



Performance of UASB reactor treating synthetic textile wastewater: effect of physicochemical pretreatment

Akshaya Kumar Verma^a, Puspendu Bhunia^{b,*}, Rajesh Roshan Dash^b

^aCentre for Energy and Environmental Engineering, National Institute of Technology Hamirpur, Hamirpur, Himachal Pradesh 177 005, India, email: akv10@iitbbs.ac.in

^bDepartment of Civil Engineering, School of Infrastructure, Indian Institute of Technology Bhubaneswar, Bhubaneswar, Odisha 751 013, India, Tel. +91 674 2306 355; Fax: +91 674 2301 983; emails: pbhunia@iitbbs.ac.in (P. Bhunia), rrdash@iitbbs.ac.in (R.R. Dash)

Received 3 April 2014; Accepted 4 February 2015

ABSTRACT

The study explores the influence of physicochemical pretreatment on the performance of upflow anaerobic sludge blanket (UASB) reactors treating synthetic textile wastewater. Physicochemical pretreatment in this study utilized a new composite coagulant magnesium chloride added with aluminum chlorohydrate which produced nearly complete color removal and a partial chemical oxygen demand (COD) removal (~55%) efficiency. Various parameters such as volatile fatty acids (VFA), bicarbonate alkalinity (B-Alk.), gas production, total aromatic amines (TAAs) generation, COD, and color removal efficiency were monitored in the UASB reactors operated at different operating conditions. For the UASB reactor treating pretreated textile wastewater, a maximum of 99% COD removal was obtained at an organic loading rates (OLRs) of 1.2 kg COD m⁻³ d⁻¹ and hydraulic retention time (HRT) of 20 h. Whereas in case of without pretreatment, a maximum of both 92% COD and color removal efficiency were achieved at an OLR of 2.4 kg COD m⁻³ d⁻¹ and HRT of 20 h. However, in this case, highly toxic, carcinogenic, and mutagenic TAAs were observed to produce in the range of 6.9–8.1 mg L⁻¹. VFA/B-Alk. ratios were found in the range of 0.05–0.15, indicating the sufficient buffering capacity for stability of the reactor. The study demonstrates the significance of physicochemical pretreatment on the performance of UASB reactor for the treatment of textile wastewater. Nevertheless, it also shows the importance of introducing pretreatment in order to avoid the production of harmful aromatic amines in the treated UASB effluent.

Keywords: Aromatic amines; COD removal; Color removal; Pretreatment; Textile wastewater; UASB reactor

1. Introduction

The rapid growth of textile industries to meet the global textile demand has degraded our environment

in various ways. Out of different types of environmental issues, pollution due to colored wastewater can be considered as one of the major environmental concerns. The unused materials from different textile processing steps generate the effluents which are generally characterized by their intense color, high

*Corresponding author.

biological oxygen demand (BOD), chemical oxygen demand (COD), turbidity, pH and toxic chemicals, low biodegradability, and the presence of recalcitrant organic compounds [1,2]. Out of several synthetic dyes used for dyeing of fiber, more than 50% dye loss is associated with the reactive azo dyes because of their poor fixation efficiency [3,4]. Azo dyes are the most extensively used dye type and constitute about 60–70% of the total dyes produced [5,6].

Most of these dyes and their intermediates can undergo reductive cleavage in the aquatic environment and transform to the harmful products such as aromatic amines. The toxic and carcinogenic effects of these aromatic amines have been well explained by numerous researchers [7,8]. Toxicity tests have demonstrated the acute toxicity due to the monocyclic aromatic amines on the different test models, where 96-h LC_{50} for the fish was reported in the range from 16.4 to 49.5 $mg L^{-1}$ [9].

Generally, two or three treatment methods are utilized in integrated manner in order to achieve adequate level of treatment [10,11]. Application of traditional anaerobic processes such as upflow anaerobic sludge blanket (UASB) reactor technology was effectively used for the treatment of textile wastewater; however, the process was recently reported to produce potentially harmful aromatic amines [12,13]. Physicochemical treatment such as chemical coagulation/flocculation using suitable coagulant has been reported to decolorize such textile wastewaters efficiently but fails in removing COD effectively [14]. Out of various methods utilized for the treatment of textile wastewaters, chemical coagulation followed by aerobic biological treatment has been observed as one of the most effective combinations [15]. This integrated process has an advantage to remove majority of the dyes and some percentage of COD through physicochemical coagulation, and then reduce the remaining carbonaceous organics in the wastewater with the subsequent aerobic biological process. Pretreatment using chemical coagulation/flocculation decolorizes the wastewater by the physical removal of the dye molecules from the textile wastewaters and not by the partial decomposition of the dyes. The partial decomposition of dyes can lead to an even more potentially harmful and carcinogenic aromatic compounds [14,16], which are resistant to degradation even under aerobic conditions.

The aerobic biological post-treatment process effectively reduces the residual COD from the physicochemically pretreated wastewater but produces significant amount of active biological sludge, limiting its applicability as a viable post-treatment option. This limitation can be avoided using anaerobic biological

processes such as UASB reactor technology as a post-treatment option [10].

The effects of using physicochemical coagulation as a pretreatment stage on the subsequent anaerobic biological treatment processes have not been fully investigated. For example, if the traditional UASB reactor technology is used for the treatment of textile wastewater, the process would produce potentially harmful aromatic amines [12,13]. These aromatic amines production can be prevented if the dyes are eliminated before the anaerobic treatment, e.g. using the integrated process of physicochemical coagulation as a pretreatment stage. However, the performance of the UASB reactor in terms of COD removal, aromatic amines removal, and overall decolorization for treating the physicochemically pretreated textile effluent has not been explored.

Therefore, in the present study, we made an effort to investigate the effectiveness of the integrated process in which UASB reactor technology was employed as a post-treatment option for physicochemically pretreated textile wastewater. The effectiveness of the integrated process in terms of COD removal, aromatic amines removal, and overall decolorization was explored. Furthermore, the effect of organic loading rates (OLRs) and hydraulic retention time (HRT) on the treatment efficiency was also scrutinized.

2. Materials and methods

2.1. Textile wastewater

Synthetic textile wastewater with a suitable dye concentration ($200 mg L^{-1}$) was prepared as per the reported chemical constituents of real textile wastewater [17,18]. The synthetic textile wastewater was prepared by mixing three different categories of commercial dyes, namely reactive black 5 (RB5), congo red (CR), and disperse blue 3 (DB3) in tap water, in an equal ratio along with the various chemical additives which are used during textile processing in textile industries (Table 1). Dyes were procured from Sigma-Aldrich, Germany. The characteristic wavelength of simulated dye wastewater was determined by running a scan of the dye solution on a UV-Vis spectrophotometer (Perkin-Elmer, Lambda 25), and the maximum absorbance wavelengths (λ_{max}) for RB5, CR, and DB3 were found as 591, 502, and 638 nm, respectively. The color content of the wastewater containing mixture of dyes was determined by taking the sum of the absorbencies measured at 591, 502, and 638 nm [19]. The synthetic textile wastewater was having COD of $1,944\text{--}2,007 mg L^{-1}$, pH of 10.4–10.6, Abs (mixture) = Abs (591) + Abs (502) + Abs (638) = 2.3992.

Table 1
Chemical constituents used for the preparation of synthetic textile wastewater

Materials used	Concentration (mg L ⁻¹)	Function
Starch	1,000	Sizing agent
Acetic acid	200	Sizing agent
Sucrose	600	Sizing agent
Dyes	200*	Coloring agent
NaOH	500	Hydrolysis
H ₂ SO ₄	300	pH neutralization
Na ₂ CO ₃	500	Fixing agent
NaCl	3,000	Fixing agent
Sodium lauryl sulfate	100	Scouring agent

*Total dye concentration in equal ratios for the three dyes together ($3 \times 66.67 = 200$ mg L⁻¹) used for the preparation of wastewater.

The percentage decolorization efficiency was determined using Eq. (1):

$$\text{Decolorization efficiency(\%)} = [(A_b - A_t)/A_b] \times 100 \quad (1)$$

where A_b and A_t are the absorbencies of the solution before treatment and after treatment of the textile wastewater, respectively. Tap water was used as a reference.

2.2. Chemicals

Extra pure magnesium chloride (MC) and industrial grade (purity 30% w/w) aluminum chlorohydrate (ACH) were used as coagulants. Powdered lime (Ca(OH)₂) was used to adjust the optimum pH, since it is well established that lime can be used as a coagulant aid as well as pH regulator [20]. All the chemicals used for analysis of different parameters and for the preparation of the synthetic wastewater were of analytical grade.

2.3. Physicochemical treatment

A newly developed composite coagulant MC + ACH was used in the pretreatment step during chemical coagulation for the efficient decolorization of textile wastewater containing different classes of textile dyes [17,21]. This composite coagulant was demonstrated to remove more than 99% of dyes and 55% of COD at their designated combined dosage and optimized pH of 800 mg L⁻¹ and 12, respectively [21]. The optimum pH value and coagulant dosage required for efficient color removal were determined

by the jar test method. 1 L beakers, containing 500 mL of wastewater, were used for the coagulation experiments. 1.0 M NaOH or 1.0 M H₂SO₄ were added to each beaker for pH adjustment. The composite coagulant was added and mixed for 3 min under rapid mixing condition at 80 rpm. The solution was then mixed at 30 rpm for 15 min and then allowed to settle down for 20 min. The supernatant from the beaker was taken for analysis.

2.4. Description of UASB reactors, operational conditions, and experimental runs

The second stage of biological anaerobic treatment was carried out in the UASB reactors. Two different sizes of UASB reactors in multiple numbers were used in the study. These UASB reactors were made of plexiglas; one type had an effective volume of 4.62 L with the dimension of 80 × 75 × 770 mm and the other type was 12.18 L with the dimension of 105 × 105 × 1,105 mm. Different experimental runs were designed based on the selected variables such as HRT, influent COD, and pretreatment (Yes/No). The reactors were operated for the treatment of original (without pretreatment) as well as physicochemically pretreated textile wastewater.

The pH of wastewater was adjusted to about neutral (~7.4) using 1.0 M H₂SO₄, and nutrients were added as per the composition suggested by Bhunia and Ghangrekar [22] before being fed to the UASB reactor. Matured cow dung slurry was obtained from a nearby cattle farm and was anaerobically digested by constantly feeding C and N source for about one month. The reactors were seeded with this digested sludge. Mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) of the inoculums were in the range of 50–62 and 35–48 g L⁻¹,

respectively. In order to reduce the time to achieve the steady state or in other words to accelerate the microbial activity of seed sludge, the reactors were initially operated with the synthetic feed containing simple sugar (sucrose) as the only carbon source equivalent to 1,000 mg L⁻¹ COD along with necessary macro and micro nutrients. This synthetic feed was free from other chemical additives as of the synthetic textile wastewater. After achieving 75% COD removal, the reactors were fed with synthetic textile wastewater having the characteristics and composition as mentioned in Table 1. The reactors were operated at ambient temperatures, ranging between 22 and 27°C.

The details of the experimental runs and their operating conditions have been summarized in Table 2. The performance of the reactors was monitored regularly till achieving the steady state. The steady state was considered, when all the parameters such as pH, bicarbonate alkalinity (B-Alk.), volatile fatty acids (VFA), COD removal, color removal, and gas production were appeared as nearly constant and within 5% variation for consecutive 4 d in each of the reactor. Similar operation conditions were maintained in the runs and during acclimatization for a particular run.

2.5. Analytical procedures

Color of the effluents was measured after filtration of supernatant through Whatman 42 filter paper. Subsequently, the absorbance of the sample was measured using a UV-Vis spectrophotometer (Perkin-Elmeyer, Lambda 25). COD was analyzed as per the closed reflux colorimetric method [23] after digestion of the

samples in a COD reactor (Model DRB 200, HACH, USA), and then absorbance was measured by COD spectrophotometer (Model DR 2800, HACH, USA) at 600 nm. B-Alk. (mg L⁻¹ as CaCO₃) and VFA (mg L⁻¹ as CH₃COOH) were measured with the titrimetric method proposed by Beydilli et al. [24]. In this method, the samples were titrated with 0.1 N standard H₂SO₄ to pH 5.1 and then to pH 3.5. pH was measured with the pH meter (HQ40D, HACH, USA). Total gas was measured with liquid displacement method by passing it through a liquid containing 2% (v/v) H₂SO₄ and 10% (w/v) NaCl [25], while methane gas was monitored using liquid containing 3% NaOH (w/v) [26]. Total aromatic amines (TAAs) were measured calorimetrically as per the method suggested by Oren et al. [27]. It was reported that RB5 and CR produce sulfanilic acid and benzidine-like aromatic amines, respectively, after their reductive cleavage under the anaerobic environment [28,29]. Therefore, these amines were served as standards while measuring aromatic amines calorimetrically using spectrophotometer at 440 nm by reacting with p-dimethyl amino benzaldehyde in acidic medium. All other parameters such as BOD, MLSS, and MLVSS were measured according to the standard methods [23].

3. Results and discussions

3.1. Variation of VFA, B-Alk., COD, and color removal efficiency

All the experimental runs as shown in Table 2 were performed using UASB reactors treating

Table 2
Experimental runs and operational condition in UASB reactors

Run	Pretreatment	Influent COD to UASB reactor (mg L ⁻¹)	HRT (h)	Effective OLR (kg COD m ⁻³ d ⁻¹)	Upflow velocity (m h ⁻¹)
1	No	1,000	24	1.0	0.046
2	No	3,000	16	4.48	0.048
3	No	2,000	20	2.4	0.038
4	Yes	500	16	0.75	0.048
5	No	1,000	16	1.5	0.048
6	Yes	500	24	0.5	0.032
7	Yes	1,500	16	2.25	0.048
8	Yes	1,500	24	1.5	0.032
9	Yes	1,000	20	1.2	0.054
10	Yes	1,000	20	1.2	0.054
11	No	3,000	24	3.0	0.046
12	Yes	1,000	20	1.2	0.0385
13	No	2,000	20	2.4	0.038
14	No	2,000	20	2.4	0.038

pretreated and without pretreated textile wastewater. The UASB reactors treating without pretreated textile wastewater took comparatively longer time to reach the steady state. The time to reach the steady state for the reactors treating pretreated textile wastewater was in the range of 44–62 d, while it was in the range of 80–110 d for the reactors treating without pretreated textile wastewater. The requirement of longer time might be related to the reduced activity of microbial consortia in the presence of toxic dyes and higher organic loads. However, the reactors irrespective of pretreated and without pretreated textile wastewater follow almost similar trends with respect to variation in different parameters such as VFA, B-Alk., COD removal efficiency, and color removal efficiency. The representation of these variations with days of operation is shown in Fig. 1 for both the cases at central points (Experimental runs 10 and 14).

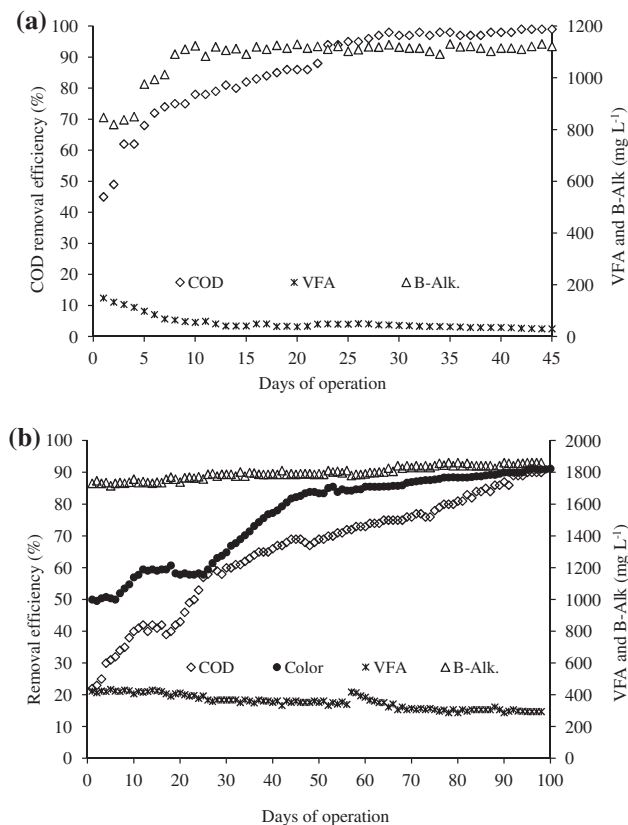


Fig. 1. Variation in VFA, B-Alk., COD, and color removal efficiency during operation of UASB reactor treating; (a) physicochemically pretreated textile wastewater (operating COD = 1,000 mg L⁻¹, HRT = 20 h) and (b) without pretreated textile wastewater (operating COD = 2,000 mg L⁻¹, HRT = 20 h).

In both the cases, B-Alk. was sufficient enough to prevent the VFA accumulation throughout the operation of the UASB reactor. However, VFA accumulation was comparatively higher in the case of reactor treating without pretreated textile wastewater. The VFA/B-Alk. ratio in both the cases was well below the critical value of 0.4, indicating the stable operation of the UASB reactors. It is also interesting to note that the removal of color took place in three distinct phases (Fig. 1(b)), where considerable color removal efficiency (~50%) was observed during the first day itself which became constant upto next 7 d of operation. This phase may be viewed as the acclimatization phase. Bio-adsorption would have been the predominant in this phase, which removes dyes by adsorbing them onto the surface of sludge [30,31]. After 7 d of operation, the color removal efficiency in the second phase increased sharply up to 61% and became constant again till the end of two more weeks. This could be the initiation of biodegradation of dyes after initial acclimatization of the seed sludge. Further, the reactor took slightly higher time (three more weeks) to accelerate the color removal efficiency from 61 to 81% in the third phase, beyond which the color removal efficiency was almost constant till the end of experimental runs. The removal efficiency in the last phase corresponds to the maximum color removal by the reactor under the given operating conditions. In this phase, biodegradation would have played a vital role in removing color by the UASB reactor.

In contrast, COD removal rate was lesser than the color removal rate. The COD removal efficiency significantly dropped when synthetic textile wastewater was introduced. Only about 20% COD removal efficiency was appeared at the end of day one, which then increased to 40% at the end of 10 d operation. The observation can be related to the toxicity of textile dyes along with sudden increase in organic loads due to which a swift drop in COD removal efficiency was observed at the beginning of introducing the synthetic textile wastewater to the reactor. COD removal efficiency was observed to improve with time due to acclimatization of seed sludge inside the reactor. At steady state, which arrived at the end of 84 d for the experimental run 14, COD removal efficiency of 89% was achieved.

3.2. Biogas production in the UASB reactors

Total gas and methane gas production were continuously increasing with increase in the OLRs. Comparatively higher production rates were observed in the case of UASB reactor treating pretreated textile wastewater.

In case of the UASB reactor treating pretreated textile wastewater, a total gas and methane gas production rates of 600 and 360 mL d⁻¹, respectively, were obtained at a minimum OLR of 0.5 kg COD m⁻³ d⁻¹, while gas production rates were increased to 3,880 and 2,020 mL d⁻¹, respectively, at the OLR of 2.25 kg COD m⁻³ d⁻¹ (Fig. 2). However, a maximum total gas and methane gas production rates of 6,040 and 2,910 mL d⁻¹, respectively, were obtained at the highest OLR of 4.48 kg COD m⁻³ d⁻¹. The results also showed that the fraction of methane gas in the total gas was comparatively higher for the UASB reactor treating pretreated textile wastewater than the reactor treating without pretreated textile wastewater. For UASB reactor with pretreated textile wastewater, the methane fraction in the total biogas was found to be 0.61 to 0.52, with the increasing OLR, while it was 0.51 to 0.47 for the reactor treating without pretreated textile wastewater. Similar observation of decrease in methane fraction with higher loading rates was also demonstrated by numerous researchers [12,32].

Biogas production rates also depend on the COD removal efficiency apart from the organic loads. The cases where pretreated textile wastewater gave excellent COD removal efficiency, increased biogas production rates were observed. In such cases, methane contents in the total gas were also appeared to be higher because of the efficient conversion of VFA into the methane gas. On the other hand, UASB reactors treating without pretreated textile wastewater were observed to produce lesser COD removal efficiency, which subsequently reduced the biogas production rate. In such cases, the methane contents of the total biogas were also found to be comparatively lower in fraction. This might be related to the complexity of wastewater, toxicity of textile dyes present, and the inhibition of acetoclastic methanogens. It is

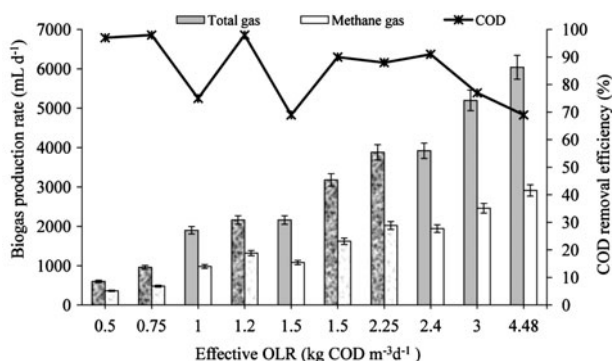


Fig. 2. Variation of biogas production rates in UASB reactor treating pretreated (textured) and without pretreated (flat) wastewater.

important to note that methanogens are more sensitive than acid-forming bacteria. In addition to this, the experimental methane gas production rates were found to be lesser than the theoretical methane gas production rates at the selected OLRs [11]. The lesser experimental methane gas production rates of the order from 20 to 47% as compared to the theoretical methane gas production rates as per the stoichiometric relationship might be related to the loss of soluble methane gas in dissolved form along with the effluent [10].

3.3. Effect of HRT and influent COD on the performance of UASB reactor

The effect of increasing HRTs on COD removal efficiencies for UASB reactor treating pretreated and without pretreated textile wastewater under different experimental runs was shown in Fig. 3. A good COD removal over 88% was observed at all the HRTs, while a maximum COD removal efficiency of close to 99% was appeared at an HRT of 20 h for the UASB reactor treating physicochemically pretreated textile wastewater (Fig. 3(a)). It can also be observed from the Fig. 3(a), which even at the same HRT of 16 h, COD removal efficiencies were different for different influent COD concentrations (97% for 500 mg L⁻¹ and 88% for 1,500 mg L⁻¹). Similar trends in the COD removal efficiency were observed for influent COD of 500 and 1,500 mg L⁻¹ at 24 h HRT. Thus, it can be said that interactions between influent COD and HRT play a vital role on the performance of UASB reactor. At a particular HRT, increase in influent COD leads to lower COD removal efficiency. This could be due to improper substrates utilization rate with the increasing organic loading. From Fig. 3(a), it can also be said that there exists an optimum HRT, at which COD utilization rate is maximum. Approximately, a HRT of 20 h was observed to give maximum COD removal efficiency in the case of pretreated textile wastewater.

Similar observations on the COD removal efficiency with the HRT and influent COD were also observed in the UASB reactor treating without pretreated textile wastewater. In this case, a maximum of 92% COD removal was obtained at an HRT of 20 h with an influent COD concentration of 2,000 mg L⁻¹ (Fig. 3(b)). However, at lower HRT, COD removal efficiency was observed to reduce.

It is a well-established fact that the methanogens are slow in biochemical reaction, and thus require sufficient contact time to utilize and/or convert the produced VFAs into methane. This could be the prime reason behind lower COD removal efficiency

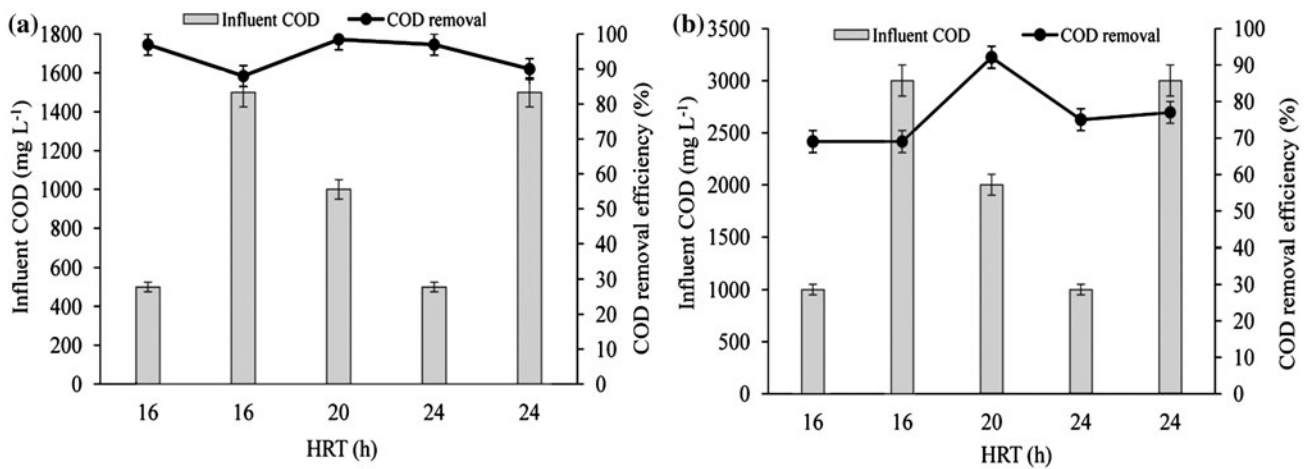


Fig. 3. COD removal efficiencies at different HRTs in UASB reactor treating; (a) physicochemically pretreated and (b) without pretreated textile wastewater.

at lower HRTs. The other possible reasons could be the effect of effective OLRs and inhibition of the microbial activity inside the reactor due to toxicity of dyes [33]. Comparatively, without pretreated textile wastewater possesses higher OLRs at a particular HRT (Table 2) over the physicochemically pretreated textile wastewater, and therefore, the microbial consortia may require a longer contact time for effective utilization of the carbonaceous organics. Similar observations of decrease in COD removal efficiency with increase in HRT were also reported earlier [34,35] for the UASB reactor treating simulated textile wastewater.

3.4. Effect of OLR on the performance of UASB reactor

The effect of OLR on COD and color removal efficiency in UASB reactor treating physicochemically pretreated and without pretreated textile wastewater was shown in Fig. 4. As mentioned previously, nearly complete color removal was observed after physicochemical pretreatment of textile wastewater. The residual COD was eliminated in the UASB reactor under different experimental runs. It can be seen from the Fig. 4(a), which at all the selected OLRs, at least 88% COD removal efficiency was observed including the highest OLR of 2.25 kg COD m⁻³ d⁻¹. As OLR

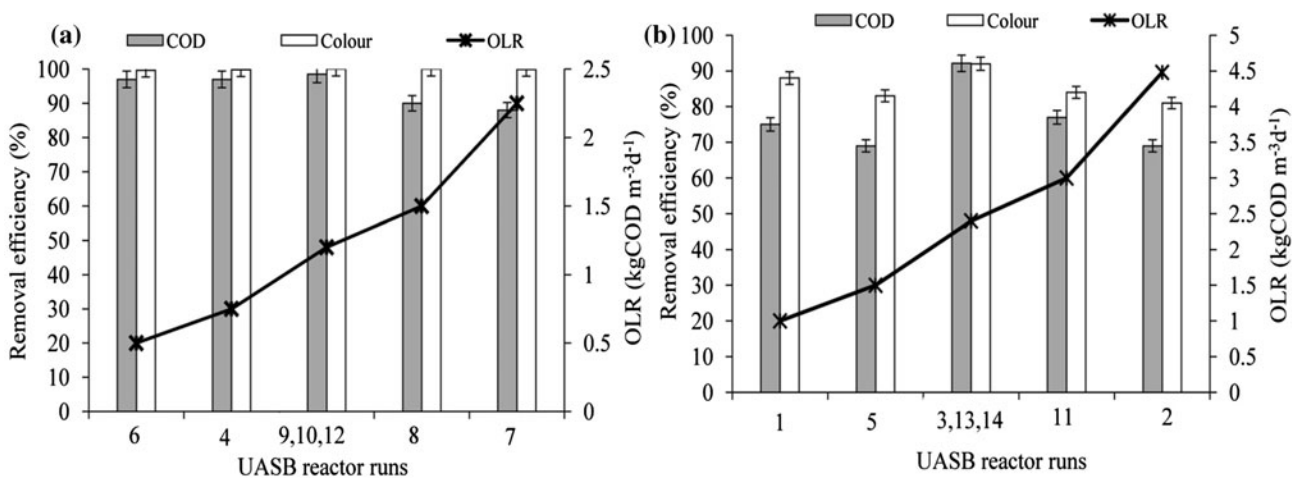


Fig. 4. Effect of OLRs on COD and color removal efficiency in UASB reactor treating; (a) physicochemically pretreated and (b) without pretreated textile wastewater.

increased from 0.5 to 2.25 kg COD m⁻³ d⁻¹, COD removal efficiency decreased from 97 to 88%. However, a maximum COD removal of close to 99% was obtained in the middle at an OLR of 1.2 kg COD m⁻³ d⁻¹ (Fig. 4(a)). The observation may also be related to the superior microbial activity at all the selected OLRs due to nonexistence of toxic dyes and availability of sufficient alkalinity by the pretreatment step to cope up the VFA accumulation inside the UASB reactors.

COD and color removal efficiencies were observed to decrease with increase in the OLR from 1.0 to 1.5 kg COD m⁻³ d⁻¹ (Fig. 4(b)). This was because of the reduction of HRT from 24 to 16 h. Increase in OLR by reducing HRT might have released intermediate metabolites through the decolorization of mixed dyes which could not be mineralized effectively, resulting in lower COD and color removal efficiencies. For UASB reactor treating without pretreated textile wastewater, there exists an OLR (2.4 kg COD m⁻³ d⁻¹) at which the efficiencies were found to be maximum, which might be assumed as an optimum OLR. At this OLR, a maximum of 92% COD as well as color removal efficiency were observed. Beyond the optimum OLR, both the COD and color removal efficiencies were observed to decrease (Fig. 4(b)).

Comparing the COD removal in the UASB reactors treating without pretreated textile wastewater under low and high OLRs, it can be seen that there exists an optimum OLR at which the activity of microbial consortia for substrate utilization appears to be maximum and therefore improves the treatment efficiency of the UASB reactor. Consequently, with low OLR, the reactor seems to be running inefficiently, while with higher OLR beyond optimum, a risk of treatment failure may occur due to the overloading of organics as explained by Chen et al. [36]. In addition to this, low treatment efficiency at high OLRs could probably due to the physiologic inhibition of sludge microbes at high organic loads [37].

The variations in VFA accumulation, B-Alk. and VFA/B-Alk. ratio with increasing OLRs in UASB reactor treating pretreated as well as without pretreated textile wastewater have been shown in Fig. 5. VFA accumulation in the reactor treating pretreated textile wastewater was well below 100 mg L⁻¹ even at the highest OLR of 2.25 kg COD m⁻³ d⁻¹. The observations in Fig. 5(a) depict that there was sufficient alkalinity in UASB reactor throughout its operation under different OLRs. This also indicates the balanced activity of the microbial sludge present inside the reactor. The total alkalinity was sufficient enough to prevent the instability of the UASB reactor by neutralizing the excess VFA.

Comparatively higher and increasing amount of VFA was produced with increase in the OLR from 1 to 4.48 kg COD m⁻³ d⁻¹ in UASB reactor treating without pretreated textile wastewater (Fig. 5(b)). Approximately, 400 mg L⁻¹ VFA was produced at the highest OLR of 4.48 kg COD m⁻³ d⁻¹. However, the alkalinity present inside the reactor for both the cases was sufficient enough to maintain the buffering capacity of the reactors during the operation. The VFA/B-Alk. ratios in the UASB reactor treating both the types of textile wastewater at the selected OLRs were always well below the critical value of 0.4, indicating the stable operation of the reactors [12,38]. The ratios also ensure the effective utilization and mineralization of the produced VFA into methane by the methanogens.

3.5. Variation of COD, color removal efficiency, and production of TAAs with HRT

The effect of HRT on COD and color removal efficiency along with the production of TAAs in the UASB reactor without pretreated textile wastewater has been shown in Fig. 6. As described previously, at an optimum HRT of 20 h and OLR of 2.4 kg COD m⁻³ d⁻¹, a maximum of 92% COD and color removal efficiency were obtained. Fig. 6 also depicts that HRT does not influence much on the color removal efficiency since a promising color removal of more than 80% was obtained at all the selected HRTs.

Thus, it can be said that effective reductive cleavage of azo bond containing dyes can occur even at a lower HRT of 16 h. The decomposition of azo bond occurs under strictly reductive environment by the electrons produced from the carbon sources present in the wastewater [39]. The high color removal could be attributed to the catabolism of sucrose, starch, and other carbonaceous compounds present in the wastewater for the removal of reduced enzyme cofactors through the cleavage of azo bonds as reported by Isik and Sponza [12] and Carliell et al. [40].

The decrease in COD removal efficiency with an increase in TAAs production in the UASB reactor treating without pretreated textile wastewater is evident from Fig. 4. A maximum of 8.1 mg L⁻¹ TAAs in the treated effluent were observed for the reactor operating at an OLR of 4.48 kg COD m⁻³ d⁻¹, producing a minimum COD removal efficiency of 69%. However, the TAAs production diminished with the improvement in COD removal efficiency. The minimum TAAs concentration of 6.9 mg L⁻¹ was observed corresponding to a maximum 92% of COD removal efficiency. The decolorization of textile azo dyes and simultaneous production of aromatic amines under

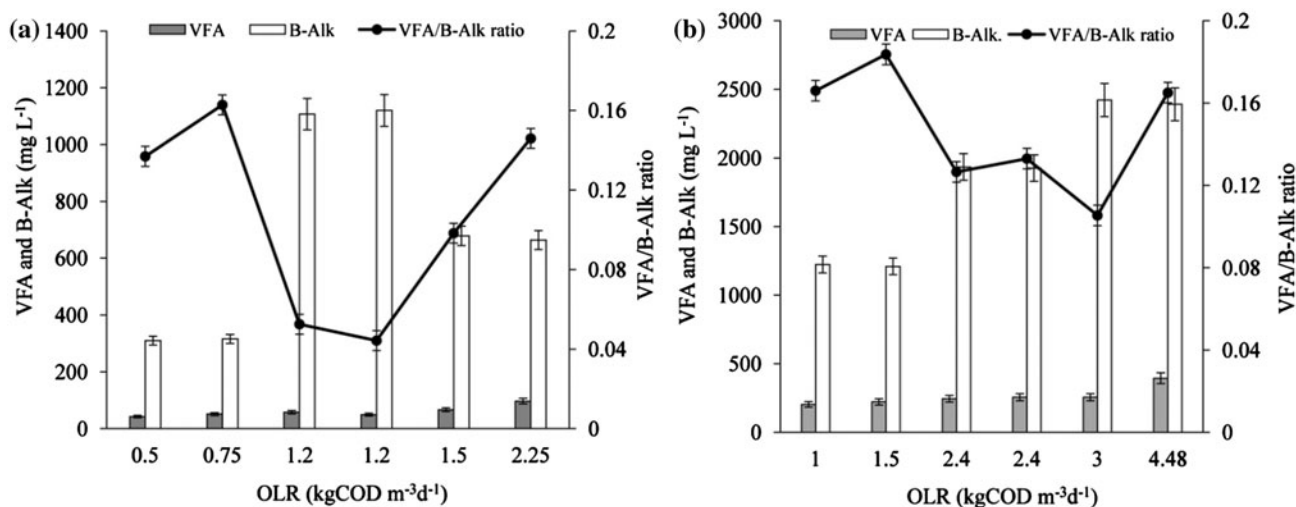


Fig. 5. Effect of increasing OLRs on VFA accumulation, B-Alk., and VFA/B-Alk. ratios in UASB reactor treating; (a) physicochemically pretreated and (b) without pretreated textile wastewater.

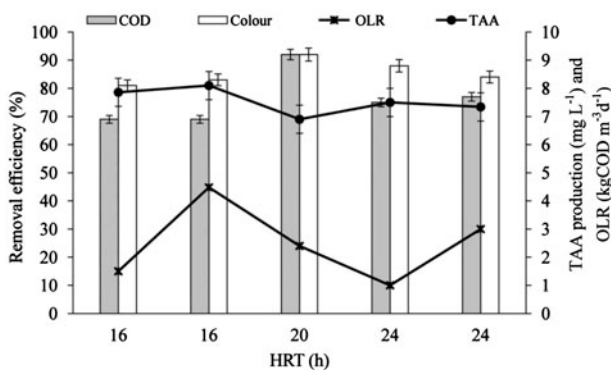


Fig. 6. COD removal efficiency, color removal efficiency, and TAAs production at different HRTs.

reductive environment have already been reported earlier. The production of aromatic amines in the UASB reactor treating textile wastewater containing azo dyes also contributes to COD of the treated effluent [41] and thereby reduces the COD removal efficiency with increasing TAAs concentration. These aromatic amines are recalcitrant in nature and therefore resist further degradation anaerobically [12].

4. Conclusions

The present experimental study demonstrates that the performance of UASB reactor treating physicochemically pretreated textile wastewater was significantly higher than that of without pretreatment. Apart from the pretreatment, the combination of COD and

HRT or more specifically influent OLR plays a vital role on the performance of UASB reactor. The UASB reactor decolorizes textile wastewater efficiently, but at the same time produces significant concentration of carcinogenic aromatic amines. The production of aromatic amines also reduces the COD reduction efficiency of the UASB reactor. A maximum of 99% COD and nearly complete color removal were obtained when physicochemical pretreatment was adopted before UASB reactor. Higher methane fraction in the total biogas also demonstrates the efficacy of physicochemical pretreatment for the treatment of textile wastewater using UASB reactor. The findings not only demonstrate the importance of pretreatment for the performance augmentation of UASB reactor treating textile wastewater but also for the elimination of recalcitrant, carcinogenic, and mutagenic aromatic amines being produced by the UASB reactor.

5. Future scope of research

Significant amount of easily dewaterable sludge produced during physicochemical coagulation of textile wastewater. The investigations on the management and handling of chemical sludge are very much required to establish the complete solution to the pollution remediation due to textile wastewater. Vermicomposting may be one of the options to manage the sludge generated from physicochemical treatment of textile wastewater. The transformation of industrial sludge into vermicompost is of double interest; on the one hand, waste is converted into a value-added product such as fertilizer and, on the other, it manages

waste that is a consequence of increasing industrialization. The solidification of the sludge using some type of binder such as Portland cement, clay, etc. and use of the solidified sludge for useful purpose such as brick making may be the other option. The monitoring of the durability of bricks made in such a way is very much required, which will determine the applicability of this option to manage industrial sludge.

Acknowledgments

The authors would like to acknowledge the funding received from Ministry of Human Resource Development, India and School of Infrastructure, Indian Institute of Technology Bhubaneswar, India, for providing facilities for carrying out research work in the related area.

Abbreviations

UASB	–	upflow anaerobic sludge blanket
HRT	–	hydraulic retention time
COD	–	chemical oxygen demand
BOD	–	biochemical oxygen demand
OLR	–	organic loading rate
TAA _s	–	total aromatic amines
VFA	–	volatile fatty acids
B-Alk.	–	bicarbonate alkalinity
MLSS	–	mixed liquor suspended solids
MLVSS	–	mixed liquor volatile suspended solids

References

- [1] I. Arslan-Alaton, G. Tureli, T. Olmez-Hanci, Treatment of azo dye production wastewaters using photofenton-like advanced oxidation processes: Optimization by response surface methodology, *J. Photochem. Photobiol. A* 202 (2009) 142–153.
- [2] M. Kornaros, G. Lyberatos, Biological treatment of wastewaters from a dye manufacturing company using a trickling filter, *J. Hazard. Mater.* 136 (2006) 95–102.
- [3] B. Manu, S. Chaudhary, Anaerobic decolorization of simulated textile wastewater containing azo dyes, *Bioresour. Technol.* 82 (2002) 225–231.
- [4] G. McMullan, C. Meehan, A. Conneely, N. Kirby, T. Robinson, P. Nigam, I.M. Banat, R. Marchant, W.F. Smyth, Microbial decolourisation and degradation of textile dyes, *Appl. Microbiol. Biotechnol.* 56 (2001) 81–87.
- [5] M. Jonstrup, N. Kumar, M. Murto, B. Mattiasson, Sequential anaerobic–aerobic treatment of azo dyes: Decolourisation and amine degradability, *Desalination* 280 (2011) 339–346.
- [6] H. Øllgaard, L. Frost, J. Galster, O.C. Hansen, Survey of azo-colorants in Denmark: Consumption, use, health and environmental aspects, Danish Environmental Protection Agency. No. 509, 1998, p. 209.
- [7] E.H. Koupaie, M.R. Moghaddam, S.H. Hashemi, Post-treatment of anaerobically degraded azo dye acid red 18 using aerobic moving bed biofilm process: Enhanced removal of aromatic amines, *J. Hazard. Mater.* 195 (2011) 147–154.
- [8] P.L. Skipper, M.Y. Kim, H.L. Patty Sun, G.N. Wogan, S.R. Tannenbaum, Monocyclic aromatic amines as potential human carcinogens: Old is new again, *Carcinogenesis* 31(1) (2010) 50–58.
- [9] USEPA, Screening-level Hazard Characterization: Monocyclic Aromatic Amines Category, Hazard Characterization Document (2009).
- [10] A.K. Verma, P. Bhunia, R.R. Dash, Carbonaceous organics removal kinetics in an upflow anaerobic sludge blanket (UASB) reactor treating physico-chemically pre-treated textile wastewater, *Desalin. Water Treat.* (2014), doi: [10.1080/19443994.2014.888687](https://doi.org/10.1080/19443994.2014.888687).
- [11] Metcalf and Eddy Inc, *Wastewater Engineering: Treatment, Disposal And Reuse*, fourth ed., McGraw Hill Co., New York, NY, 2003.
- [12] M. Isik, D.T. Sponza, Anaerobic/aerobic treatment of simulated textile wastewater, *Sep. Purif. Technol.* 60 (2008) 64–72.
- [13] S. Sandhya, K. Sarayu, K. Swaminathan, Determination of kinetic constants of hybrid textile wastewater treatment system, *Bioresour. Technol.* 99 (2008) 5793–5797.
- [14] A.K. Verma, P. Bhunia, R.R. Dash, Effectiveness of aluminum chlorohydrate (ACH) for decolorization of silk dyebath effluents, *Ind. Eng. Chem. Res.* 51 (2012) 8646–8651.
- [15] F. El-Gohary, A. Tawfik, Decolorization and COD reduction of disperse and reactive dyes wastewater using chemical coagulation followed by sequential batch reactor (SBR) process, *Desalination* 249 (2009) 1159–1164.
- [16] V. Golob, A. Vinder, M. Simonic, Efficiency of coagulation/flocculation method for treatment of dye bath effluents, *Dyes Pigm.* 67 (2005) 93–97.
- [17] A.K. Verma, P. Bhunia, R.R. Dash, Applicability of a new pre-hydrated industrial grade polyaluminium salt for the decolourisation of textile wastewater, *Desalin. Water Treat.* 52 (2014) 4553–4561, doi: [10.1080/19443994.2013.803776](https://doi.org/10.1080/19443994.2013.803776).
- [18] N. Daneshvar, A. Oladegaragoze, N. Djafarzadeh, Decolorization of basic dye solutions by electrocoagulation: An investigation of the effect of operational parameters, *J. Hazard. Mater.* 129 (2006) 116–122.
- [19] Y. Wang, B.Y. Gao, Q.Y. Yue, J.C. Wei, W.Z. Zhou, R. Gu, Color removal from textile industry wastewater using a composite flocculants, *Environ. Technol.* 28 (2007) 629–637.
- [20] B.Y. Gao, Q.Y. Yue, Y. Wang, W.Z. Zhou, Color removal from dye-containing wastewater by magnesium chloride, *J. Environ. Manage.* 82 (2007) 167–172.
- [21] A.K. Verma, P. Bhunia, R.R. Dash, Reclamation of wastewater using composite coagulants: A sustainable solution to the textile industries, *Chem. Eng. Trans.* 42 (2014) 175–180.
- [22] P. Bhunia, M.M. Ghangrekar, Analysis, evaluation, and optimization of kinetic parameters for performance appraisal and design of UASB reactors, *Bioresour. Technol.* 99 (2008) 2132–2140.

- [23] G.K. Anderson, G. Yang, Determination of bicarbonate and total volatile acid concentration in anaerobic digesters using a simple titration, *Water Environ. Res.* 64 (1992) 53–59.
- [24] M.I. Beydilli, S.G. Pavlostathis, W.C. Tincher, Decolorization and toxicity screening of selected reactive azo dyes under methanogenic conditions, *Water Sci. Technol.* 38(4–5) (1998) 225–232.
- [25] E. Razo-Flores, M. Luijten, B. Donlon, G. Lettinga, J. Field, Biodegradation of selected azo dyes under methanogenic conditions, *Water Sci. Technol.* 36(6–7) (1997) 65–72.
- [26] C.K. Lim, H.H. Bay, T.C. Kee, Z.A. Majid, I. Zaharah, Decolourisation of reactive black 5 using *Paenibacillus* sp. immobilised onto macrocomposite, *J. Bioremed. Biodegrad.* S1:004, (2011) (special issue), doi: [10.4172/2155-6199](https://doi.org/10.4172/2155-6199).
- [27] A. Oren, P. Gurevich, Y. Henis, Reduction of nitro substituted aromatic compound by the eubacteria *Haloanaerobium praevalens* and *Sporohalobacter marismortui*, *Appl. Environ. Microbiol.* 57(11) (1991) 3367–3370.
- [28] M. Isik, D.T. Sponza, Aromatic amine degradation in a UASB/CSTR sequential system treating congo red dye, *J. Environ. Sci. Health A Toxic. Hazard. Subst. Environ. Eng.* 38(10) (2003) 2301–2315.
- [29] APHA (American Public Health Association), AWWA (American Water Works Association), WEF (Water Environment Federation), *Standard Methods for the Examination of Water and Wastewater*, twentieth ed., Washington, DC, 1998.
- [30] Z.K. Bagewadi, A.G. Vernekar, A.Y. Patil, A.A. Limaye, V.M. Jain, Biodegradation of industrially important textile dyes by actinomycetes isolated from activated sludge, *Biotechnol. Bioinf. Bioeng.* 1(3) (2011) 351–360.
- [31] Y. Fu, T. Viraraghavan, Fungal decolorization of dye wastewater: A review, *Bioresour. Technol.* 79 (2001) 251–262.
- [32] W.W. Eckenfelder Jr., *Industrial Water Pollution Control*, second ed., McGraw Hill Inc., Singapore, 1989.
- [33] G.F. Chan, N.A. Abdul Rashid, L.L. Koay, S.Y. Chang, W.L. Tan, Identification and optimization of novel NAR-1 bacterial consortium for the biodegradation of Orange II, *Insight Biotechnol.* 1(1) (2011) 7–16.
- [34] C. O’Niell, F.R. Hawkes, D.L. Hawkes, S.R.R. Esteves, S.J. Wilcox, Anaerobic–aerobic biotreatment of simulated textile effluent containing varied ratios of starch and azo dye, *Water Res.* 34(8) (2000) 2355–2361.
- [35] D.T. Sponza, M. Isik, Reactor performance and fate of aromatic amines through decolorization of direct black 38 dye under anaerobic/aerobic sequential, *Process Biochem.* 40 (2005) 35–44.
- [36] Y. Chen, B. Rößler, S. Zielonka, A.M. Wonneberger, A. Lemmer, Effects of organic loading rate on the performance of a pressurized anaerobic filter in two-phase anaerobic digestion, *Energies* 7 (2014) 736–750.
- [37] R.M. Kassa, *Biological Organic Matter and Nutrient Removal from Textile Wastewater Using Anaerobic–Aerobic Bioprocess*, Addis Ababa University School of Graduate Studies Environmental Science Programme, Piazza, Addis Ababa, Ethiopia, 2007.
- [38] E. Behling, A. Diaz, G. Colina, M. Herrera, E. Gutierrez, E. Chacin, E. Fernandez, C.F. Forster, Domestic wastewater treatment using a UASB reactor, *Bioresour. Technol.* 61 (1997) 239–245.
- [39] T.C. Zhang, Y.C. Fu, P.L. Bishop, M. Kuperlc, S. Fitzgerald, H.H. Jiang, C. Harmer, Transport and biodegradation of toxic organics in biofilms, *J. Hazard. Mater.* 41 (1995) 267–285.
- [40] C.M. Carliell, S.J. Barclay, N. Naidoo, C.A. Buckley, D.A. Mulholland, E. Senior, Microbial decolourisation of a reactive azo dye under anaerobic conditions, *Water SA* 21(1) (1995) 61–69.
- [41] V. Murali, S.A. Ong, L.N. Ho, Y.S. Wonga, Evaluation of integrated anaerobic–aerobic biofilm reactor for degradation of azo dye methyl orange, *Bioresour. Technol.* 143 (2013) 104–111.