Mixed- and Plug-Flow Performances of an Anaerobic Biofilter Treating 2-Ethylhexanoic Acid

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ABSTRACT

The performance of a 20-L anaerobic biofilter treating 2-ethylhexanoic acid (2-EHA) operating with the effluent recirculated was compared with that of the same biofilter operated without any recirculation. The recirculation of effluent was at a rate of 60 L/h through the biofilter. Tracer experiments were carried out to study the hydrodynamics in the biofilter under different modes of operation. The dispersion number (D/UL) obtained from these tracer experiments for the biofilter operated with and without effluent recirculation were 0.65 and 0.06, respectively. These values show that the recirculation was effective in achieving a mixed-flow pattern in the biofilter, whereas the biofilter operated without recirculation was essentially a plugflow column with a moderate level of axial dispersion.

The feed consisted of 2-EHA at a concentration of 8200 mg/L, which is equivalent to a COD of 20,000 mg/L. The optimal performance of the mixed-flow biofilter was at a hydraulic retention time (HRT) of 1.1 d, with a COD removal efficiency of 92.8% and a biogas production rate of 6.44 L/L biofilter vol/d. The biofilter failed at 0.83 d HRT, as a result of washout of biomass at this high hydraulic loading rate. By comparison, the optimal performance achieved for the plugflow system was at 2 d HRT. The COD removal efficiency was 74.1%, and biogas production rate was 2.13 L/L biofilter vol/d. When the HRT was lowered to 1.5 d, failure occurred owing to inhibition as indicated by the low methane yield of 0.192 L/g COD removed. The

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superior performance of the mixed-flow mode can be attributed to the presence of the recycle stream, which diluted and evenly distributed the feed.

Index Entries: Mixed- and plug-flow anaerobic biofilter; 2-ethylhexanoic acid degradation; branched-chain fatty acid; biofilter performance; tracer studies.

INTRODUCTION

Anaerobic digestion processes are widely used for treating agricultural wastes and are finding increasing application in treating high-strength industrial wastes (1–14). The process allows a high degree of waste stabilization, has a low production of excess sludge, and forms methane, which can be recovered and stored for use as fuel.

However, a distinct problem of anaerobic treatment is process instability at high loading rates, and this is associated with the slow growth rates of certain bacteria in the anaerobic system. The slowest growing bacteria are the acetoclastic methanogens, which convert the intermediate volatile fatty acid (VFA), ethanoic acid, to CH₄ and CO₂. Their maximum specific growth rate is between 0.17–0.33 d⁻¹ (2,15), requiring a minimum operating retention time of 6 d in conventional suspended culture digesters. Operation at high hydraulic loading rates, equivalent to retention times shorter than 6 d, would result in washout of the acetoclastic methanogens, which would, in turn, lead to accumulation of intermediate VFAs and the eventual souring of the digester.

An important development in anaerobic digestion is the biofilter, in which the anaerobic bacteria are allowed to grow as biofilm on surfaces of packing media. An increased biomass concentration is achieved, which overcomes the disadvantage of the low rates of anaerobic digestion. The anaerobic biofilter has been reported to handle higher hydraulic loading rates than conventional suspended culture digesters, thus enabling more economical treatments (2,4–6,12,16).

In high-rate anaerobic biofilters, adequate mixing is essential to ensure uniform distribution of substrate and to prevent localized accumulation of VFAs (17). This is usually achieved by recirculating biogas or effluent through the packed bed. DeWalle and Chian (18) reported that an effluent recycle, while diluting the influent concentration, maintained the COD removal efficiency with respect to the diluted influent. In a separate study, Thirumurthi (19) used a 14.8-L upflow anaerobic biofilter, packed with toroidal biorings, to study the effect of effluent recycle rate on COD removal efficiency. The biofilter was found to be in its optimal performance when the recycle velocity was between 66–680 cm/h, which is equivalent to recirculating the entire liquid content of the biofilter 0.4–4.2 times an hour. Sloughing of biofilm occurred at recycle velocities higher than 680 cm/h.

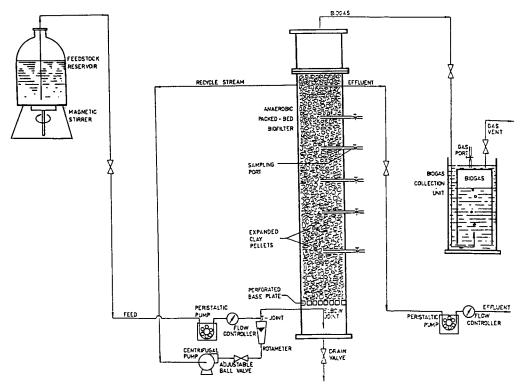


Fig. 1. Experimental setup of biofilter system.

In this study, a 20-L anaerobic upflow biofilter was used to treat 2-ethylhexanoic acid (2-EHA), a branched-chain fatty acid present in a chemical industry effluent. Feed concentration of 2-EHA was 8200 mg/L (20,000 mg COD/L). The performance of the biofilter, operated in the mixed-flow mode, with effluent recycle, and the plug-flow mode, without effluent recycle, was compared in terms of COD removal efficiency and biogas production rate at various hydraulic loading rates. The fluid flow patterns through the packed bed were confirmed by carrying out tracer stimulus-response studies.

METHODS

Biofilter Design

The experimental setup of the biofilter system is shown in Fig. 1. The biofilter used was fabricated from a cylindrical plexiglass pipe with an internal diameter of 0.14 m and an overall height of 2.15 m. The packing medium consisted of fire-expanded clay pellets of average diameter 0.015 m. The rough and irregular surfaces of the pellets enabled attachment, as well as trapping of biomass in the interstices. The packed filter was filled to a depth of 2 m with the packing medium supported by a perforated

liquid-dispersion base plate. This resulted in an effective void vol of 20 L. The headspace, with a perforated plate, was designed to hold the pellets against their buoyancy and to enable disengagement of biogas before collection.

To achieve the mixed-flow condition, effluent was drawn from the top of the biofilter column and recirculated through the bottom at 60 L/h. This was equivalent to recirculating the entire liquid content of the biofilter three times an hour. To ensure proper mixing and dilution of the feed, the recycle stream joined the influent stream via a T-joint, and these were directed, by means of an elbow joint, towards the bottom of the column. The feed was introduced by a twin-headed peristaltic pump, which also withdrew effluent from the top of the column. This setup enabled an approximately constant volume of filter liquor to be maintained. In the plugflow operation, the effluent recycle stream was cut off. The biogas was collected, by displacing acidified water, in an inverted plexiglass tank of 30-L capacity.

Start-Up Procedure and Biofilter Operation

Anaerobic digester sludge from a domestic waste-water treatment plant, screened with a 2-mm sieve to remove coarse particles, was used to seed the biofilter. The feed consisted of 2-EHA at 8200 mg/L, supplemented with NH₄CL and KH₂PO₄ to obtain a C:N:P ratio of 120:5:1. Since 2-EHA has a low solubility in water, the feed was prepared in the form of sodium 2-ethylhexanoate by adding sodium hydroxide. It was further supplemented with trace elements and thiamine hydrogen chloride as the growth factor.

After seeding, the biofilter was allowed to acclimatize gradually to the feed at 20 d HRT. When the biofilm was firmly established on the surfaces of the packing medium, the biofilter was operated in the mixed-flow mode for 425 d at HRTs of 15, 10, 8, 6, 3, 2, 1.5, 1.1, and 0.83 d, and allowing stable operation to be attained at each HRT. The effluent from the top of the biofilter was sampled three times a week, and analyzed for COD, TSS, VSS, pH, 2-EHA, and intermediate VFA concentrations. Biogas production rate was measured daily after equilibrating the gas to atmospheric pressure, while biogas quality was analyzed in terms of percentage of methane, carbon dioxide, and nitrogen.

Reseeding and acclimatization, after the mixed-flow biofilter experiment was terminated, were carried out relatively easily because of the acclimatized biomass retained from the previous operations. The biofilter was then operated in the plug-flow mode for 220 d at the same HRTs as the mixed-flow operation until it failed. The same analyses as described above were carried out.

The experiments were carried out at ambient temperature, which was between 28–30°C. During the operation, no pH adjustment was necessary, since the pH of the digester liquor remained between 6.5–8.0.

Tracer Experiments— Flow Dynamics in the Packed Bed

Ideally, tracer experiments should be carried out when the biofilter is in actual operation. However, a large extent of "noise" owing to the dissolved components in the liquor of an active biofilter would have interfered with the response signals of the tracer.

The tracer experiments were carried out with the clean biofilter filled with water, with the assumption that the effect of biofilm on flow pattern was insignificant. This assumption was based on the fact that the void volume of the clean biofilter was determined to be 20 L and that of the operational biofilter was 19 L, which indicated that the volume of interstitial space occupied by the biomass was small and could be neglected.

Tracer stimulus-response techniques described by Levenspiel (20) and Wakao and Kaguel (21) were used to obtain information on the residence time distribution (RTD) and flow patterns through the packed bed of the biofilter. Experiments were carried out with the biofilter operating at a feed rate equivalent to a HRT of 2 d with and without recycle.

Each tracer consisted of a pulse of 30 mL of sodium chloride at a concentration of 500 g/L, which was injected by means of a high-speed peristaltic pump at the bottom of the biofilter. Sodium chloride solution was used as the tracer, because it is inert, does not disturb the flow pattern in the biofilter, and can be easily detected. For each experiment, the tracer was injected only after steady-state conditions were reached inside the packed bed, as indicated by a constant flow through the bed. Response was detected as a time record of the total dissolved solids (TDS) leaving the top of the biofilter column by an off-line conductivity meter (LTH Electronics Ltd., Type PB5 with a Type CMC5/10/TIK electrode).

Analytical Methods

COD, TSS, and VSS of the biofilter effluent samples were determined in accordance with Standard Methods (22). 2-EHA and VFAs were determined with a Shimadzu model GC-14A gas chromatograph with a Chromosorb WAW 100/120 mesh, FFAP (15%) and H_3PO_4 (1%) column. Biogas quality was examined by a Varian model 3300 gas chromatograph with a 2-m Porapak Q 80/100 mesh column.

RESULTS AND DISCUSSION

Flow Dynamics in the Packed Bed

The flow patterns in a closed vessel, such as the biofilter, can be modeled by the one-parameter dispersion model, which correlates the mean residence time and the variance of the RTD curve by the following relationship:

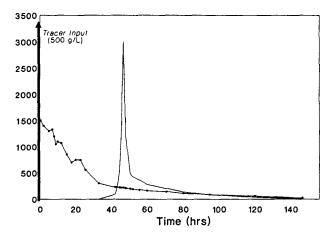


Fig. 2. RTD of the biofilter in different modes of operation. —■— With recycle-60 L/h. — Without recycle.

$$(S^2/t^2) = 2(D/UL) - 2(D/UL)^2 [1 - e^{-(UL/D)}]$$
 (1)

where, S^2 = variance of the RTD curve, h^2 , t = mean residence time of the RTD curve, h, D/UL = dispersion number, dimensionless, D = axial dispersion coefficient, m^2/h , U = interstitial fluid velocity, m/h, and L = length of biofilter column, m.

The dimensionless dispersion number (D/UL) is the parameter that measures the extent of axial dispersion and gives an indication of the flow pattern in the packed bed. It approaches zero for ideal plug flow and infinity for ideal mixed flow.

The mean residence time (*t*) locates the center of gravity of the RTD curve and is calculated by

$$t = \left[\sum \left(t_i C_i \Delta t_i \right) / \sum \left(C_i \Delta t_i \right) \right] \tag{2}$$

where, t_i = time after the tracer was introduced, h, C_i = concentration of sodium chloride in the sample taken from the biofilter at time t_i , mg/L, Δt_i = interval between successive samples, h, and Σ denotes the summation of the argument in the parentheses through each tracer experiment. The variance describes how the RTD curve spreads out in time and is given by:

$$S^{2} = \left[\sum \left(t_{i}^{2} C_{i} \Delta t_{i} \right) / \sum \left(C_{i} \Delta t_{i} \right) \right] - t^{2}$$
(3)

An ideal tracer input is a discontinuous pulse represented mathematically by the Dirac delta function, which is defined as a function of time with an infinite height, zero width, and when integrated gives an area of unity. The actual tracer input used in this experiment, however, was approximated by a tall, narrow square wave because the peristaltic pump used for injecting the tracer could not achieve a true instantaneous injection.

Figure 2 shows the RTD curves in response to the tracer in the biofilter with and without recycle, which are plotted in terms of mg/L of TDS vs

Table 1
Results from the Tracer Studies

Mode of operation	Mean residence time t, h	Variance S², h²	Dispersion number
With recycle at 60 L/h Without recycle	46.39	1373.46	0.65*
	62.59	486.92	0.06

^{*}A recycle rate of 300 L/h, which is more than adequate to create complete-mixed conditions in a packed bed (2), gave a dispersion number of 1.63, which was only 2.6 times higher than that when the recycle rate was at 60 L/h. Therefore, the recycle rate of 60 L/h can be considered to have achieved effective mixing in the packed bed of the biofilter.

Table 2 Values of Dispersion Number at Various Extends of Mixing*

Extend of mixing	Typical values of dispersion number
Ideal plug flow	0
Small amount of dispersion	0.002
Intermediate amount of dispersion	0.025
Large amount of dispersion	0.200
Ideal mixed flow	Approaches infinity

^{*}Based on the results published by Levenspiel (20).

time in hours. The response signal for the biofilter with recycle resembles the typical profile of an ideal mixed-flow system, which can be represented mathematically by an exponential decay function. The response to the tracer input was almost instantaneous with a short lag time of about 10 min (not visible with the resolution of Fig. 2). The response signal for the biofilter without recycle was a skewed peak that had a sharp, rapidly increasing positive slope and a slow decreasing tail. The lag time was about 46 h, which agreed very closely with the operating HRT of 2 d. This is a typical response configuration of a plug-flow system with moderate amounts of dispersion.

The mean residence time, variance, and dispersion number of the biofilter under different modes of operation, as calculated by Eqs. (1)–(3), are tabulated in Table 1. Table 2 summarizes the values of dispersion number, published by Levenspiel (20), for various extends of mixing as predicted by the dispersion model. The dispersion numer of 0.65 obtained for the biofilter with recycle (at a rate of 60 L/h) falls into the regime where there is a large extent of dispersion (D/UL>0.2). When the recycle rate was at 300 L/h, which is more than adequate to create complete-mixed conditions in a packed bed (2,19), the dispersion number of 1.63 was only 2.6 times higher than that when the recycle rate was at 60 L/h. Therefore, the recycle rate of 60 L/h can be considered to have achieved effective mixing in the packed bed of the biofilter. However, a series of tests with recycle rate that varies between 60–0 L/h has to be carried out before an optimum recycle rate just achieving effective mixing (D/UL=0.2) can be determined. The dispersion number of 0.06 obtained for the biofilter without recycle indicated that an intermediate amount of dispersion was present. This observed dispersion, which resulted in the deviation from the truly plugflow hydrodynamics, was attributed to diffusion and eddies generated when fluid flowed through the interstitial channels of the packed bed.

Biofilter Performances

The performances of the biofilter operated in the mixed- and plugflow modes are summarized in Table 3.

COD Removal

The biofilter, in both the mixed- and plug-flow modes, demonstrated similar performances in terms of COD removal at long HRTs ranging from 15-6 d. As the HRT was reduced to 3 d, the effects of the recycle stream in distributing and diluting the feed affected the performance of the biofilter. The COD removal of the mixed-flow biofilter was higher than that of the plug-flow biofilter. The difference between the two reactors' performances became more pronounced as the HRT was lowered. The COD removal rate of the mixed-flow biofilter reached an optimum of 335.6 g/d, with COD removal efficiency of 92.3%, at 1.1 d HRT and organic loading rate of 18.2 g COD/L/d. The COD removal rate of the plug-flow biofilter reached an optimum of 148.2 g/d, with COD removal efficiency of 74.1%, at 2 d HRT and organic loading rate of 10.0 g COD/L/d. These results show that the mixed-flow biofilter can be operated more efficiently than the plug-flow biofilter. However, the plug-flow mode is a more attractive option at long HRTs, between 15-6 d, because it can achieve COD removal efficiencies that are comparable to that attained by the mixed-flow biofilter while maintaining a lower cost of operation without the recycle stream. Failure of the mixed- and plug-flow biofilters occurred when the HRT was lowered to 0.83 and 1.5 d, respectively, and this was indicated by a drastic drop in their COD removal efficiencies.

These performances surpassed that reported by Sachs et al. (12) for a plug-flow biofilter treating a pharmaceutical waste water with a much lower organic strength (2000 mg/L). The reported COD removal was 70–80% at an HRT of 3.6 d and organic loading rate of 0.56 g COD/L/d.

Biogas Production

The biogas production rates increased with decreasing HRT. The highest rate of biogas production for the mixed-flow biofilter was 128.7 L/d (6.44 L/L biofilter vol/d) at HRT of 1.1 d and 42.6 L/d (2.13 L/L biofilter vol/d) at HRT of 2 d for the plug-flow biofilter.

Table 3 Mixed- and Plug-Flow Performance of the Biofilter

Biogas	OD removal Biogas
rod. rat L/d	efficiency, prod. rat % L/d
a	IFa FPb MFa
	97.6 7.1
	98.8 16.2
	97.8 16.6
	98.7 26.1
.3 42.1	98.1 92.3 56.3 42
	74.10 67.2
	11:
	13.3 106.7
.7e	
ь.	

^a Biofilter operated in mixed-flow mode.
^b Biofilter operated in plug-flow mode.
^c All concentrations were measured at the top of biofilter.
^d N.D.—not detectable.
^c Optimum performance.

The methane composition of the biogas recorded over the entire duration of this investigation was very stable (between 74.1–87.4%). These methane compositions are in agreement with the findings of Lo et al. (4) and Ng and Chin (5), but are substantially higher than those reported by other workers (6,11). The high methane content can be attributed to the dissolution of carbon dioxide in the liquor of the biofilter.

The methane yield of the mixed-flow biofilter was between 0.24–0.36 L/g COD removed at all the HRTs studied. These values were very close to the theoretical maximum of 0.35 L/g COD removed, indicating that a very high proportion of 2-EHA degraded in the biofilter was converted to biogas, and a much less proportion was being converted to biomass. This was advantageous for the operation of the biofilter, because the problem of biomass accumulation leading to clogging of the packed bed would be reduced. It is worth noting that, even when the mixed-flow biofilter was failing at 0.83 d HRT, the methane yield remained high at 0.32 L/g COD removed. A balanced population of acid formers and methanogens was still being maintained. Failure of the biofilter was attributed to sloughing of biomass and not to the high organic load. This consistency in methane yield was markedly different from the behavior of the mixed-flow biofilter described by Ng and Chin (5), with the methane yield increasing from 0.17 to 0.53 L/g COD removed as the HRT was reduced from 6.3 to 2.1 d.

The methane yield of the plug-flow biofilter was 0.19 L/g COD removed when the biofilter was failing at HRT of 1.5 d. This suggested that inhibition owing to the high organic loading rate was the cause of failure.

Acid Levels

2-EHA and VFA concentrations in the effluent of the mixed-flow bio-filter were very low at HRTs between 15–1.1 d. When the HRT was reduced to 0.83 d, 2-EHA concentration in the effluent increased to 4407 mg/L, which represented a 2-EHA removal efficiency of 46.3%. Between HRT 1.1 and 0.83 d, the highest levels of ethanoic and propanoic acid concentrations were 250 mg/L and 312 mg/L, respectively. However, these high levels of intermediate VFAs were not sustained; they reduced to an average total of 97 mg/L within the next few days. The pH of the filter liquor remained around neutrality. These results again suggested that failure of the mixed-flow biofilter was not because of inhibition of methanogenic activity, since the latter would have led to an accumulation of intermediate VFAs, lowering the pH of the filter liquor, and eventual souring of the biofilter.

2-EHA and VFA concentrations also remained low in the effluent of the plug-flow biofilter at HRTs between 15–6 d. At the HRT of 3 d, the intermediate VFAs started to accumulate to an average total concentration of 1058 mg/L. This indicated that the high loading rate started to inhibit methanogenic activity. When the HRT was reduced to 2 d, the acid formers were also inhibited as indicated by an increase in 2-EHA concentration to 3117 mg/L. 2-EHA remained largely undergraded when the HRT was re-

duced further to 1.5 d, and the concentration in the effluent was 7106 mg/L. This represented a 2-EHA removal efficiency of 13.3% and marked the point of failure for the plug-flow biofilter.

Biomass Production

The biomass wastage from the mixed-flow biofilter at HRTs between 15–3 d was low, averaging between 0.05–0.30 g/d, which is in agreement with the general characteristics of biofilters treating wastes with low solid contents (2,6,12). Much higher wastage, averaging between 1.30–2.15 g/d, was observed at shorter HRTs between 2–0.83 d. The high hydraulic loading rates at short HRTs, with the added effect of the recycle stream, resulted in a very high surface flow velocity (632 cm/h at 0.83 d HRT) as experienced by the biofilm on the surface of the packing medium. The luxuriant growth of biofilm on the packing medium decreased drastically at these short HRTs and had almost disappeared during operation at 0.83 d HRT. Therefore, the gradual wash-out of biomass owing to high hydraulic loading rates, or low HRTs, was proposed to be the cause of failure of the mixed-flow biofilter.

The biomass wastage of the plug-flow biofilter was very much higher than that of the mixed-flow biofilter at all the HRTs studied. This difference was most obvious for HRTs between 15–3 d, during which the biomass wastage varied from 0.60 to 3.58 g/d, which were between 10–24 times higher than that in the mixed-flow biofilter. It was proposed that a large proportion of biomass from the seed was retained in the plug-flow biofilter as suspended biomass in the interstices of the packed-bed and loosely held biofilm on the packing medium. This biomass was gradually being displaced as the HRT was reduced, accounting for the high biomass wastage observed. In the mixed-flow biofilter, on the other hand, the hydraulic flow of the recycle stream helped to establish a uniform and firmly attached biofilm on the support, and enabled the excess biomass from the seed to be displaced during the acclimatization period, prior to actual operation.

In the plug-flow biofilter, scum formation had caused clogging at the upper section of the packed bed. This reduced the effective volume of the biofilter and impeded the release of biogas into the head space. Occasional agitation was necessary to break the scum layer. This problem did not occur in the mixed-flow biofilter, since the scum was dispersed by the recycle stream.

REFERENCES

- 1. Barford, J. P., Cail, R. G., Callander, I. J., and Floyd, E. J. (1986), Biotech. Bioeng. 28, 1601.
- 2. Denac, M. and Dunn, J. (1988), Biotech. Bioeng. 32, 159.

- 3. Koepp, H. J., Schoberth, S. M., and Sahm, H. (1985), Conservation and Recycling 8(1/2), 211.
- 4. Lo, K. V., Whitehead, A. J., Liao, P. H., and Bulley, N. R. (1984), Agricultural Wastes 9, 175.
- 5. Ng, W. J. and Chin, K. K. (1987), Biol. Wastes 20, 157.
- 6. Russo, C., St Anna, G. L., and de Carvalho Pereira, S. E. (1985), Agricultural Wastes 14, 301.
- 7. Schwitzguebel, J. P. and Peringer, P. (1988), Proc. of Fifth Int. Symp. on Anaerobic Digestion, 579.
- 8. Britz, T. J., Meyer, L. C., and Botes, P. J. (1983), Biotech. Lett. 5(2), 113.
- 9. Gijzen, H. J., Schoenmakers, T. J. M., Caerteling, C. G. M., Vogels, G. D. (1988), *Biotech. Lett.* **10(1)**, 61.
- 10. Gijzen, H. J., Zwart, K. B., Verhagen, F. J. M., and Vogels, G. D. (1988), Biotech. Bioeng. 31, 418.
- 11. Mosey, F. E. (1978), J. Wat. Pollut. Control, (3), 370.
- 12. Sachs, E. F., Jennet, J. C., and Rand, M. C. (1982), J. Env. Eng. 108(EE2), 297.
- 13. Speece, R. E. (1983), Env. Sc. Tech. 17(9), 416A.
- 14. Stronach, S. M., Rudd, T., and Lester, J. N. (1986), *Biotech. Monographs*, vol. 2, Springer-Verlag, Berlin, Hiedelberg.
- 15. Mosey, F. E. (1983), Wat. Sc. Tech. 15, 209.
- 16. Henze, M. and Harremoes, P. (1983), Wat. Sc. Tech. 15, 1.
- 17. Stafford, D. A. (1982), Biomass 2, 43.
- 18. DeWalle, F. B. and Chian, E. S. K. (1976), Biotech. Bioeng. 18, 1275.
- 19. Thirumurthi, D. (1988), Wat. Research 22(4), 517.
- 20. Levenspiel, O. (1972), Chemical Reaction Engineering, John Wiley, pp. 253-325.
- 21. Wakao, N. and Kaguei, S. (1982), Heat and Mass Transfer in Packed Beds, Gordon and Breach, Science Publishers, New York.
- 22. APHA (1980), Standard Methods for the Examination of Waste and Wastewater, 15th ed., APHA, AWWA, WPCF, Washington, D.C.