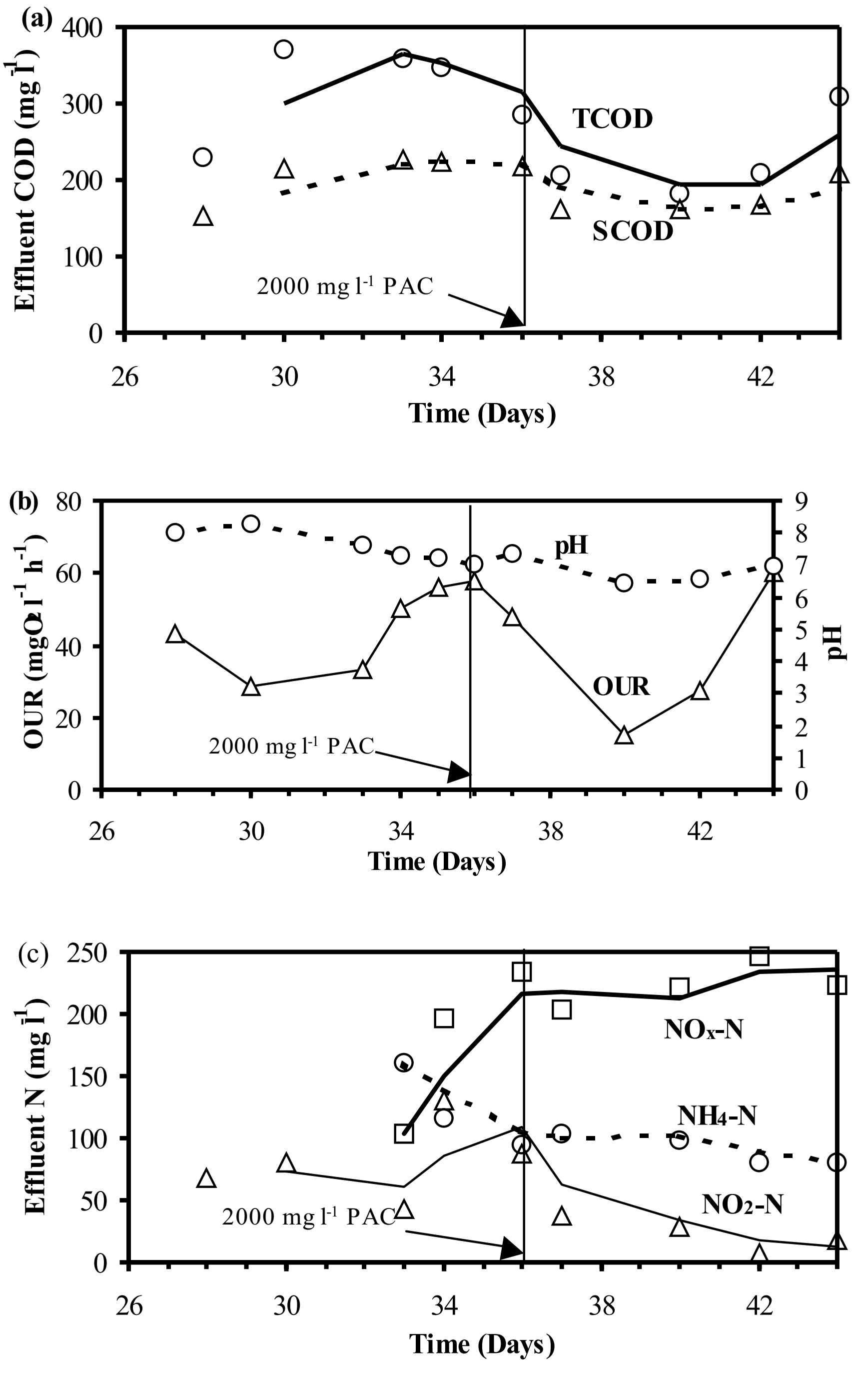

Figure 6

Profiles in PERIOD II of CF operation (with feed concentrations of TCOD 1 854 mg·ℓ^{1}, SCOD 1 626 mg·ℓ^{1}, TKN 406 mg·ℓ^{1}, NH_4-N 345 mg·ℓ^{1}, NO_x-N 15 mg·ℓ^{1}, and feed pH of 7.46)

(a) Effluent total COD (TCOD) and soluble COD (SCOD) concentrations
(b) OURs and pH in the reactor
(c) Effluent NH_4-N, NO_x-N and NO_2-N concentrations

The latter was similar to the final SCOD of SCFB Runs 1 and 2, showing that SCFB operation could simulate continuous-flow operation in that respect. In the period before PAC addition (0 to19 d) the effluent stream contained non-biodegradable COD originating from leachate.

The slug PAC addition on the 19th day led to an immediate effect (Fig. 5a) and in the effluent the mean TCOD decreased from 161±28 mg·ℓ^{-1} to 92±20 mg·ℓ^{-1}, and the mean SCOD decreased from 124±15 mg·ℓ^{-1} to 41±18 mg·ℓ^{-1}, respectively. This effect of PAC lasted for about 4 d, but then the effluent COD tended to increase to levels before PAC addition (Fig. 5a), indicating the loss of effectiveness after saturation of PAC.

The OUR profiles illustrated in Fig. 5b exhibited a pattern similar to COD profiles. OUR was higher when micro-organisms were exposed to higher concentrations of biodegradable substrate in the reactor. When biodegradable COD decreased, OUR tended to decrease (Fig. 5c). Hence, it was deduced that OUR serves as a sensitive parameter in reflecting the responses to substrate changes and PAC additions, especially in the case of continuous-flow operation.

In the period from 0 to 19 d, NH_4-N removal and NO_x-N production were similar to SCFB operation. In this period, the second step of nitrification, conversion of nitrite to nitrate, was inhibited and a major portion of NO_x-N existed in the form of nitrite (Fig. 5c) as in former SCFB Runs 1 and 2.

As seen from the NH_4-N and NO_x-N profiles in Fig. 5 c and the values in Table 3b, after the PAC addition on the 19th day NH_4-N removal and NO_x-N production rates increased. NO_x-N production rate (Table 3b) far exceeded those reached in SCFB runs in which nitrification improvement was not visible. The reason was the saturation of PAC with biodegradable and non-inhibitory organic matter and loss of effectiveness in those SCFB runs. In spite of this increased NO_x-N production, NO_2-N concentrations did not rise apparently in continuous-flow operation, showing that inhibition of *Nitrobacter* was prevented to some extent after PAC addition. This was not observed in any of the former batch (Aktas and Çeçen, 2001) and SCFB Runs.

Period II

In this period lasting from 26 to 36 d the reactor received a feed with an increased leachate ratio (13.3% by volume) as seen in Table 3a and 3b. The feed concentrations were: TCOD:1 854 mg·ℓ^{-1}, SCOD: 1 626 mg·ℓ^{-1}, TKN: 406 mg·ℓ^{-1}, NH_4-N: 345 mg·ℓ^{-1} and NO_x-N :15 mg·ℓ^{-1}. The loading rate was 1.25 gTCOD·gMLVSS^{-1}·d^{-1}. 59% of this

COD loading was attributed to leachate-COD.

No new PAC had been added since the 19th day of operation. In spite of this fact, the effect of PAC seemed to last longer in comparison to SCFB operation. As seen in Table 3a, the steady-state effluent TCOD and SCOD concentrations were about 340±39 mg·ℓ^{-1} and 221±5 mg·ℓ^{-1}, respectively. It was seen that PAC became saturated and the effluent SCOD concentrations tended to increase slightly on days 34 to 36 (Fig. 6a). The new PAC addition on the 36th day improved COD removal further. After this PAC addition, TCOD and SCOD were again decreased to 198±15 mg·ℓ^{-1} and 165±3 mg·ℓ^{-1}, respectively (Fig. 6a, Table 3a).

Generally, the effect of PAC was more pronounced in continuous-flow operation than in SCFB operation. This difference was attributed to the difference in operating conditions. In a continuous-flow reactor at steady-state, PAC was always exposed to much lower effluent concentrations than the influent. On the other hand, due to the once-a-day feeding pattern in the SCFB reactor, PAC was initially exposed to high substrate levels and probably became saturated with biodegradable COD, thereby decreasing its effectiveness.

The main differences between SCFB and CF operations were then observed when the ratio of leachate increased. In the SCFB reactors, micro-organisms were exposed to higher concentrations of toxic and inhibitory organics after each once-a-day feeding. However, in a CF reactor they were exposed to lower toxic and inhibitory concentrations due to the more steady operation and therefore a better COD removal was observed. In both SCFB and CF operations, however, PAC was not bioregenerated, at least not under the conditions of this study. Also in other studies a combination of PAC and biological treatment seemed not to be synergistic (Çeçen, 1994; Xiaojian et al., 1991). If bioregeneration did take place, the filled PAC pores would be purified leading to further substrate uptake even if no new PAC was added. Also in batch reactors no visible bioregeneration of PAC was observed (Aktas and Çeçen, 2001). Bioregeneration is a means of reducing PAC requirements. If this is not obviously seen like in our case, PAC should be continuously added to the reactor in order to bring about a permanent removal in COD and other parameters.

Also during this period OUR values (Fig. 6b) usually followed the COD pattern, but remained at a higher level than in PERIOD I since in PERIOD II substrate loads and effluent concentrations were higher. Also, the enhancement of NO_x-N production may have contributed to this higher OUR level in this period.

NO_x-N and NO_2-N concentrations did not change significantly in the first 5 to 6 d after the increase of leachate ratio (Fig. 6c). But on the 34th day an improvement in nitrification was observed. Obviously some time was required to reach steady-state and acclimate nitrifiers to new feeding conditions. After the shock PAC dose on the 36th day, both NH_4-N removal and NO_x-N production increased (Fig. 6c). A greater percentage of NH_4-N was converted into NO_x-N. As seen in Table 3 b, the maximum NO_x-N production rate amounted to 0.160 gNO_x-N·$gMLVSS^{-1}$·d^{-1} which far exceeded those achieved in SCFB operation. Figure 6b also shows that effluent pH decreased apparently accompanying nitrification. But the most striking effect of PAC was the achievement of complete nitrification. A smaller fraction of effluent NO_x-N consisted of NO_2-N and the NO_2-N concentration was decreased from above 100 mg·ℓ^{-1} to about 10 mg·ℓ^{-1} indicating that inhibition of *Nitrobacter* had been almost completely prevented (Fig. 6c).

Throughout this continuous-flow operation, FA concentrations were below 6 mg·ℓ^{-1}. FA concentrations between 1 and 6 mg·ℓ^{-1} might have contributed to *Nitrobacter* inhibition, but this was also observed in periods when FA was below 1 mg·ℓ^{-1} that would not be inhibitory. Hence, an additional factor in nitrification inhibition seemed to be also the presence of inhibitory organics and metals in leachate.

Conclusions

The study brought a novel approach in combined leachate and domestic wastewater treatment by showing how and under which circumstances the negative impact of leachate could be relieved by PAC addition in semi-continuous and continuous-flow operations. As the ratio of leachate in the feed increased, the positive effect of PAC became more apparent and total COD and soluble COD concentrations could be decreased to low levels. At increased leachate ratios nitrification became generally more inhibited, primarily due to the increase in free ammonia. With PAC addition this inhibition could be relieved to some extent. Generally PAC addition had a more pronounced effect on nitrification than on organic carbon removal.

The study also emphasised the differences between SCFB and CF operations. The positive effect of PAC on COD reduction and nitrification was more striking in CF operation than in SCFB operation. For practical purposes the results in SCFB operation implied that under intermittent substrate loadings the effect of PAC would be less compared to steady CF operation. Another observation made during the study was that PAC was not bioregenerated. Therefore a continuous PAC addition was necessary when PAC became saturated. The depletion of organic matter could be successfully monitored by OUR measurements which was best observed in CF operation.

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