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Journal of Hazardous Materials B96 (2003) 79–90
Journal of Hazardous Materials
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Biological treatment of mixed industrial wastewaters in a fluidised bed reactor

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Received 18 March 2002; received in revised form 18 June 2002; accepted 19 June 2002

Abstract

A study has been carried out on the operating parameters that influence the biodegradation of petroleum and brewery wastewaters, with a low-density biomass support. The biodegradation rate of a mixture of two wastes was compared with that of the separate wastes. A low aspect ratio reactor was employed, and this made it possible to operate at low superficial gas and liquid velocities. The gas distributor used created a fluid flow pattern similar to that of a draft tube, which enhanced axial mixing. At a particles loading of 12% (v/v), the optimum superficial gas velocity was 2.5 cm/s for the mixture. The interstice structure of the biomass-support particles, improved microbial attachment due to the resulting large surface area. There was a low biomass concentration when petroleum wastewater was treated alone, however, for a mixture of petroleum and brewery wastewaters, an increase in the concentration was observed. There was a higher gas hold up in the mixture than in the petroleum wastewater, but lower than in the brewery wastewater. An improved biodegradation was achieved when a mixture of brewery and petroleum wastewaters was treated, and this gave an indication that nutrient deficient wastes can be treated together with phosphate and nitrate rich food industry wastewaters.

Keywords: Fluidised bed reactors; Biological treatment; Petroleum; Brewery; Wastewater

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PII: S0304-3894(02)00166-8

Nomenclature

A, B, n	empirical constants
d_p	particle diameter (mm)
D_c	reactor diameter (m)
H	reactor static bed height (m)
H/D_c	aspect ratio
$K_L\mathrm{a}$	volumetric mass transfer coefficient (s^{-1})
U_L	superficial liquid velocity (cm/s)
U_g	superficial gas velocity (cm/s)
U_{mf}	minimum fluidisation velocity (cm/s)
TSS	total suspended solids (ppm)
V_L	liquid volume (m^3)
V_r	reactor volume (m^3)
V_s	support particle volume (m^3)
w_d	dry biomass concentration (g/m^3)

Greek letters

ε_g	gas hold up
ρ_L	density of the liquid (kg/m^3)
ρ_p	density of the support particles (kg/m^3)

Subscripts

C	column
d	dry
g	gas
L	liquid
mf	minimum fluidisation
p	particle

1. Introduction

The pursuit for a clean environment creates the need to develop industrial wastewater treatment methods with better performance efficiencies than the conventional methods of stabilisation ponds and activated sludge. The choice of either biological or chemical methods for treatment of industrial wastewaters depends on the composition of the wastes. Industrial wastes from food industries typically contain a significant amount of biodegradable compounds. These compounds contain phosphates and nitrates, which need to be removed in order to control eutrophication, which is a consequence of their discharge into the water bodies.

Wastes from mine drainage, on the other hand, contain toxic chemicals including heavy metals, which can be removed by precipitation in a fluidised bed [1,2]. Aromatic hydrocarbon compounds found in wastewaters such as those of petroleum refinery, are not easily biodegradable due to the presence of the toxic compounds of the phenolic group. Such recalcitrant compounds can be removed by an adsorption or a coagulation method [3]. The latter methods are expensive as compared to the biological methods. Thus, biodegradation, though less rapid in degradation of wastes, is a much widely applied method due to low operating costs.

Application of biological methods such as fluidised bed bioreactors has generated a lot of interest in the recent past. The major advantage of fluidised bed bioreactor over other biodegradation systems is a higher biomass concentration, and a higher mass transfer, resulting in a higher rate of biodegradation [4]. The application of the fluidised bed bioreactor makes it possible to achieve phase homogeneity and larger solid–liquid contact area. These characteristics of a fluidised bed bioreactor enable an operation at a high volumetric loading, a fact that makes a fluidised bed an appropriate choice for treatment of toxic effluents [5].

The homogeneity of the fluid temperature and the concentration profile depend on the stirring effect caused by the gas flow through the bed. Since the minimum fluidisation velocity (U_{mf}) marks the boundary between fixed bed and fluidised bed reactors, it is a very important hydrodynamic parameter. The minimum fluidisation velocity can also give an insight into the power requirement for fluidisation operation. A high minimum fluidisation velocity will invariably result in a high fluidisation velocity, and this leads to an increase in power consumption. Fluidisation should, therefore, be kept as low as possible but high enough to enhance mass transfer by increasing gas hold up.

The gas fluidisation velocity (U_{g}) and gas hold up (ε_{g}) are correlated by [6–8]

$$\varepsilon_{\mathrm{g}} = AU_{\mathrm{g}}^{n} \tag{1}$$

where A and n are empirical constants. It has been reported by Lee et al. [9] that there is a simple linear correlation between gas hold up and mass transfer coefficient ($K_{\mathrm{L}}\mathrm{a}$)

$$K_{\mathrm{L}}\mathrm{a} = 1.53\varepsilon_{\mathrm{g}} \tag{2}$$

From Eqs. (1) and (2), the correlation between gas velocity and mass transfer is given by

$$K_{\mathrm{L}}\mathrm{a} = BU_{\mathrm{g}}^{n} \tag{3}$$

where the values of the empirical constants, B and n, depend on the type of system (gas and liquid) used and the operating conditions. The value of 'n' tends to unity for most homogeneous phase mixtures and varies with the flow regime in a given system, and a value of 0.9 has been reported by Koichi et al. [10], at a very low superficial gas velocity range (0.0278–0.83 cm/s).

Treatment of mixed wastewaters requires an understanding of both chemical and physical characteristics, as well as the resulting characteristics of the mixture, in order to identify the complementary factors of the respective wastes. A study of the effect of hydrodynamics on biodegradation of brewery has been reported separately [11]. Having studied the hydrodynamic factors that are important in the design of a fluidised bed reactor, the main objective of this study is to evaluate the possibility of employing a fluidised bed for treating mixed industrial wastewaters.

2. Materials and methods

The reactor (Fig. 1) was made of Duran glass with the upper part, disengagement cylinder, made of stainless steel. A distributor with 9.8% open area [12] was used, with more orifice at the centre, in order to simulate draft tube flow pattern. The diameter of the reactor was 16 cm, and the ratio of static bed height (H) to the reactor diameter (D_c), referred to as aspect ratio, was 10.

Preliminary experiments comprising chemical analysis and investigation of the hydrodynamics preceded biodegradation experiments. Hydrodynamic experiments were carried out, to quantify parameters such as fluidisation velocity, gas hold, minimum fluidisation velocity and particle loading. This was done with tap water as well as with industrial wastewaters at ambient conditions, in a 170 l reactor. Low-density (960 kg/m^3) polyethylene biomass support particles were employed, and these particles had a surface area to mass ratio of 2.13 m^2/kg. The particles were large ($d_p = 10$ mm) enough to enable determination of fluidisation velocity by visual observation [4]. Tap water was used as a reference system, and the hydrodynamic parameters of the wastewaters were compared with those of the tap water. A pre-calibrated rotameter was used to measure the gas flow rate.

Microbial concentration was measured with a spectrophotometer (Spectronic 21D-Milton Roy), where turbidity measurements were translated into concentrations [13]. High performance liquid chromatograph (HPLC) was used to measure hydrocarbon compounds. The chemical oxygen demand (COD) was determined by the redox method using hydrocheck (HC 6016). Results of these analyses are shown in Tables 1 and 2.

Samples from the industry had a COD range of 28,000–38,000 ppm and 30,000–60,000 ppm for the brewery and petroleum wastewater, respectively. The initial prepara-

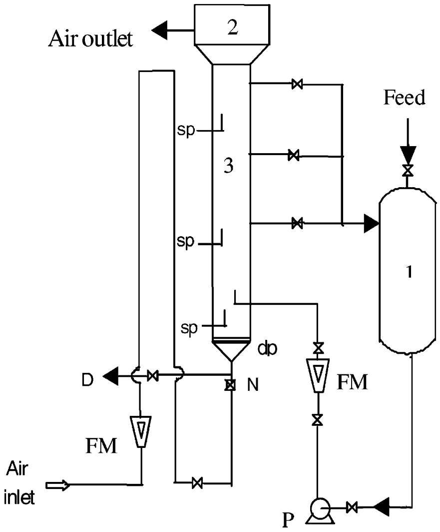

Fig. 1. Schematic diagram of the apparatus: 1, settling tank; 2, disengagement cylinder; 3, reactor column; P, pump; D, drainage pipe; dp, distributor plate; sp, sampling point; and FM, flowmeter.

Table 1
Composition of brewery wastewater

Parameter	Mean value
PO_{4-}-P (ppm)	70
COD (ppm)	33000
BOD_5 (ppm)	1000
TSS (ppm)	4800
pH	6.8

Table 2
Composition of petroleum wastewater

Parameter	Mean concentration (ppm)
Phenol	600
2,4-Dimethyl phenol	720
TSS	1800
Benzene	500
Toluene	95
1-Xylene	15
BOD	15600
COD	45000

tion of the wastes involved removal of coarse solid particles, that were collected with the wastewater, and adjusting the COD and BOD by dilution with tap water. Dilution was done to obtain a constant initial feed concentration, and the solids were removed to avoid damage to the pump used. Brewery wastewater contained more total suspended solids (TSS) that the petroleum wastewater. Seeding for a mixed population culture was obtained from a petroleum waste separation pond at a local refinery. Biodegradation was carried out batch wise in the reactor, and samples were taken at a time interval of 10% of the hydraulic retention time (HRT) of 24 h.

3. Results and discussion

Tap-water-particle mixture was used as a reference system, and the hydrodynamic parameters of the wastewaters were compared with those of the reference system. Since the reactor aspect ratio was low, fluidisation was achieved at a gas flow rate, and the COD reduction was influenced by gas flow rate. Liquid flow rate had a negligible effect on both the bed fluidisation and on the COD reduction.

4. Hydrodynamics

The onset of fluidisation of the water-particles system occurred when the gas superficial velocity was 0.28 cm/s, and this was the minimum fluidisation velocity (U_{mf}) for tap water.

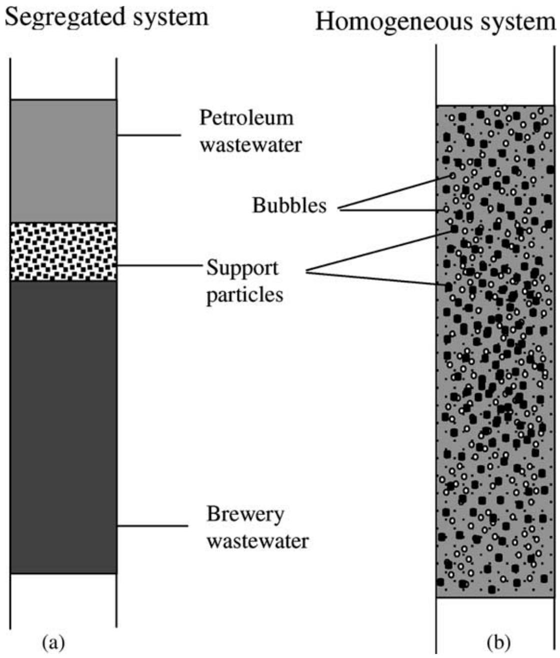

Fig. 2. Mixture of brewery and petroleum wastewaters (a) segregated and (b) homogeneous mixtures.

The large bubbles moved upwards while the small ones moved downwards due to the induced draft tube like flow pattern. A similar flow pattern could not be easily visualised in highly concentrated petroleum wastewater samples due to the dark colour of the waste. Visualisation of the flow pattern was only possible after addition of tap water or brewery wastewater.

There were two distinct layers of the liquids with the particles sand-witched between the petroleum and brewery wastewaters (Fig. 2). The particles were denser than the petroleum wastewater but lighter than tap water and the brewery wastewater. The phases could not mix until a gas superficial velocity of 0.22 cm/s caused sufficient bed turbulence. The minimum fluidisation velocity achieved with the mixture was lower than that achieved in the tap water system.

Solid hold up was taken as the ratio of the volume of the particles to the volume of the mixture in the reactor (V_s/V_r), and this was in the range of 3–13%. The particles being lighter than water, initially floated on the surface of the water, and fluidisation could not be achieved with the flow of water alone. Fig. 3 shows that low solid hold up (less than 5%) resulted in high U_{mf}, which was due to the influence of static bed height. For solid hold up exceeding 10%, the influence of particle loading predominated. The high U_{mf} was as a result of a tendency toward fixed bed, and this is consistent with results reported earlier, [11] where same reactor configuration as in the present work was used. A solid hold up of 12% was, therefore, adopted for the investigation of the gas hold up and further experimental investigations.

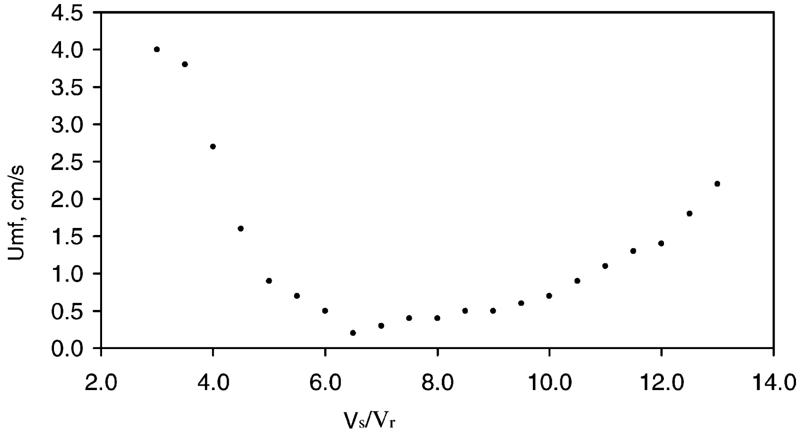

Fig. 3. Variation of particle hold up with U_{mf} of the mixture.

The particles employed in this work had a high surface area to mass ratio (2.13 m^2/kg), and this is a factor that is very important, not only for the attachment of the micro-organisms but also for fluidisation power economy. High surface area to mass ratio enables an operation with a low particle loading, leading to a low power requirement as a result of the low gas flow rate required to fluidise a bed with low solid hold up.

The experimental data points shown in Fig. 4 were fitted to the correlation equation (Eq. (1)) and a near linear relation between the increase in gas hold up and the gas superficial velocity resulted. The lowest gas hold up was observed in the petroleum wastewater and the highest in the brewery wastewater, with the hold ups in tap water and in the mixture being in between the two. The high gas hold up in brewery wastewater was due to

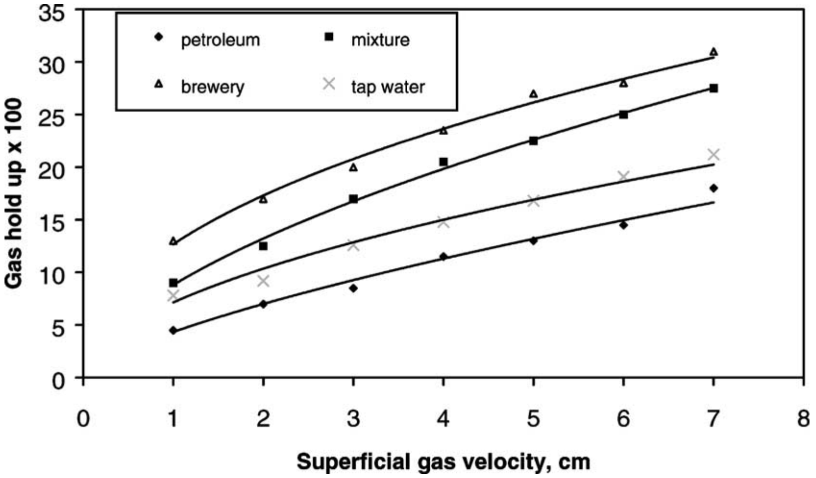

Fig. 4. Variation of gas hold up with gas velocity.

Table 3
Correlation equation for gas hold up [4]

U_g (cm/s)	ε_g	Correlation	References
20–800	0.2–0.9	$\varepsilon_g = 0.417U_g^{0.44}$	[7]
20–800	0.2–0.9	$\varepsilon_g = 0.628U_g^{0.237}$	[8]
1–8	0.05–0.3	$\varepsilon_g = 0.71U_g^{0.535}$	Present work
0.1–1.8	0.003–0.045	$\varepsilon_g = 1.45U^{0.8}$	[16]

the low viscosity (1.1 mPa), the presence of surface-active alcohols and proteineous compounds. Similar observation has been reported [14,15]. The high viscosity (4.3 mPa) of the petroleum wastewater resulted in large fast moving and stable bubbles with low residence time, consequently, leading to low phase hold up. Only the small bubbles could be dragged by the downward flow of fluid adjacent to the walls, and this resulted in high residence time.

Gas hold up correlations from literature for different ranges of gas flow rates are compared with the present results in Table 3. The values of gas hold up reported here are lower than those reported by Kito et al. [7] and Vunjak-Novakovic et al. [8], where the values of n were 0.44 and 0.237 as compared to the n value of 0.535 for the present work. This can be explained by the fact that the range of gas velocity used here (1–8 cm/s), was low compared to the range (20–800 cm/s) reported in the fore mentioned literature. However, Chisti et al. [15] operated at a much lower gas velocity (0.1–1.8 cm/s) than the present work, and obtained a larger value of n (0.80). Fluidisation was possible with such a low gas flow rate due to the low reactor aspect ratio and low particle density employed. It is an established fact that at low gas flow rates, there is almost a linear relation between ε_g and U_g. It is, therefore, expected that an operation at low gas flow rates should result in a correlation with a higher value of ‘n’ (Eq. (1)), and the present work confirms this. Such a correlation may suffice for engineering purposes, however, a correlation based on known physical parameters can generally be more predictive [17].

5. COD reduction

In separate treatment of brewery wastewater, there was an initial foam formation and an increase in temperature (from 25 to 35 °C). Up to 74% COD reduction were observed after 24 h with the bulk fluid dry biomass concentration (w_d) of 165 g/m^3. Conversely, a temperature drop (from 25 to 20 °C) occurred in the system of petroleum wastewater and a COD reduction of 36% over the same period, for w_d of 78 g/m^3. The percentage COD reduction is comparable to the 35.4% COD reduction reported by Holubar et al. [18]. The low reduction could be attributed to the presence of poly nuclear hydrocarbons (PAH) and low gas hold up in the petroleum wastewater.

The mixing ratio of about 1:2, of the petroleum wastewater to that of brewery provided a more homogeneous mixture at a low fluidisation velocity. Up to 64% COD reduction was observed with the mixture of the two wastewaters, with relatively stable temperature of about 26.5 °C, and no foaming occurred. Initially, emulsions of petroleum wastewater occurred in the mixture. These disappeared after 20% of the residence time, for w_d of 158 g/m^3.

Bloor and Anderson [19] obtained a high reduction (97%), which can be attributed to high nutrient (COD:P:N = 100:5:1) used. In the present work, nutrients were added (to obtain a COD:P:N ratio of 100:1:0.4 [20]) only for comparison purposes, to check the dependence of COD reduction on the nutrients. A reduction of 90% in the mixture was achieved (after the HRT of 24 h), showing that a higher reduction can be obtained with nitrates and phosphates enriched wastes. Similarly, this shows that the 64% reduction was achieved at a shorter HRT when nutrients were added. The COD/BOD ratios of 1.99 and 8.1 for the brewery wastewater and petroleum wastewater, respectively, indicate that the brewery wastewater is more biodegradable than the petroleum wastewater. An increase in the amount of the brewery wastewater would increase the biodegradability of the mixture, however, it is necessary that the amount of the petroleum be kept high enough in order to obtain a significant reduction for the latter. The relative volumes of the respective wastewaters depend on the physical and chemical characteristics of the wastes.

Variation of biodegradation with superficial gas velocity shows a similar trend of the biodegradation process for the brewery and petroleum wastewaters (Fig. 5). The fact that the brewery wastewater was more biodegraded than the mixture and the petroleum wastewater shows the dependence of biodegradation on the nutrients. At a higher gas flow rate there was a higher decrease in COD reduction for the petroleum wastewater as compared to the brewery wastewater. This can be attributed to the increase in bubble diameter with increasing gas flow rate. The high viscosity of the petroleum wastewater enhanced the stability of large bubbles, leading to a decrease in mass transfer. The optimum superficial gas velocity for both wastes, treated separately, was 2.7 cm/s as compared to 2.5 cm/s for the mixture.

Initial concentrations of the mixture and the petroleum wastewaters were adjusted to 38,000 ppm, which was the maximum concentration of brewery wastewater. Biodegradation rates of the mixed, petroleum and brewery waste waters were compared in Fig. 6, and for all these wastes, there was a slow COD reduction in the first 4 h, which represents microbial growth period. At this stage, the population of micro-organisms was still too low

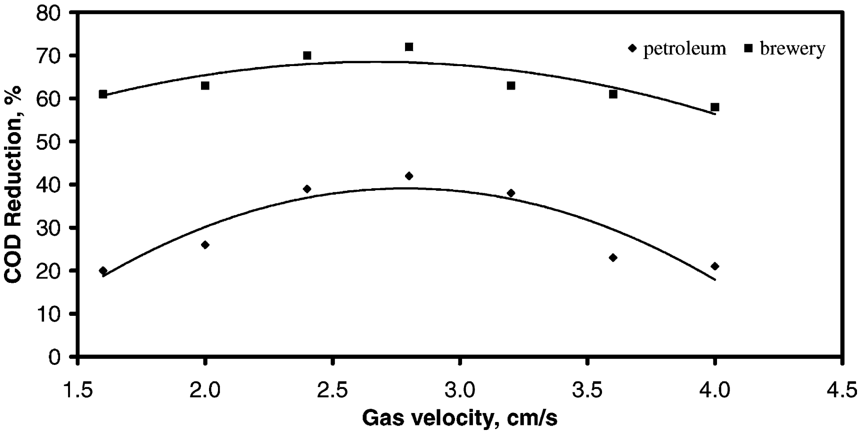

Fig. 5. Variation of biodegradation with gas velocity.

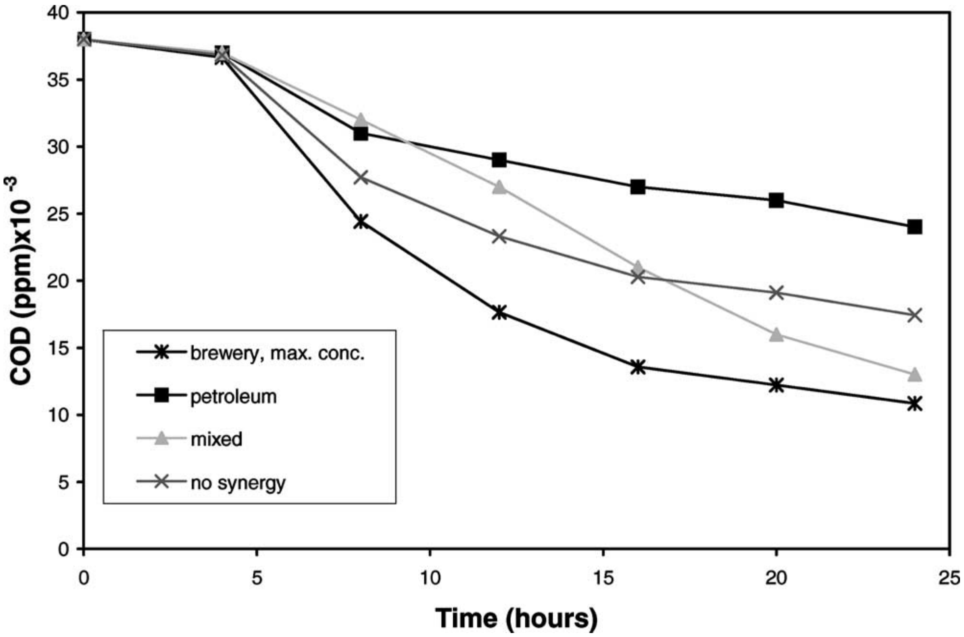

Fig. 6. Degredation of COD in brewery, petroleum and mixed wastewaters.

to cause a significant COD reduction, and an increased reduction rate was observed after this period. The increased population of micro-organisms caused the rapid reduction for about 20 h, after which the rate slowed down. The last slow step was due to the exhaustion of the nutrients. This can also be attributed to the formation of inert COD, as a result of the metabolic activity of the micro organisms, as has been reported [21]. Fig. 6 shows that for equal initial concentration of the petroleum wastewater and the mixture, a higher COD reduction was obtained with the mixture. If the action of the micro-organisms was additive, the theoretical curve (no synergy) in Fig. 6 could have been obtained for the mixture. The biodegradation rate for the mixture was lower than that of the separate wastes, however, it was more steady for a longer period of time (about 80% of the HRT). This could be as a result of compounded factors; both hydrodynamic and biochemical in nature. The theoretical curve predicts a reduction trend much similar to that of the brewery wastewater. This was due to the higher volume ratio of the brewery wastewater used. The theoretical curve accounts for the interaction of the factors that influence biodegradation in a simple statistical manner. However, the change in the microbial environment and hence the performance of the micro-organisms cannot be predicted by such a statistical comparison. Biodegradation of such waste is system specific, and knowledge of the hydrodynamics is necessary for reactor design. However, additional information on the nature and the performance of the micro-organisms is also required to predict the biodegradability more precisely. Further studies on the nature and the activity of the micro-organisms can provide an explanation to the observed trend.

6. Conclusion

As indicated with the high COD/BOD ratio, petroleum wastewater contains a considerable amount of recalcitrant materials that may result in high treatment cost. Waste from food products can enrich the nutrient deficient petroleum wastewater, resulting in shorter HRT for the mixture. There was a more homogeneous phase mixing and high gas hold up for the mixture, though, the low percentage COD reduction (without addition of nutrients) indicated that the nutrients in the brewery wastewater were not sufficient for the high concentrated petroleum wastewater used. Operation at a low gas fluidisation velocity, due to the use of low density particles and low aspect ratio, and the attainment of up to 64% COD reduction without the use of nutrients, suggest that a system of this nature can be economical to run.

Acknowledgements

This work was supported by the Faculty of Engineering (University of Dar es Salaam) and the German Academic Exchange Service (DAAD). Dr. Harro von Blotnittz's analysis of results is highly acknowledged.

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