



Occurrence of anionic surfactants in treated sewage: Risk assessment to aquatic environment

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ABSTRACT

A comparative evaluation of occurrence of and risk to aquatic environment due to anionic surfactants (AS) in treated effluents from three main treatment processes, i.e. activated sludge process (ASP), oxidation pond (OP), and upflow anaerobic sludge blanket reactor (UASBR) is presented. UASBR effluents contained substantial concentrations of AS (4.25–5.91 mg/L as average AS removal was not found to exceed 18%). Post-treatment of UASBR effluent using 1–1.6 days detention, anaerobic polishing ponds (PP) was also found quite ineffective. In UASBR–PP combine, AS reduced only up to 30%. Effluents from OP based sewage treatment plants (STPs) also contained significant concentrations of AS. On the contrary, effluent AS or linear alkylbenzene sulfonate (LAS) concentrations recorded in ASP effluents were quite low (less than 0.2 mg/L). Unlike UASBR, LAS or AS removals greater than 99% are achieved in ASP. Treated effluents from UASBR and OP based STPs when discharged to aquatic ecosystems are likely to cause substantial risk to aquatic environment due to the presence of AS while effluents from ASP are not supposed to pose risk. Need to find an effective aerobic post-treatment unit to UASBR for desired removal of AS is emphasized.

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1. Introduction

Anionic surfactants (AS) in sewage are found as a result of the use of consumer products like detergents, cleaning and dish washing agents, and personal care products. The largest group of AS is linear alkylbenzene sulfonate (LAS). AS may enter the aquatic environment when raw or partially treated sewage is discharged. Range of LAS concentration in raw sewage of 3–21 mg/L has been reported by several investigators [1,2]. The removal efficiency of surfactants depends on the method of treatment employed. Aerobic methods like activated sludge process (ASP), and oxidation pond (OP) and anaerobic method like upflow anaerobic sludge blanket reactor (UASBR) are used widely for sewage treatment.

The removal of LAS in ASP based sewage treatment plants (STPs) includes sorption to the sludge particles and biodegradation with a total removal of 95–99% [3–12]. It is widely accepted that LAS are readily degradable under aerobic conditions. Under aerobic conditions, total mineralization of LAS proceeds through degradation of the alkyl group by means of ω -oxidation, β -oxidation, desulfonation, and finally degradation of the phenyl ring [13].

Biodegradation of AS under anaerobic conditions has historically been believed not to occur as known mechanisms that precede

the aerobic mineralization require molecular oxygen [14]. However, recently LAS has been reported to degrade anaerobically under certain conditions [15–17]. The limited information indicates that (a) LAS can be used as a source of sulfur by anaerobic bacteria under sulfur limited conditions [18], and (b) benzenesulfonic acid and benzaldehyde may be produced as metabolites during anaerobic LAS degradation under thermophilic range [16]. Lobner et al. [19] observed that anaerobic reactors operated under the same conditions sometimes exhibited very different degradation capabilities. They found 40–80% removal of LAS in bench-scale UASB reactors under mesophilic and thermophilic conditions. Sanz et al. [17] found that LAS degraded more in a UASB reactor without co-substrate than a UASB reactor where it was used with a co-substrate. It has been suggested that some microorganisms take AS when they have no other option.

Detergents, which contain surfactants, can seriously damage the environment. In India, per capita consumption of detergents was projected to rise to over 4 kg per annum by 2005 [20]. The surfactant toxicity is primarily a function of the ability of the surfactant to adsorb and penetrate the cell membrane of aquatic organisms [21,22]. It is also reported that LAS concentration from 0.02 to 1.0 mg/L can damage fish gills, cause excess mucus secretion, decrease respiration in the common goby, cause reduced settling rate, and damage swimming patterns in blue mussel larva. Surfactants are also responsible for causing foam in rivers and effluents of treatment plants and reduction of water quality. A review by Venhuis and Mehrvar [22] regarding the acute effects of LAS on

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freshwater plankton and organisms (including bacteria to crustaceans) under field conditions revealed that LAS has a negative impact on the survival of heterotrophic nanoflagellates and ciliates at very low concentrations. Fairchild et al. [23] has also found that LAS concentration of 0.36 mg/L had no effect on biological population. Schroder [24] determined LAS concentrations under realistic worst-case conditions (i.e. low dilution rates) in sections of Rur river affected by the discharge of ASP effluent. At all the sections studied, when predicted environmental concentrations (PEC) were compared with predicted no effect concentrations (PNEC), values of risk quotient (RQ) were found below 1. Elimination of LAS in river water has been credited to biodegradation under aerobic conditions [25,26]. A risk assessment study by Schroder [24], Takada et al. [25], Rapaport et al. [28], and Temara et al. [29] showed that LAS was environmentally safe due to its high removal of over 99% in activated sludge process.

Recently, 16 full-scale UASBR based STPs with a total installed capacity of 598 ML/d have been constructed in northern part of India in towns situated along river Yamuna and its tributary Hindon. However, in spite of the full-scale application of UASBR since over fifteen years, real-time data on removal or biodegradation of AS in an actual UASBR based STP is not available in literature. Whatever little work has been done [15–19] is based on laboratory or pilot scale research and reported results are varying in nature. Removal in oxidation ponds is also not reported. This paper presents a comparative evaluation of occurrence of AS in treated effluents from three main processes, i.e. ASP, OP, and UASBR and the assessment of risk it may pose to aquatic environment. More number of UASBR based STPs were selected as removal of AS has not been reported in full-scale UASBRs.

2. Material and methods

Eight, UASBR, OP, and ASP based STPs located in Haridwar (29°58'N, 78°13'E), Saharanpur (29°58'N, 77°23'E), Muzaffarnagar (29°28'N, 77°44'E), Ghaziabad (28°40'N, 77°28'E), and Noida (28°20'N, 77°30'E) were selected for the study (Fig. 1). Their installed capacities vary from 9 to 70 ML/d. Some relevant details are included only for UASBR based STPs as ASP and OP are in use for quite some time.

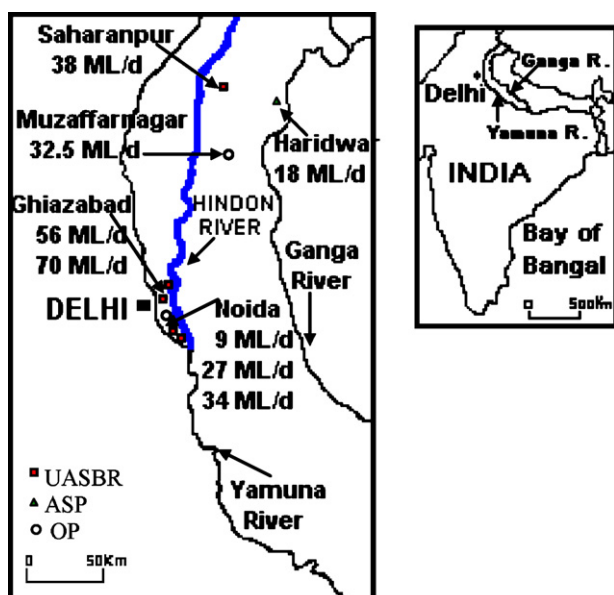


Fig. 1. Locations of investigated STPs with their treatment capacities.

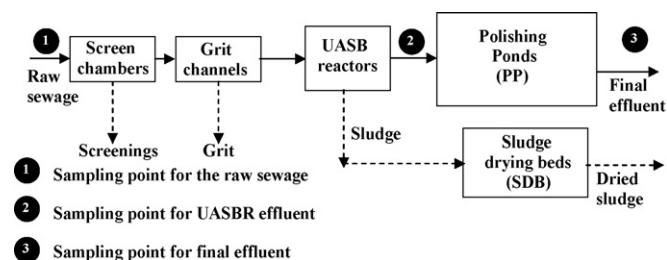


Fig. 2. Typical flow diagram of UASBR based STPs studied.

2.1. UASBR based STPs

A general schematic flow diagram of the combined UASBR–PP (polishing pond) system is shown in Fig. 2. Main characteristics are summarized in Table 1. Same sequence is followed at all UASBR based STPs. Study was carried over a period of 21 months (August 2004–April 2006) covering different seasons. The combined (UASBR–PP) systems were designed to handle 200 mg/L of influent biochemical oxygen demand (BOD, 5 days; 20°C), and 400 mg/L of influent suspended solids (SS) for meeting the required Indian standards of 30 mg/L of BOD and 100 mg/L of SS in the final effluent. Sewage after preliminary treatment (screening and grit removal) is uniformly distributed at the bottom of UASB reactors. The UASBR effluents are discharged to 1–1.6 days detention polishing ponds for tertiary treatment. Finally the effluents are discharged to nearby water bodies.

2.2. Oxidation ponds based STPs

Two OP based STPs of installed capacities of 32.5 and 9 ML/d located at Muzaffarnagar and Noida, respectively, were selected for the study. Both the STPs have same sequence of units, i.e. screen chambers–grit channels–primary OPs and secondary OPs. Wastewater samples (raw and treated sewage) were collected over a period of 10 months (April 2005–January 2006). Treated sewage is used for irrigation by nearby farmers. Whenever not required by farmers, it is discharged in a stream.

2.3. Activated sludge process based STP

One conventional activated sludge process based STP of 18 ML/d capacity situated at Haridwar was selected for the study. Samples (raw and treated sewage) were collected between February 2005 and March 2005.

2.4. Analysis

At all the STPs considered in the present work, sewage reaches STPs after multistage pumping. It is primarily because of flat topography of the cities and presence of number of water channels. At every stage, sewage is detained for a short time and gets mixed up in the sump. It is finally collected at the main pumping station (MPS) just ahead of STP. From MPS, it is pumped round the clock more or less at a uniform rate. It flows through the STPs by gravity. Prior to August 2004, the 2-hourly samples were composited at the plants (based on 2-hourly average flow) to prepare a 24-h flow-weighted composite sample. Composite samples were analyzed along with 2-hourly grab samples. This exercise was repeated a number of times at every STP. Results are not reported in this paper. Distinct diurnal variations in characteristics were not observed. It is presumably due to a general leveling effect during collection system (due to multistage pumping), and treatment (due to retention times in reactors). Based on this, it was decided to collect only grab samples during the present study.

Table 1
Technical characteristics of investigated UASBR based STPs

Parameters					
Installed capacity (ML/d)	27	34	38	56	70
Locations	Noida	Noida	Saharanpur	Ghaziabad	Ghaziabad
Operating capacity (ML/d)	24.7	32.1	30.4	42.3	60.3
Start of operation	April 2000	October 2001	March 2000	July 2002	July 2002
Design parameters					
COD (mg/L)	450	450	600	450	450
BOD (mg/L) (5 d, 20 °C)	200	200	200	200	200
SS (mg/L)	400	400	400	400	400
Sewage temperature (°C)	15	15	15	15	15
UASB reactors					
Numbers	3	4	4	4	4
Dimensions, $L \times W \times D$ (m ³) (each)	24 × 28 × 6.10	24 × 24 × 6.25	28 × 24 × 6.05	32 × 32 × 6.10	32 × 40 × 6.38
Effective depth (m)	5.55	5.90	5.55	5.60	5.88
Effective volume of reactors (m ³)	≈11,200	≈13,600	≈15,000	≈23,000	≈30,000
HRT (at average flow) (h)	9.9	9.6	9.4	9.8	10.3
Polishing ponds					
Numbers	2	2	2	2	2
Surface area, $L \times W$ (m ²) (each)	110 × 120	237.4 × 55.1	12700	180 × 120	190 × 144
Effective depth (m)	1.6	1.3	1.5	2.0	1.75
Total volume of ponds (m ³)	42,000	34,000	38,000	86,000	96,000
HRT (at average flow) (d)	1.6	1	1	1.5	1.4

AS were measured in samples of sewage as methylene blue active substances (MBAS) as prescribed in Standard Methods [30]. LAS (Hach, USA) was taken as a reference. AS in non-filterable residues from sewage samples were extracted by soxhlet extraction technique using methanol [31] and then analyzed using MBAS method. All AS concentrations are reported in this paper as "mg/L (calculated as LAS, mol. wt., 318)". Other conventional pollutional parameters were also analyzed as per Standard Methods [30]. Samples for biochemical oxygen demand (BOD) determinations were incubated for 3 days at 27 °C. Dissolve oxygen (DO) was measured by using a DO meter (Senso Direct OX 24, Aqualytic, Germany). A spectrophotometer (DR/4000, Hach, USA,) was used for colorimetric measurements.

3. Results and discussion

3.1. UASBR based STPs

Twenty-one months data was used to find range, mean, and standard deviations of different parameters for each STP. For the discussion in present paper, along with AS, results of BOD also have been considered. Wherever, trend was same, result of all the five UASBR based STPs have been presented together. Average composition of raw sewage at five STPs is given in Table 2. It represents a typical Indian sewage. Wide variations in influent characteristics were noticed. Over the period of twenty one months (August 2004–April 2006), sewage temperature ranged between

Table 2
Average composition of the raw sewage (August 2004 to April 2006) received at five UASBR based STPs studied

Parameters	Range	(Mean ± S.D.)
Sewage temperature (°C)	12.0–36.6	(25 ± 5.20)
pH	6.90–7.90	(7.37 ± 0.21)
Suspended solids (mg/L)	196–510	(337 ± 71.00)
Volatile suspended solids (mg/L)	101–301	(191 ± 50.00)
Total BOD (mg/L)	109–272	(168 ± 29.50)
Soluble BOD (mg/L)	51–197	(83 ± 19.50)
Total COD (mg/L)	162–683	(398 ± 120.85)
Soluble COD (mg/L)	102–381	(184 ± 55.68)
Dissolved oxygen (mg/L)	0	0
Filterable AS (mg/L)	1.25–6.93	(3.52 ± 0.79)
Particulate AS (mg/L)	0.11–4.42	(1.93 ± 0.81)

12 and 36.6 °C. COD varied from 162 to 683 mg/L, BOD from 109 to 272 mg/L, and SS from 196 to 510 mg/L. AS ranged from 2.18 to 9.82 mg/L. Filterable fraction of AS ranged from 1.25 to 6.93 mg/L with a mean concentration of 3.52 mg/L while particulate fraction varied from 0.11 to 4.42 mg/L (mean 1.93 mg/L). Methylene blue active substances appear to be very insignificant part of total organic mass in all the wastewater samples at different STPs. On an average, filterable organics were almost equal to particulate form of organics (measured as BOD) except at 70 ML/d STP at Ghaziabad where filterable BOD was only around 40% of total BOD (Fig. 4). On the other hand, AS were observed significantly more in filterable form than particular form (Fig. 3; Table 2). At 38 ML/d STP at Saharanpur, on an average filterable AS were found to be even more than double compared to particulate fraction.

3.1.1. AS removal in UASB reactors

Similar to raw sewage, wide variations in characteristics of secondary or UASBR effluents were also noticed (Figs. 3 and 4: IV, V and VI bars for each STP). Average total BOD in UASBR effluent ranged from 54 to 75 mg/L, accounting to average removal of 56–68%. Total BOD removal was quite comparable with 72% at STP at Kanpur [27], and 63% at STP at Mirzapur [32], which served as the models for constructing these STPs. Overall mean AS removal ≈11% did not match with mean BOD removal of ≈63% in these UASBRs. On an average for five STPs, UASBR effluent contained 4.25 to 5.91 mg/L AS. Gasi et al. [33] also found that UASBR effluent (120 m³ cylindrical UASBR, Brazil) is rich in AS concentration. They found it to have 4.63–5.30 mg/L AS (as MBAS). UASB reactors contain very large amount of SS (≈92000 mg/L) which provide large surface area to filterable/non-filterable AS to adhere to. In a UASBR, biosolids are retained for 30–50 days (i.e. solids retention time, SRT) while hydraulic retention time (HRT) is only between 1/3 and 1/2 of a day. Depending on the operating conditions and process stability, AS are released due to desorption or solubilization from sludge bed to the over flowing wastewater [34]. Similar mechanism was also described by Cowan et al. [35] for ASP based STPs. They stressed that, the total amount of LAS (i.e. dissolved plus sorbed) is available for biodegradation and the time for biodegradation is equal to the hydraulic residence time (HRT) as in ASP, HRT ≈ SRT. On the contrary in a UASBR, SRT ≫ HRT resulting in solubilization/hydrolysis of AS. This fact is very well reflected in Fig. 3 (UASBR effluents, V

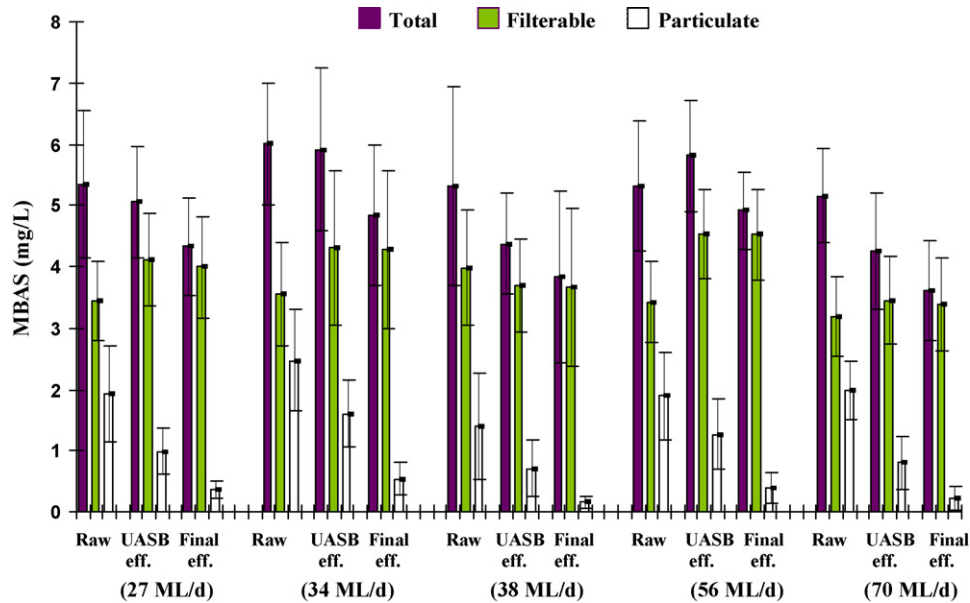


Fig. 3. UASBR based STPs: average MBAS in raw sewage, UASBR effluent, and in final effluent.

bar for each STP). The filterable fraction of AS in secondary effluent is more than that in raw sewage except at 38 ML/d STP. At 56 ML/d STP even total AS concentration in secondary effluent was consistently found to be more than that in raw sewage. The reasons for increase in total AS after UASBR at 56 ML/d plant are not clearly known. Possibility of the production of bio-surfactants [36,37] or extracellular polymers (ECP) [38,39] in UASBRs has been suggested by some researchers. At STPs of 27, 34, and 70 ML/d capacities, although filterable fraction of AS increases in secondary effluent, but this increase is compensated by decrease in particulate fraction resulting in overall reduction of total AS compared to raw sewage. Average ratio of filterable to total BOD, in UASBR effluent increased from 0.49 (in influent) to 0.65 (in effluent), and filterable AS to total AS from 0.65 (in influent) to 0.80 (in effluent), respectively. Compared to average removal of 45% of particulate AS, filterable fraction of AS was found to increase rather than decrease except at 38 ML/d capacity STP at Saharanpur where $\approx 7\%$ reduction was observed. Overall average AS reduction in UASBR ranged from 2% to 18% (mean $\approx 11\%$) only. Results have been summarized in Table 3.

3.1.2. AS removal in polishing ponds

Polishing ponds have been designed to have HRTs ranging from 1 to 1.6 days. Algal growth (and associated aerobic conditions) cannot be expected at pond detention times less than the multiplication rate of algal cells (2–2.5 days at 20 °C) [40]. As expected, algae have not been found to be growing during the entire sampling period of 21 months. DO was also absent in pond effluents throughout the study. Based on the parametric study, ponds could be classified as 1–1.6 days detention, non-algal, shallow, anaerobic ponds (Table 1). Average removals of BOD and AS in polishing ponds were found to be $\approx 49\%$ and $\approx 15.2\%$, respectively. Like UASBR, removal of AS remained low compared to BOD. However, removals of both filterable and non-filterable fractions of AS improved at tertiary stage. Overall elimination of AS in PPs was calculated to range from 12.8% to 18.3%.

3.1.3. Overall AS removal at UASB based STPs

Overall AS and BOD removals at five STPs are summarized in Table 4 (columns 5 and 6). Reduction in total AS were found to be in the range of 8–30%. It did not match with the BOD reduction,

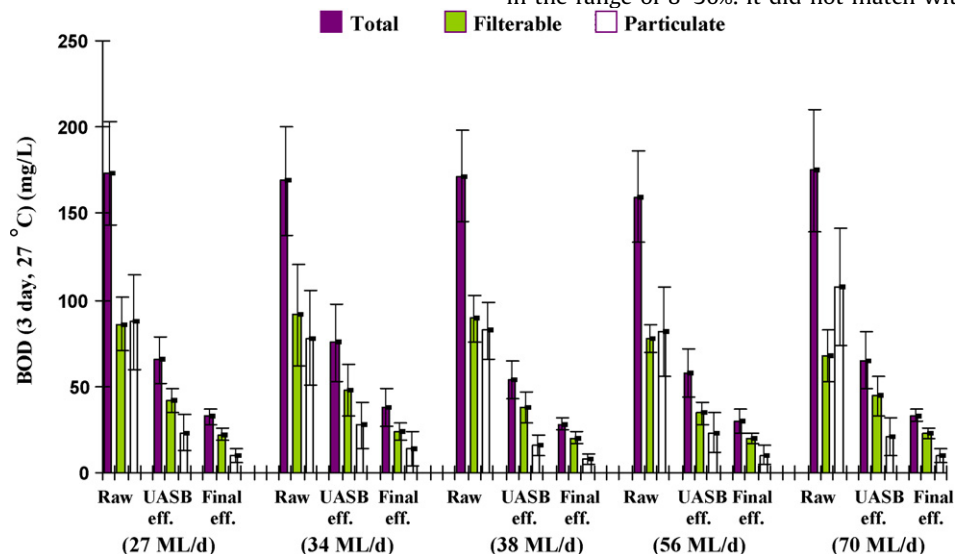


Fig. 4. UASBR based STPs: average BOD in raw sewage, UASBR effluent, and in final effluent.

Table 3
UASBR based STPs: changes in BOD and AS

	UASBR		PP		UASBR-PP	
	BOD	AS	BOD	AS	BOD	AS
Filterable	D (35–57%)	I ^a (8–33%)	D (43–50%)	NC (0.4–3%)	D (65–81%)	I ^a (6–32%)
Particulate	D (65–81%)	D (33–60%)	D (49–56%)	D (64–76%)	D (82–91%)	D (78–89%)
Total	D (56–68%)	D (2–18%)	D (48–49%)	D (13–18%)	D (78–84%)	D (8–30%)

D = decreases, I = increases, NC = no change.

^a At 4 out of 5 STPs.

which was found in the range of 78–84% (mean \approx 81%). However, particulate fraction of AS reduced appreciably (78–89%, mean 83%) compared to filterable fraction, which was found to increase rather than decrease (except at 38 ML/d capacity STP). In case of BOD also, better reduction of particulate fraction compared to filterable one was noticed. Increase in the ratio of filterable to particulate BOD (raw WW-0.97, secondary WW-1.91, and tertiary WW-2.14) and AS (raw WW-1.90, secondary WW-3.99, and tertiary WW-11.61) is quite noticeable as the wastewater passes through the various treatment units. This indicates significant change in the form of organics from particulate to soluble, more noticeable in case of AS than BOD. UASBR-PP effluent discharges substantial amount of AS, on an average ranging from 3.60 to 4.91 mg/L. It could be concluded that in an UASBR-PP combine (a) only up to 30% reduction of total AS takes place, (b) on an average greater than 80% reduction of particulate AS is achieved, (c) solubilization of AS in UASBR results in noticeable increase in filterable form of AS in UASBR as well as UASBR-PP effluents, and (d) solubilization and substantial reduction in particulate form of AS results in considerable increase in ratio of filterable to particulate AS from <2 to >11 in treated sewage.

In a UASBR-PP based STP, aerobic conditions do not develop even in polishing ponds. PP effluents were found to be devoid of oxygen. Influent and effluent PP oxidation reduction potential (ORP) values ranged from –150 to –100, and –145 to –90 mV, respectively indicating little change in reducing state of wastewater in PP (or immediate demand of O₂ by PP effluent). Due to low ORP, O₂ demand of anaerobically treated effluent is always greater than aerobically treated wastewaters. Absence of DO results in limited reduction of AS. Selection of such PPs for post-treatment of anaerobically treated sewage does not appear to be a good choice from the point of view of removal of AS. The second author did extensive monthly monitoring at many of these UASBR-PP based STPs over a period of greater than 3 years. The treated effluent has been found to contain significant amounts of organics, suspended solids, coliform, nutrients, and sulfides, etc. exceeding the maximum permissible levels (unpublished results). Installation of a more effective (compared to PP) post-treatment unit to UASBR effluent is, therefore, warranted. Based on the present work, AS could be added in to the list of parameters not being effectively tackled by UASBR-PP system.

Table 4
UASBR, OP and ASP based STPs: effluent concentrations and estimated PEC, PNEC and RQ values

STP	Capacity (ML/d)	Average AS concentration (mg/L)		Average %removal		PEC _{water} (mg/L)	PNEC _{water} (mg/L)	RQ
		Influent	Effluent	AS	BOD			
UASBR	27	5.35	4.33	19	81	0.433	0.027	16.04
UASBR	34	6.01	4.83	20	78	0.483	0.027	17.89
UASBR	38	5.36	3.83	29	84	0.383	0.027	14.19
UASBR	56	5.32	4.91	8	82	0.491	0.027	18.19
UASBR	70	5.16	3.60	30	81	0.360	0.027	13.33
OP	9	6.22	3.31	47	76	0.331	0.027	12.26
OP	32.5	5.57	0.67	88	80	0.067	0.027	2.48
ASP	18	2.05	0.13	94	92	0.013	0.027	0.48

Various post-treatment options (physicochemical and biological) have been researched for the treatment of secondary anaerobic effluents. However, from economic point of view, biological processes still appear to be ideal option. Most investigated biological processes are [41,42]: (i) biofilm processes (downflow hanging sponge, rotating biological contactor, trickling filter, submerged biofilter, anaerobic filter), (ii) pond processes, (iii) activated sludge process, and (iv) soil/plant processes (rapid infiltration, superficial irrigation, overland flow, constructed wetlands). A research programme on feasible technologies for UASBR post-treatment was carried out by a network of 15 Brazilian Universities. Design values for different post-treatment units such as trickling filter (TF), aerated submerged filter, dissolved air flotation, aerated ponds and activated sludge have been suggested [42]. However, research has been mainly restricted to the use at either laboratory-scale or pilot scale using natural or synthetic wastewaters.

The applicability of ASP for the post-treatment of anaerobic effluents in full-scale plants has been already demonstrated [43]. Duckweed ponds, polishing ponds and aerated lagoons are also being used at UASBR based STPs in India. However, not much data is available. Moreover, fate of AS has not been evaluated in any of the post treatment options studied so far. Use of aerobic processes like ASP, downflow hanging sponge (DHS), and aerated lagoon as post-treatment may result in desired reduction of AS in treated sewage. In a recent publication result of long-term evaluation of a combination of UASBR and DHS post treatment unit has been reported [44]. The system demonstrated removal efficiency constantly greater than 95% for unfiltered BOD. Dissolved oxygen in the final effluent was 5–7 mg/L although no mechanical aeration was provided in DHS system. Therefore, although LAS/AS were not tested, it is expected that such a combination of anaerobic-aerobic processes (UASBR-DHS) may reduce AS in final effluent up to such a level that it might not have any negative effect on aquatic environment. Ozonation has been found [33] to improve the effluent characteristics of UASB reactor treating domestic sewage. With a contact time of 50 min and ozone application dosage of 16.7 mg/L, 91% removal of AS were achieved.

3.2. OP based STPs

Average composition of raw sewage received at two OP based STPs during the period of ten months of the study was almost sim-

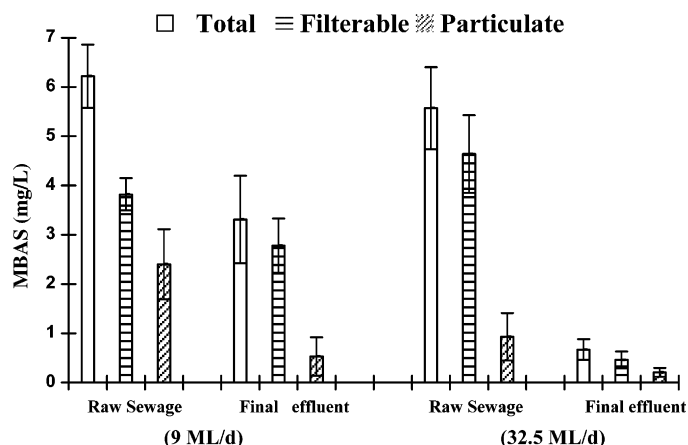


Fig. 5. Oxidation pond based STPs: average AS in raw sewage and final effluent.

ilar to the raw sewage composition summarized in Table 2. The sewage temperature and pH varied from 17 to 32.5 °C, and 7.0 to 7.9, respectively. The organics measured as COD and BOD varied from 222 to 685 mg/L (average 417 mg/L), and 148 to 234 mg/L (average 188 mg/L), respectively. Anionic surfactants measured as MBAS varied from 3.53 to 7.59 mg/L (average 5.89 mg/L), out of which the filterable fraction ranged from 2.84 to 5.61 mg/L (average 4.23 mg/L) and particulate from 0.22 to 3.66 mg/L (average 1.66 mg/L). Average AS and BOD values in sewage and final effluent are given in Figs. 5 and 6, respectively. On an average filterable BOD in incoming sewage was less than the particulate BOD at both the STPs. In case of AS, it was reverse.

Removal of AS at two STPs varied widely. The average concentrations of AS in treated sewage were found 3.31 and 0.67 mg/L (Fig. 5) resulting in average removals of ~47% and ~88% at 9 and 32.5 ML/d STPs, respectively. At 32.5 ML/d STP at Muzaffarnagar, DO in treated effluent was found to range from 3.5 to 29.3 mg/L and pH from 8.3 to 9.8. Most of the time DO exceeded saturation concentration. Contrary to this at 9 ML/d STP, DO concentration of 1.9 mg/l was detected only once and pH was observed only between 7.5 and 7.9. DeLeenheer [34] reported that minimum DO of 0.2 mg/L is required for aerobic degradation of AS. Because of good algal growth final effluent of Muzaffarnagar plant always appeared green while that from STP at Noida appeared blackish.

The high level of algal photosynthetic activity not only raises the pH of the pond at Muzaffarnagar but also increases its DO content. Removals in OPs are multi-factorial, dependent on a synergistic interaction between pH, DO, humic substances, and light, etc. The multi-parametric synergistic interactions as expected in OPs do not seem to occur in OP system at Noida resulting in unacceptable levels

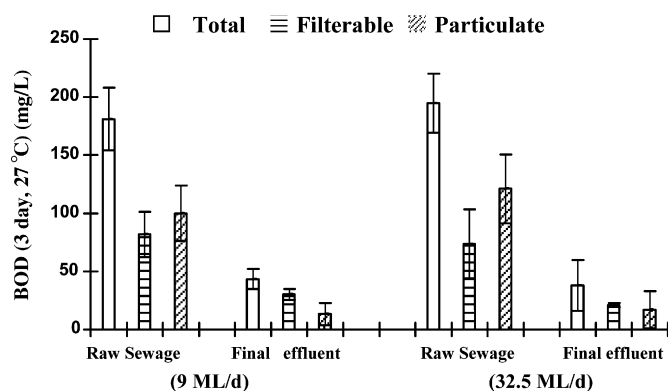


Fig. 6. Oxidation pond based STPs: average BOD in raw sewage and final effluent.

of AS removal. Although both STPs were initially designed as oxidation ponds adopting same design criteria, the one at Noida was not being properly operated and did not qualify to be designated as OP.

3.3. ASP based STP

Final effluent contained on an average 0.13 mg/L AS with a total removal of ~94%. Removal of AS was found to be much higher compared to that found in UASBR.

3.4. Efficiencies of removals of surfactants in different treatment systems studied

The average AS concentration in the treated effluents and percentage removals for different STPs are given in Table 4. AS removals ranged from 8% to 30%, 47% to 88%, and ~94% for UASBR, OP, and ASP based STPs, respectively. Concentrations of LAS or AS in treated effluents of ASP, OP, and UASBR based STPs from previous studies and present work are compiled in Fig. 7. Low effluent LAS or AS concentrations (less than 0.2 mg/L) in case of ASP are quite clear. Compared to this UASBR effluents contain high concentrations of AS (greater than 2.5 mg/L). Percentage removals for different technologies are shown in Fig. 8. LAS or AS removals greater than 99% have been reported by several researchers for ASP. Percentage BOD removals for some of these studies are shown in Fig. 9. In ASP, AS removals greater than BOD removals seems to be a common feature while it is just reverse in UASBR process.

3.5. Risk assessment to aquatic environment

The risk assessment to aquatic environment due to presence of AS in treated sewage was evaluated according to the procedure laid down in European Union Technical Guidance Document (EU TGD) [45]. Risk is assessed depending on (a) PEC, and (b) PNEC, i.e. the concentration below which unacceptable effects on organisms are not likely to occur.

3.5.1. PEC_{water}

The measured average concentrations of anionic surfactants in final effluents from different STPs are summarized in Table 4, column 4. EU TGD has suggested a dilution factor of 10 (TGD default dilution coefficient) which was used to calculate predicted environmental concentration in receiving water (PEC_{water} , Table 4, column 7).

3.5.2. $PNEC_{water}$

No observed effect concentration (NOEC) of 0.27 mg/L has been experimentally found based on long-term laboratory screening tests on broad array of freshwater plants/organisms at different trophic levels and utilized for assessment of risk to aquatic environment by many researchers [12,46–53]. Value reported is for LAS while in the present work AS were determined and not LAS. However, since LAS predominate among AS, NOEC value reported for LAS (i.e. 0.27 mg/L) was used to calculate PNEC. An assessment factor of 10 has been suggested [45] for the estimation of PNEC values for LAS. This yields lowest value of predicted no effect concentration in receiving water ($PNEC_{water}$) of 0.027 mg/L (Table 4, column 8).

3.5.3. Risk quotient (RQ)

The values of RQ were calculated using Eq. (1).

$$RQ = \frac{PEC_{water}}{PNEC_{water}} \quad (1)$$

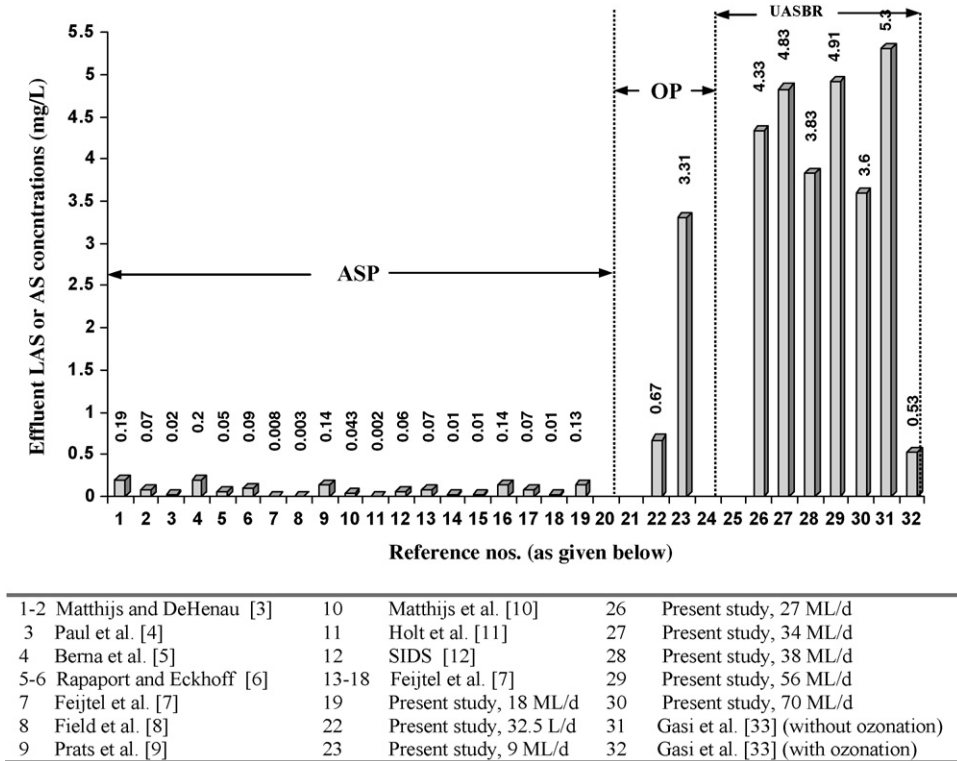


Fig. 7. ASP, OP and UASBR based STPs: concentration of LAS or AS in treated effluent.

RQ greater than 1 indicates a risk of adverse effect to the aquatic environment. Calculated values of RQ are given in Table 4, column 9. Values of RQ from literature and present work for three treatment options are shown in Fig. 10. It ranged from 2.0 to 19.6 for UASBR based STPs, much greater than desired value of less than 1. Even after ozonation of UASBR effluent it was found greater than 1 [33]. Biodegradation of AS under anaerobic conditions is limited. Treated effluents from UASBR based STPs when discharged to

aquatic ecosystems are likely to generate substantial risk. There is a need to provide effective aerobic post-treatment to UASBR effluent. The RQ values calculated for two OP based STPs (12.26 and 2.48) showed wide variation as one of the STPs was not properly maintained. The concentration of AS in treated effluents from OP based STPs may also generate risk to the aquatic environment. The RQ values in case of ASP reported by various research workers and also found in present work were less than 1. Compared to UASBR and

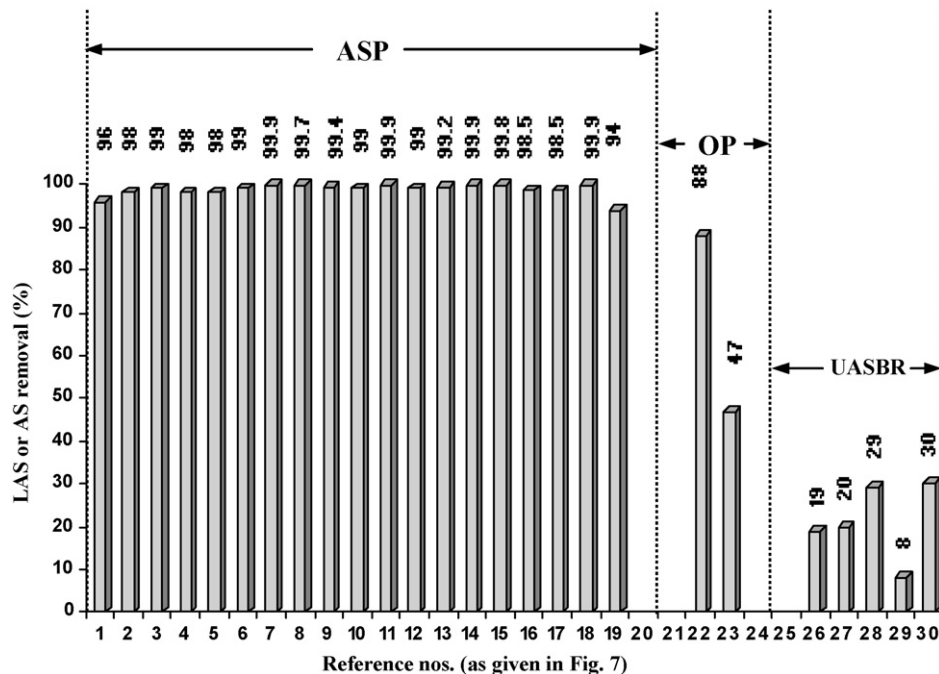
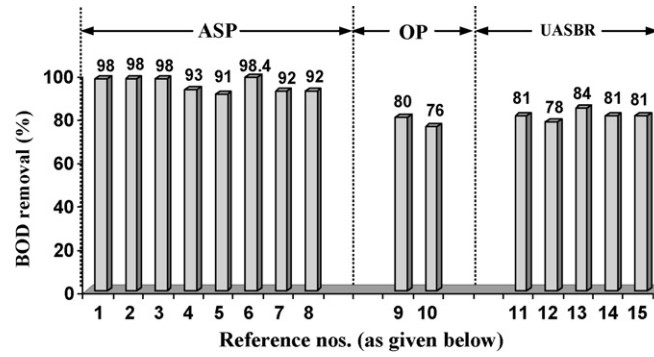


Fig. 8. ASP, OP and UASBR based STPs: percent removals of LAS or AS.



1 Feijtel et al. [7]	5 Feijtel et al. [7]	9 Present study, 32.5 ML/d	13 Present study, 38 ML/d
2 Feijtel et al. [7]	6 Feijtel et al. [7]	10 Present study, 9 ML/d	14 Present study, 56 ML/d
3 Feijtel et al. [7]	7 Prates et al. [9]	11 Present study, 27 ML/d	15 Present study, 70 ML/d
4 Feijtel et al. [7]	8 Present study, 18 ML/d	12 Present study, 34 ML/d	

Fig. 9. ASP, OP and UASBR based STPs: percent BOD removal.

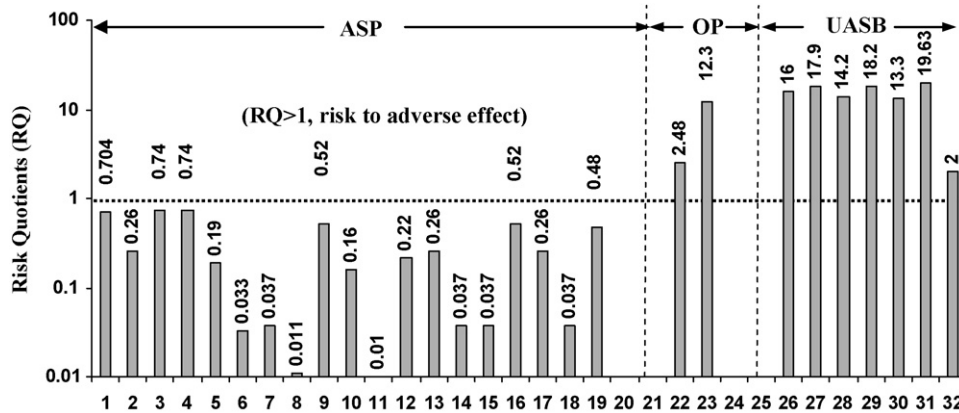


Fig. 10. ASP, OP and UASBR based STPs: values of risk quotients to aquatic environment due to discharge of treated effluents.

OP based STPs, RQ for ASP is quite low. Petersen et al. [54] selected two Norwegian plants to find RQ. First plant employed chemical precipitation with aluminium sulfate. RQ was found greater than 1. It was concluded that a STP with only chemical treatment may lead to risk quotients greater than 1. At second plant biological treatment included anaerobic and aerobic processes. RQs for LAS were well less than 1.

4. Conclusions

- In UASBR reactors at 4 out of 5 STPs, average removals of AS ranged from only 2% to 18%. At fifth STP, AS were even found to increase by around 8%. Effluents contained substantial concentrations of AS (4.25–5.91 mg/L). Particulate fraction is reduced by around 45% while soluble fraction increases. Although, anaerobic biodegradation of LAS or AS has been reported in bench-scale reactors, however, based on present work on 5 actual STPs for considerable duration, it appears that anaerobic environment of UASBR does not seem to favour appreciable removal of AS.
- Post treatment of UASBR effluent using 1–1.6 days detention polishing ponds was also found largely ineffective. Need to find an effective aerobic post-treatment unit to UASBR (like UASBR–ASP, UASBR–DHS, UASBR–ozonation, and UASBR–aerated lagoon) is felt.
- In a UASBR–PP combine, removals of total and adsorbed AS observed were less than or equal to 30% and greater than 80%, respectively. On the other hand, filterable AS increases and ratio

of filterable to adsorbed AS increases by over 5-folds as sewage passes through STP.

- Effluent AS or LAS concentrations recorded in ASP effluents are quite low (<0.2 mg/L). Unlike UASBR, removals of LAS or AS exceeded 99%. It was even found to be greater than BOD removal.
- Effluent from ASP is not supposed to pose any risk to aquatic environment due to the presence of AS. Contrary to this, treated effluents from UASBR based STPs are likely to pose substantial risk of AS toxicity to aquatic life forms unless an effective post-treatment is adopted.
- In case of OPs, RQ was found greater than 1 indicating risk of adverse effect to aquatic environment due to presence of AS in the treated sewage.

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References

- [1] M.J. Scott, M.N. Jones, The biodegradation of surfactants in the environment (Review), *Biochimica et Biophysica Acta* 1508 (2000) 235–251.
- [2] M.S. Holt, J. Waters, M.H.I. Comber, AIS/CESIO environmental surfactant monitoring programme. SDIA sewage treatment pilot study on linear alkylbenzene sulfonate (LAS), *Water Res.* 29 (1995) 2063–2070.
- [3] E. Matthijs, H. de Henau, Determination of LAS, *Tenside Surf. Det.* 24 (4) (1987) 193–198.
- [4] H. Paul, Brunner, S. Capri, A. Marcomini, W. Giger, Occurrence and behaviour of linear alkylbenzenesulfonate, nonylphenol, nonylphenol mono- and nonylphenol diethoxylates in sewage and sewage sludge treatment, *Water Res.* 22 (12) (1988) 1465–1472.
- [5] J.L. Berna, J. Ferrer, A. Moreno, D. Prats, F. Ruiz, The fate of LAS in the environment, *Tenside Surf. Det.* 26 (1989) 101–107.
- [6] R.A. Rapaport, W.S. Eckhoff, Monitoring linear alkyl benzene sulfonate in the environment: 1973–1986, *Environ. Toxicol. Chem.* 9 (10) (1990) 1245–1257.
- [7] T.C.J. Feijtel, E. Matthijs, A. Rottiers, G.B.J. Rijs, A. Kiewiet, A. de Nijs, AIS/CESIO environmental surfactant monitoring programme. Part 1: LAS monitoring study in “de Meer” sewage treatment plant and receiving river, Leidsche Rijn, *Chemosphere* 30 (6) (1995) 1053–1066.
- [8] J.A. Field, M.A. Field, T. Poiger, H. Siegrist, W. Giger, Fate of secondary alkane sulfonate surfactants during municipal wastewater treatment, *Water Res.* 29 (1995) 1301–1307.
- [9] D. Prats, F. Ruiz, B. Vazquez, M. Rodriguez-Pastor, Removal of anionic and nonionic surfactants in a wastewater treatment plant with anaerobic digestion: a comparative study, *Water Res.* 31 (8) (1997) 1925–1930.
- [10] E. Matthijs, M.S. Holt, A. Kiewiet, G.B.J. Rijs, Environmental monitoring for linear alkylbenzene sulfonate, alcohol ethoxylate, alcohol ethoxy sulfate, alcohol sulfate, and soap, *Environ. Toxicol. Chem.* 18 (1999) 2634–2644.
- [11] M.S. Holt, K.K. Fox, M. Daniel, H. Buckland, LAS and Boron monitoring in four catchments in the UK contribution to GREAT-ER, *Sci. Total Environ.* 314–316 (2003) 271–288.
- [12] SIDS. Sponsor Country: USA, Dossier on LAS (draft), 2005.
- [13] F. Haagensen, A.S. Mogensen, I. Angelidaki, B.K. Ahring, Anaerobic treatment of sludge: focusing on reduction of LAS concentration in sludge, *Water Sci. Technol.* 46 (2002) 159–165.
- [14] G.G. Ying, Fate, behavior and effects of surfactants and their degradation products in the environment, *Environ. Int.* 32 (3) (2006) 417–431.
- [15] I. Angelidaki, A.S. Mogensen, B.K. Ahring, Degradation of organic contaminants found in organic waste, *Biodegradation* 11 (2000) 377–383.
- [16] A.S. Mogensen, B.K. Ahring, Formation of metabolites during biodegradation of linear alkylbenzene sulfonate in an up-flow anaerobic sludge bed reactor under thermophilic conditions, *Biotechnol. Bioeng.* 77 (2002) 483–488.
- [17] J.L. Sanz, E. Culubret, J. deferrer, A. Moreno, J.L. Berna, Anaerobic biodegradation of linear alkylbenzene sulfonate (LAS) in upflow anaerobic sludge blanket (UASB) reactors, *Biodegradation* 14 (2003) 57–64.
- [18] K. Denger, A.M. Cook, Note: linear Alkylbenzene sulphonate (LAS) bioavailable to anaerobic bacteria as a source of sulphur, *J. Appl. Microbiol.* 86 (1999) 165–168.
- [19] T. Lobner, L. Torang, D.J. Batstone, J.E. Schmidt, I. Angelidaki, Effects of process stability on anaerobic biodegradation of LAS in UASB reactors, *Biotechnol. Bioeng.* 89 (7) (2005) 759–765.
- [20] Toxic Links, 2002, <http://www.toxiclinks.org/>.
- [21] R.A. Kimerle, Aquatic and terrestrial ecotoxicology of LAS, *Tenside Surf. Det.* 26 (1989) 169–176.
- [22] S.H. Venhuis, M. Mehrvar, Health effects, environmental impacts, and photochemical degradation of selected surfactants in water, *Int. J. Photoenergy* 6 (2004) 115–125.
- [23] J.F. Fairchild, F.J. Dwyer, T.W. LaPoint, S.A. Burch, C.G. Ingersoll, Evaluation of a laboratory-generated NOEC for linear alkylbenzene sulfonate in outdoor experimental streams, *Environ. Toxicol. Chem.* 12 (1993) 1763–1775.
- [24] F.R. Schroder, Concentration of anionic surfactants in receiving river water, *CLER Rev.* 3 (1) (1997) 44–53.
- [25] H. Takada, K. Mutoh, N. Tomita, T. Miyadzu, N. Ogura, Rapid removal of LAS by attached biofilm in an urban shallow stream, *Water Res.* 28 (1994) 1953–1960.
- [26] C. Lee, N.J. Russell, G.F. White, Modelling the kinetics of biodegradation of anionic surfactants by biofilm bacteria from polluted riverine sites: a comparison of five classes of surfactants at three sites, *Water Res.* 29 (1995) 2491–2498.
- [27] H. Draaijer, J.A.W. Maas, J.E. Schaapman, A. Khan, Performance of the 5 MLD UASB reactor for sewage treatment at Kanpur, India, *Water Sci. Technol.* 25 (1992) 123–133.
- [28] R.A. Rapaport, R.J. Larson, D.C. McAvoy, A.M. Nielsen, M. Trehy, The fate of commercial LAS in the environment, *CLER Rev.* (1995) 20–30.
- [29] A. Tamara, G. Carr, S. Webb, D. Versteeg, T. Feijtel, Marine Risk assessment: LAS in the North Sea, *Mar. Pollut. Bull.* 42 (8) (2001) 635–642.
- [30] Standard methods for the examination of water and wastewater, 20th ed., American Public Health Association, Washington, DC, USA, 1998.
- [31] A. Marcomini, W. Giger, Simultaneous determination of LAS, alkylphenol polyethoxylates, and nonylphenol by high performance liquid chromatography, *Anal. Chem.* 59 (1987) 1709–1715.
- [32] S.M. Hammad, Performance of a full scale UASB domestic wastewater treatment plant, *J. Inst. Public Health Eng. India* 1 (1996) 11–19.
- [33] T.M.T. Gasi, L.A.V. Amaral, C.E.M. Pacheco, A.G. Filho, A.D. Garcia, S.M.M. Vieira, R. Francisco, P.D. Orth, M. Scoparo, M.S.R.D. Dias, M.L. Magri, Ozone application for the improvement of UASB reactor effluent. 1: Physical-chemical and biological appraisal, *Ozone Sci. Eng.* 13 (2) (1991) 179–193.
- [34] A. DeLeenheer, Dynamics integrated modeling of basic water quality and fate and effect of organic contaminants in rivers, Ph.D. Thesis, Faculteit Landbouwkundige en toegepaste biologische Wetenschappen, 2004.
- [35] C.E. Cowan, R.J. Larson, T.C.J. Feijtel, R.A. Rapaport, An improved model for predicting the fate of consumer product chemicals in wastewater treatment plants, *Water Res.* 27 (4) (1993) 561–573.
- [36] N.H. Youssef, K.E. Duncan, D.P. Nagle, K.N. Savage, R.M. Knapp, M.J. McInerney, Comparison of methods to detect biosurfactant production by diverse microorganisms, *J. Microbiol. Methods* 56 (2004) 339–347.
- [37] L.M.S. Anna, G.V. Sebastian, E.P. Menezes, T.L.M. Alves, A.S. Santos, J.N. Pereira, D.M.G. Freire, Production of biosurfactants from *Pseudomonas aeruginosa* PA1 isolated in oil environments, *Braz. J. Chem. Eng.* 19 (2) (2002) 159–166.
- [38] J.W. Morgan, C.F. Forster, L. Evison, A comparative study of the nature of biopolymers extracted from anaerobic and activated sludges, *Water Res.* 24 (6) (1990) 743–750.
- [39] X.S. Jia, H.H.P. Fang, H. Furumai, Surface charge and extracellular polymer of sludge in the anaerobic degradation process, *Water Sci. Technol.* 34 (5–6) (1996) 309–316.
- [40] S.J. Arceivala, *Wastewater Treatment for Pollution Control*, 2nd ed., Tata McGraw-Hill, New Delhi, 1999.
- [41] C.A.L. Chernicharo, Post-treatment options for the anaerobic treatment of domestic wastewater, *Rev. Environ. Sci. Biotechnol.* 5 (2006) 73–92.
- [42] E.P. Jordao, I. Volschan, Cost-effective solutions for sewage treatment in developing countries, the case of Brazil, *Water Sci. Technol.* 50 (7) (2004) 237–242.
- [43] F.H. Passig, L.H. Villela, O.P. Ferreira, Piracicamirim sewage treatment plant- Conception utilizing anaerobic process followed by aerobic process-Evaluation of operational conditions and compatibility of the processes. In: preprints of the VI Latin-American workshop and seminar on anaerobic digestion. UFPE/CTG/BT/2000, Recife, Brazil, 2000, pp. 53–59.
- [44] M. Tandukar, I. Machdar, S. Uemura, A. Ohashi, H. Harada, Potential of a combination of UASB and DHS reactor as a novel sewage treatment system for developing countries: Long term evaluation, *J. Environ. Eng.* 132 (2) (2006) 166–172.
- [45] EU-TGD. Technical Guidance Document in support of the Commission directive 93/67/EEC on risk assessment for new notified substances and the Commission regulation (EC) 1488/94 on risk assessment for existing substances, 2002 (Revision of the 1996 version, Office for official publications of the European Communities, Brussels).
- [46] W.H. Konemann, Quantitative structure-activity relationships in fish toxicity studies. Part I: Relationship for 50 industrial pollutants, *Toxicology* 19 (1981) 209–221.
- [47] BKH, The use of existing data for estimation of the maximum tolerable environmental concentration of LAS. Part I: main report. Part II: data list, BKH, Delft (NL), 1993.
- [48] D.C. McAvoy, W.S. Eckhoff, R.A. Rapaport, Fate of linear alkylbenzene sulfonate in the environment, *Environ. Toxicol. Chem.* 12 (1993) 977–987.
- [49] C.F. Tabor, L.B. Barber, Fate of linear alkylbenzene sulfonate in the Mississippi River, *Environ. Sci. Technol.* 30 (1996) 161–171.
- [50] E.J. Van de Plassche, J.H.M. de Bruijn, R.R. Stephenson, S.J. Marshall, T.C.J. Feijtel, S.E. Belanger, Predicted no-effect concentrations and risk characterization of four surfactants: linear alkylbenzene sulfonate, alcohol ethoxylates, alcohol ethoxylated sulfates, and soap, *Environ. Toxicol. Chem.* 18 (1999) 2653–2663.
- [51] S.E. Belanger, J.W. Bowling, D.M. Lee, E.M. LeBlanc, D.C. McAvoy, D.H. Davidson, Integration of aquatic fate and ecological responses to LAS in model stream ecosystem, *Ecotoxicol. Environ. Saf.* 52 (2002) 150–171.
- [52] D.J. Versteeg, J.M. Rowlings, Bioconcentration and toxicity of C₁₂LAS to aquatic organisms exposed in experimental streams, *Arch. Environ. Contam. Toxicol.* 44 (2003) 237–246.
- [53] HERA, HERA-LAS Human and Environmental Risk Assessment: Linear Alkylbenzene Sulphonates, LAS. CAS No. 68411-30-3, Version 3.0, October 2007.
- [54] G. Petersen, D. Rasmussen, K. Maenpaa, T. Kallqvist, T. Madsen, J.V.K. Kukkonen, Transport and fate of surfactants in the aquatic environment, 2003, <http://www.nordicinnovation.net/nordtestfiler/tec524.pdf>.