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Carbonaceous organics removal kinetics in an upflow anaerobic sludge blanket (UASB) reactor treating physico-chemically pre-treated textile wastewater

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ABSTRACT

In the present study, physico-chemically pre-treated textile wastewater with a residual chemical oxygen demand (COD) of $780 \pm 10\,\mathrm{mg\,L^{-1}}$ was treated using a lab-scale upflow anaerobic sludge blanket (UASB) reactor at variable HRTs of 30.8 to 8 h, and organic loading rates (OLRs) of 0.62–2.4 kg COD $\mathrm{m^{-3}\,d^{-1}}$. Using a new composite coagulant at dosage of $800\,\mathrm{mg\,L^{-1}}$ for pre-treatment, more than 99% of colour was removed from the feeding influent to UASB reactor. The optimum OLR was found as 0.95 kg COD $\mathrm{m^{-3}\,d^{-1}}$ at which maximum COD reduction (98%) was achieved. Modified Stover-Kincannon, Grau second-order, Monod, Haldane and Contois models were applied to evaluate the carbonaceous substrate removal kinetics inside the UASB reactor. The experimental results of this analysis revealed that modified Stover-Kincannon and Grau second-order kinetics were suitable for predicting the performance and to estimate the kinetic coefficients of UASB reactor.

Keywords: Composite coagulant; Kinetic modelling; Textile wastewater; UASB reactor

1. Introduction

Textile industries are rapidly increasing to meet the necessities of the growing population and to contribute to the economy of the nation. However, effluents from the textile industries are one of the major sources of environmental pollution and public health concerns, particularly in many urban areas. These effluents are heavily polluted with the complex organic and inorganic chemicals which are used during various steps of textile processing and the unused materials from each process are discharged as wastewater. This wastewater possess strong colour due to the presence of residual dyes, high biological oxygen demand (BOD), chemical oxygen demand (COD), turbidity, pH and toxic chemicals. The presence of a very small concentration of residual dye in water is highly visible and therefore affects the receiving environment not only aesthetically, but also disturbs the aquatic life by obstructing the light penetration and oxygen transfer. The carcinogenic and mutagenic ability of various azo dyes and their precursors produces detrimental effects to the environment [1,2]. Therefore, to protect the water bodies, textile wastewater must be treated up to the safe discharge limits as recommended by USEPA [3].

Various physico-chemical, chemical and biological processes, as well as some of the new emerging

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techniques like sonochemical or advanced oxidation processes are normally used for treating the textile wastewater [4]. However, each of them has some limitations and drawbacks in their applications. Hence, there is no single economically and technically viable method to solve this problem and usually two or three methods have to be combined together in order to achieve adequate level of colour removal [5,6]. One of the effective combinations for the treatment of textile wastewaters is the use of physico-chemical coagulation followed by biological treatment [7]. This integrated process has an advantage to remove most of the dyes through physico-chemical coagulation and also to reduce the carbonaceous organic matters in the form of COD of the wastewater significantly, while biological process further reduce the remaining carbonaceous organics of the wastewater efficiently.

The traditional aerobic biological processes do not effectively decrease the colour of the textile wastewater [8] and also generate large quantity of active biological sludge which needs further treatment before being discharged to the environment. The anaerobic biological processes can be considered as an energy efficient technology as less energy is required for its operation, and biogas is produced as a by-product. These processes were previously used for the treatment of textile wastewaters [9,10], preferably for textile azo dye reduction. However, the azo dye reduction under anaerobic conditions leads to the formation of various types of aromatic amines, which possess the potential toxicity and carcinogenicity [11,12]. USEPA [13] provides the evidence of different types of 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 $49.5\,mg\,L^{-1}$. The carcinogenic effects of these aromatic amines were well explained by numerous researchers [14,15]. Production of these aromatic amines can be avoided using the integrated process of physico-chemical coagulation and anaerobic biological treatments. The suitability of different chemical salts as coagulants for the decolourisation of various types of textile wastewaters has been investigated previously [6,16–18].

Literature shows that studies pertaining to the anaerobic treatment of textile wastewaters are very limited. Also, very limited studies are available on the physico-chemical treatment of synthetic textile wastewater containing majority of chemical additives that are used in textile industries during various steps of textile processing. To the best of our knowledge, no such study in the literature is reported for the evaluation of the upflow anaerobic sludge blanket (UASB) reactor as anaerobic post-treatment phase, treating physico-chemically pre-treated synthetic textile wastewater containing different classes of textile dyes. In this connection, Verma et al. [18] has reported the supremacy of magnesium chloride (MC) for decolourisation of textile wastewater containing various classes of dyes. Further, the effectiveness of a novel aluminium based coagulant as aluminium chlorohydrate (ACH) has also been reported for decolourisation of synthetic as well as real textile effluents [6]. However, the reported dosage of MC was very high to achieve the desired (>99%) degree of colour removal. Therefore, in the present study a composite coagulant, i.e. mixture of MC and ACH, was used for the decolourisation of synthetic wastewater containing various classes of textile dyes such as reactive black 5, disperse blue 3 and congo red along with the other chemical constituents that are normally used during textile processing and found in the texile wastewater. The objective of the present study is to investigate the effectiveness of composite coagulant (MC + ACH) for the pre-treatment of textile wastewater and to evaluate the kinetics of carbonaceous organics removal by the UASB reactor treating physico-chemically pre-treated synthetic textile wastewater using various mathematical models.

2. Materials and methods

2.1. Chemicals

Extra pure MC and industrial grade (purity 30% w/w) aluminium chlorohydrate (ACH) were used as coagulants. 1.0 M H_2SO_4 and NaOH were used to adjust the desired pH. Lime was also used to adjust the optimum pH, since it is well established that lime can be used as a coagulant aid as well as to adjust the desired pH [16]. The other chemical additives used in the preparation of the synthetic wastewater were of analytical grade.

2.2. Textile wastewater

Synthetic textile wastewater was prepared as per the reported chemical constituents of real textile wastewater [19], with a total dye concentration of 200 $mg\,L^{-1}$. The synthetic textile wastewater was prepared by mixing three commercial dyes namely, reactive black 5 (RB5), congo red (CR) and disperse blue 3 (DB3) in tap water, in equal ratio along with the various chemical additives such as starch, acetic acid, sucrose, sodium carbonate, sodium hydroxide, sulphuric acid, detergent, and sodium chloride, which are used during textile processing in textile industries.

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 and the maximum absorbance wavelengths ($\lambda_{\max}$) for RB5, CR and DB3 were found as 591, 502 and 638 nm, respectively. The colour content of the wastewater containing mixture of dyes was determined by taking the sum of the absorbencies measured at 591, 502 and 638 nm [17]. The synthetic textile wastewater was having COD = 1944 to 2007 mg L^{-1}, pH = 10.4 to 10.6, Abs (mixture) = Abs(591) + Abs(502) + Abs(638) = 2.3992.

The percentage decolourisation efficiency was determined using the following Eq. (1):

$$\text{Decolourisation efficiency}\,(\%) = \left[\frac{(A_{\text{b}} - A_t)}{A_{\text{b}}}\right] \times 100 \quad (1)$$

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

2.3. Coagulation and flocculation test procedures

The optimum pH value and coagulant dosage required for efficient colour removal were determined by jar test method. One litre beakers containing 500 mL of wastewater were used for the coagulation experiments. About 1.0 M NaOH or 1.0 M H_2SO_4 was 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 slow flocculation at 30 rpm for 15 min and allowed to settle down for 20 min. The supernatant from the beaker was taken for analysis.

2.4. Description and operation of UASB reactors

Two identical UASB reactors made of Plexiglas having an effective volume of 4.62 L, with the dimension of 80 × 75 × 770 mm were used in the study. Physico-chemically pre-treated textile wastewater was used as an influent for the UASB reactors. The nutrients were added to influent as per the composition suggested by Bhunia and Ghangrekar [20]. Matured cow dung slurry obtained from nearby cattle farm was anaerobically digested by constantly feeding C and N source for one month. The reactors were fed with this digested sludge after having achieved the desired VSS concentration. Mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) of the inoculum were found to be 62.18 and 41.98 g L^{-1}, respectively. Initially, the reactor was operated with the synthetic feed with sucrose as the carbon source equivalent to 1,000 mg L^{-1} COD along with the nutritional composition. After achieving 75% COD reduction with the synthetic feed consisting of sucrose as the sole carbon source, the reactors were fed with physico-chemically pre-treated synthetic textile wastewater. The reactors were operated at room temperature, between 22 and 27 ℃ with five different HRTs of 30.8, 20, 15, 12 and 8 h (reactor 1 was operated at 30.8, 15 and 8 h HRT, and the reactor 2 was operated at the 20 and 12 h HRT) at different organic loading rates (OLRs). The performance of the reactors was monitored regularly till the steady state was achieved.

2.5. Analyses

Colour measurement was carried out after filtration of supernatant, obtained after chemical coagulation, through filter papers. Subsequently, the pH of supernatant sample was adjusted to neutral and then the absorbance of the sample was measured using UV-vis spectrophotometer. The biochemical oxygen demand (BOD_5), total suspended solids (TSS) and total volatile solids (TVS) were measured according to the standard methods [21]. The COD was analysed as per the closed reflux colorimetric method [21] after digestion of the samples in COD reactor (Model DRB 200, HACH, USA) and then absorbance measurement was carried out by COD spectrophotometer at 600 nm (Model DR 2,800, HACH, USA). Total gas and methane gas measurements were carried out using water displacement method as suggested by Isik and Sponza [9]. Bicarbonate alkalinity (B- alkalinity) and volatile fatty acid (VFA) were measured using a titrimetric method as proposed by Anderson and Yang [22]. Aromatic amines were also monitored colorimetrically as per the method suggested by Oren et al. [23]. Total nitrogen in the UASB reactor effluents was measured using persulphate digestion method, proposed and used by Bachman and Canfield [24].

3. Kinetic model description in UASB reactor

Mathematical models are in general used to optimise the plant design, predict the operational performance, and to evaluate the experimental results. Kinetic analysis is an accepted pathway for describing the performance of biological treatment systems and for predicting their performance. A number of models had been used previously for the treatment and operation of different types of wastewaters by UASB reactor [4,8,20,25]. However, to the best of our knowledge, kinetic modelling of UASB reactor treating physicochemically pre-treated synthetic textile wastewater is yet to be established. Therefore, in the present study, different mathematical models namely, modified Stover-Kincannon, Grau second-order, Haldane, Monod and Contois models were studied at the steady states.

3.1. Modified Stover-Kincannon model

This model considers the substrate removal rate as a function of OLR at steady state. The original Stover-Kincannon model is expressed with the Eq. (2) [26].

$$\frac{\mathrm{d}S}{\mathrm{d}t} = U_{\max} \cdot \frac{\left(Q \cdot \left(\frac{S_0}{V}\right)\right)}{K_B + \left(Q \cdot \left(\frac{S_0}{V}\right)\right)} \tag{2}$$

where $\mathrm{d}S/\mathrm{d}t$ is defined as Eq. 3.

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{Q}{V} \cdot (S_0 - S_e) \tag{3}$$

linearisation of Eqs. (2) and (3) yields Eq. (4)

$$\frac{V}{Q \cdot (S_0 - S_e)} = \frac{K_B}{U_{\max}} \frac{V}{Q \cdot S_0} + \frac{1}{U_{\max}} \tag{4}$$

The plot of $\frac{V}{Q \cdot (S_0 - S_e)}$ vs. $\frac{V}{Q \cdot S}$ will be a straight line. The intercept and the slope of this line will give $\frac{1}{U_{\max}}$ and $\frac{K_B}{U_{\max}}$, respectively.

3.2. Grau second-order multi-component substrate removal model

The general equation of the second-order kinetic model is exemplified in Eq. (5) [27]:

$$-\frac{\mathrm{d}S}{\mathrm{d}t} = k_s \cdot X \cdot \left(\frac{S_e}{S_0}\right)^2 \tag{5}$$

Integrated and linearised form of Eq. (5) is represented as Eq. (6):

$$\frac{S_0 \cdot \theta_H}{S_0 - S_e} = \theta_H - \frac{S_0}{k_s \cdot X} \tag{6}$$

Considering the second term of the right part of Eq. (6) as a constant, the Eq. (7) will be obtained [27].

$$\frac{S_0 \cdot \theta_H}{S_0 - S_e} = b \cdot \theta_H + a \tag{7}$$

$\frac{(S_0 - S_e)}{S_0}$ represents the substrate removal efficiency and is symbolised as "*E*". Therefore, Eq. (7) can be written as:

$$\frac{\theta_H}{E} = a + b \cdot \theta_H \tag{8}$$

From the linearised plot of Eq. (8), the constants "*a*", "*b*" and k_s can be obtained. The coefficient "*b*" in Eq. (8) is close to one and generally reflects the impracticality of attaining a zero value of COD.

3.3. Monod kinetic model

The rate of change of biomass and substrate in UASB reactor without biomass recycle can be expressed as Eqs. (9) and (10):

$$\frac{\mathrm{d}X}{\mathrm{d}t} = \frac{Q}{V_b} \cdot X_0 - \frac{Q}{V_b} \cdot X_e + \mu \cdot X - K_d \cdot X \tag{9}$$

$$-\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{Q}{V_b} \cdot S_0 - \frac{Q}{V_b} \cdot S_e - \frac{\mu \cdot X}{Y} \tag{10}$$

The ratio of the total biomass in the reactor to the biomass wasted per given time is called as mean cell residence time (θ_c) or sludge retention time (SRT) and calculated from the following equation:

$$\theta_c = \frac{V_b \cdot X}{Q \cdot X_e} \tag{11}$$

Specific growth rate and the concentration of rate limiting substrate can be related by Monod equation as follows:

$$\mu = \frac{\mu_m \cdot S_e}{K_s + S_e} \tag{12}$$

The concentration of the biomass in the influent X_0 can be considered as negligible at steady-state conditions, Therefore, at steady state, the following equation can be obtained after substitution of Eq. (12) in Eq. (9),

$$\frac{Q \cdot (S_0 - S_e)}{V_b . X} = \frac{1}{Y} \cdot \left(\frac{1}{\theta_c}\right) + \frac{1}{Y} \cdot K_d \tag{13}$$

The plot of $\frac{Q \cdot (S_0 - S_e)}{V_b \cdot X}$ vs. $\frac{1}{\theta_c}$ will be linear one and from this the kinetic constants Y and K_d can be determined.

3.4. Contois kinetic model

Contois model is a modification over the Monod model. In case of Contois model, cell mass growth rate depends upon the concentrations of both substrate and cell mass, and growth rate is inhibited at high concentrations of the cell mass. According to the Contois kinetic model:

$$\mu = \frac{\mu_m S_e}{\beta X + S_e} \qquad (14)$$

The substitution of Eq. (14) in Eq. (10) and linearisation gives:

$$\frac{V_b \cdot S_e}{Q \cdot Y \cdot (S_0 - S_e)} = \frac{1}{\mu_m}\left(\frac{S_e}{X}\right) + \frac{\beta}{\mu_m} \qquad (15)$$

The values of kinetic constants, μ_m and β can be obtained from the intercept and slope of the plot $\frac{V_b \cdot S_e}{Q \cdot Y \cdot (S_0 - S_e)}$ vs. $\left(\frac{S_e}{X}\right)$ s as per Eq. (15).

3.5. Haldane model

The Haldane equation has been widely used to describe substrate inhibition kinetics and biodegradation of inhibitory substrates. The Haldane kinetic model follows the equation as stated in Eq. (16) [20,28]:

$$\mu = \frac{\mu_m}{1 + \frac{K_s}{S_e} + \frac{S_e}{K_i}} \qquad (16)$$

At steady-state condition, the substrate balance for the UASB reactor as per Eq. (10) gives Eq. (17):

$$\frac{V_b \cdot S_e \cdot X}{Q \cdot (S_0 - S_e)} = \frac{(S_e)^2}{K_i \cdot k} + \frac{S_e}{k} + \frac{K_e}{k} \qquad (17)$$

where "k" represents the maximum specific substrate utilisation rate.

4. Results and discussions

4.1. Pre-treatment of synthetic textile wastewater using composite coagulant

pH plays a very important role in determining the efficiency of the coagulation process. The optimum pH for MC and ACH was investigated and reported as 9 and 12, respectively, by Verma et al. [18]. In the present study, the optimum pH for the composite coagulant was determined as 12. Lime was applied to adjust the pH of the solution up to optimum pH for further treatments using composite coagulant, since lime possess the dual characteristics, i.e. act as a coagulant aid and also increases the pH [16]. The optimum dosage of composite coagulant for efficient chemical coagulation of textile wastewater was determined by varying the coagulant dosage with two different ratios of MC + ACH (1:1) and MC + ACH (1.5:1). During the experiment, it was observed that higher dosage of composite coagulant was required to produce virtually colourless treated effluent, when composite coagulant was used in the ratio of MC + ACH as 1:1. MC was reported as a highly effective coagulant in the removal of reactive dyes as compared to ACH [18]. Therefore, the concentration of MC in the composite coagulant was increased (in the ratio of MC + ACH as 1.5:1) in view of decreasing the dosage of composite coagulant effectively by precipitating the reactive dyes present in the wastewater.

Decolourisation efficiency as a function of coagulant dosage for both the coagulant combinations is shown in Fig. 1. From Fig. 1, decoulourisation efficiencies of 99.66% and 99.85% were found for the combinations MC + ACH (1:1) and MC + ACH (1.5:1), respectively, at a dosage of 1,200 mg L^{-1}.

Although the removal efficiency by MC + ACH (1.5:1) was marginally higher as compared to MC + ACH (1:1) at the dosage of 1,200 mg L^{-1}, a very high decolourisation efficiency of around 98% was observed at a dosage of 600 mg L^{-1} of MC + ACH (1.5:1). At the same dosage (600 mg L^{-1}), 85% decolourisation efficiency was observed in case of composite coagulant MC + ACH (1:1), which is much lesser than the efficiency achieved by MC + ACH (1.5:1). Moreover, the excellent colour removal close to 99% was observed at

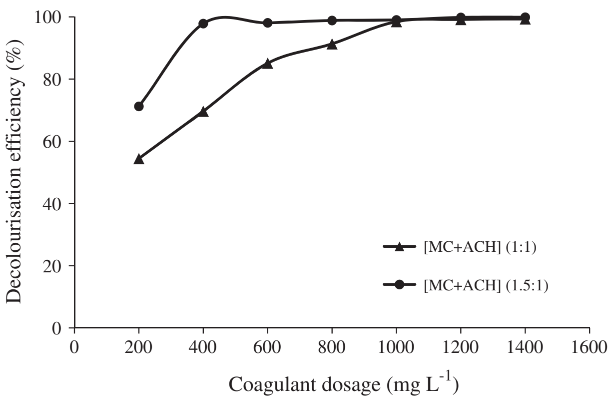

Fig. 1. Effect of composite coagulant dosage on decolourisation efficiency at two different ratios.

800 mg L^{-1} combined dosage of MC + ACH (1.5:1), which was far superior over the colour removal (~ 91%) produced by MC + ACH (1:1) at the same dosage. Therefore, the combination MC + ACH (1.5:1) was considered as the best composite coagulant at the optimum pH and a dosage of 12 and 800 mg L^{-1}, respectively. The maximum COD reduction efficiency of 55% was obtained at the optimised conditions. As the residual COD in the pre-treated wastewater is higher than the recommended limits of different countries, the wastewater must further be treated to meet the safe discharge limit.

4.2. Reactor performance

The reactors were operated at five different hydraulic retention times (HRTs) with the physico-chemically pre-treated textile wastewater to evaluate the kinetic coefficients of different kinetic models. The UASB reactors 1 and 2 were first operated simultaneously at HRT of 30.8 and 15 h, respectively. Once steady state is reached, the reactors were operated at the HRT of 20 and 12 h (for reactor 1) and at HRT of 8 h (for reactor 2). Different parameters which were measured at steady-state conditions are summarised in Table 1.

A logically justified relationship between most of the parameters monitored and HRT at steady state can be observed from the Table 1. As HRT decreased from 30.8 h to 8 h, the pH and B-Alkalinity levels also decreased, respectively, from 7.4 and 1,145 mg L^{-1} to 7.2 and 1,025 mg L^{-1}, whereas the VFA concentration increased from 50 to 140 mg L^{-1}. It was expected that the methanogens, which are slow in biochemical reaction, would not be getting sufficient contact time at lower HRTs to convert the produced VFAs into methane completely and hence, resulted in the accumulation of VFA. The variation of pH was not much significant and pH remained within the optimal range for anaerobic conditions. This is due to the fact that all the reactors were operated with sufficient buffering capacity, which is evident from the data of influent and effluent B-Alkalinity presented in Table 1.

VFAs were produced as the precursors during anaerobic stabilisation of the organic matter, which resulted in the drop of pH inside the reactor. Since methanogens are very sensitive to the variation in pH, it was required to provide the buffering environment by adding suitable concentration of buffering agent. Buffering conditions were maintained by the neutralisation of hydrogen ions released with the B-Alkalinity present inside the UASB reactor [4]. The highest VFA/B-Alkalinity ratio was observed as 0.13 at the HRT of 8 h, which is well below the ratio required (0.4) for maintaining the stability of UASB reactor. Highest COD removal efficiency of 98% was observed at the HRT of 30.8 and 20 h, which then decreased to 71% at an HRT of 8 h. The increased level of VFAs at the decreased HRTs (or at the increased OLRs) may be related to the imbalance in the activity of acetogens and methanogens for the further conversion of VFAs to produce methane gas. The BOD_5 of effluents and total N was increased with a decrease in the HRT; however, at HRT of 20 h, a reverse response was observed producing only 25 mg L^{-1} BOD_5 and 7.9 mg L^{-1} total N in the effluent. Based on these observations, it can be said that

Table 1
Steady-state experimental performance at different HRTs

	HRTs (h)				
Parameter	30.8	20	15	12	8
Influent pH	7.5 ± 0.1	7.5 ± 0.1	7.5 ± 0.1	7.5 ± 0.1	7.5 ± 0.1
Effluent pH	7.4 ± 0.1	7.4 ± 0.1	7.3 ± 0.1	7.3 ± 0.05	7.2 ± 0.1
Influent B-Alkalinity (mg L^{-1} as $CaCO_3$)	1,150 ± 10	1,130 ± 10	1,150 ± 10	1,130 ± 10	1,130 ± 10
Effluent B-Alkalinity (mg L^{-1} as $CaCO_3$)	1,145 ± 15	1,120 ± 15	1,080 ± 20	1,065 ± 15	1,025 ± 15
Effluent VFA (mg L^{-1} as CH_3COOH)	50 ± 5	55 ± 10	60 ± 5	110 ± 10	140 ± 10
Influent COD (mg L^{-1})	770 ± 10	790 ± 10	770 ± 10	790 ± 10	790 ± 10
COD reduction (%)	97.5 ± 1.5	98 ± 1.0	88 ± 1.5	82 ± 1.0	71 ± 2
OLR (kg COD m^{-3} d^{-1})	0.60	0.95	1.23	1.57	2.36
Effluent BOD_5 (mg L^{-1})	30 ± 5	25 ± 5	45 ± 5	55 ± 5	65 ± 5
Total N_{effluent} (mg L^{-1})	8.5 ± 0.3	7.9 ± 0.2	9.1 ± 0.2	13.2 ± 0.2	16.4 ± 0.5
Total aromatic amines (mg L^{-1})	BDL	BDL	BDL	BDL	BDL
Total gas production rate (mL d^{-1})	1,550 ± 50	2,355 ± 60	2,890 ± 55	3,470 ± 70	4,680 ± 60
Methane gas production rate (mL d^{-1})	735 ± 25	1,020 ± 30	1,135 ± 30	1,320 ± 35	1,650 ± 25
Operation period to achieve steady state (d)	42	34	47	35	35

the optimum operating HRT of UASB reactor treating physico-chemically pre-treated textile wastewater is 20 h at an OLR of 0.95 kg COD m^{-3} d^{-1}.

Total gas production and methane gas production were 1,550 and 755 mL d^{-1}, respectively, at the HRT of 30.8 h; whereas at HRT of 8 h, these parameters were increased to 4,680 and 1,550 mL d^{-1}, respectively. It can be seen that methane gas fraction in the total gas decreased from 51.29 to 35.25% with the increase in the OLR from 0.6 to 2.3 kg COD m^{-3} d^{-1}. This indicates the slight imbalance of the UASB process in which the rate of acid formation (VFAs) exceeds the rate of breakdown of VFAs to methane with increasing OLRs and thereby drops the percentage methane content. In addition to this, VFA accumulation at increasing OLRs produces a significant amount of carbon dioxide and therefore results in the decrease in the methane content [9]. The theoretical methane gas production rates at the selected HRTs of 30.8, 20, 15, 12 and 8 h were calculated as 1.01, 1.63, 1.90, 2.26 and 2.9 L d^{-1}, respectively [5]. The lesser experimental methane gas production rates of the order from 27 to 40% as compared to the theoretical methane gas production rates as per the stochiometric relationship may be related to the loss of soluble methane gas in dissolved form along with the effluent.

For the reactor with HRT of 30.8 and 15 h, the time taken to achieve steady state was more than the reactor having operating HRT of 20, 12 and 8 h. The change-over of the HRTs to 20 h, 12 h and then to 8 h was made to the reactors having operated for the HRT of 30.8 and 15 h only after achieving the steady state from the day when these were inoculated for the first time with seed sludge. Hence, the reactors 1 and 2 with HRT of 30.8 and 15 h, respectively, required the excess acclimatisation time compared to the runs with HRT of 20, 12 and 8 h which were operated with the pre-acclimatised sludge remained at the end of steady-state operation at HRT of 30.8 and 15 h. Almost all the observed results of this study are in good agreement with the results reported by few researchers [4,29].

4.3. Kinetic coefficients of different kinetic models

4.3.1. Modified Stover-Kincannon model

Different kinetic parameters were evaluated for five different HRTs at the steady states for all the models. Fig. 2 is plotted as per the Eq. (4) between reciprocal of organic loading removal rate and reciprocal of the total organic loading rate for determining the values of maximum utilisation rate $U_{\max}$ and saturation value constant (K_B). The linear regression method produced the values of kinetic parameters as 4.84 and 4.27 g L^{-1} d^{-1} for and $U_{\max}$ and K_B, respectively, with a very high correlation coefficient (*R*) of 0.993.

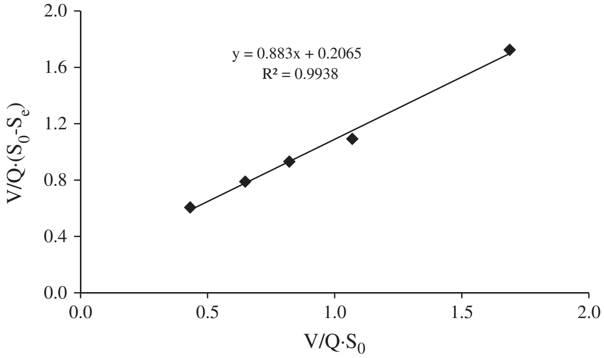

Fig. 2. Modified Stover-Kincannon model plot.

The calculated values indicate the substrate removed by the anaerobic consortia during the given time and thereby reflects the biodegradability of the organic matter under the current operating conditions [30]. The determined values of kinetic parameters are in good agreement with the results reported by Isik and Sponza [4], who had performed the kinetic modelling of UASB reactor treating simulated textile wastewater. Turkdogan-Aydinol et al. [31] have also reported the results of kinetic modelling of UASB reactor treating municipal wastewater at low temperature and found the values of $U_{\max}$ and K_B, respectively, as 1.996 and 1.536 g L^{-1} d^{-1}. The difference in the values of the kinetic parameters in the present study compared to Turkdogan-Aydinol et al. [31] may be due to different operating conditions and characteristics of wastewater used.

4.3.2. Grau second-order multi-component substrate removal model

In order to find out the kinetic coefficients (*a*, *b* and k_s), Fig. 3 is plotted as per the Eq. (7) and the values of kinetic coefficients were calculated from the intercept and the slope of straight line on the graph. The values of *a* and *b* were found to be 0.162 and 0.8786, respectively, with a very high correlation coefficient (R^2) of 0.994. The average value of k_s as calculated as 0.1 d^{-1} using the equation $a = S_0/(k_s \cdot X)$ which reflects the substrate removal rate for each unit of microorganism. Effluent substrate concentration can be determined by rearranging and substituting the value of "*a*" and "*b*" in Eq. (7). Eq. (18) can be used for predicting the effluent carbonaceous organics in physico-chemically pre-treated textile wastewater.

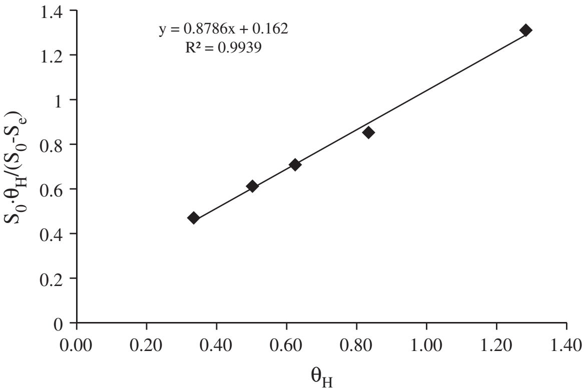

Fig. 3. Grau second-order model to determine the kinetic coefficients.

$$S_e = S_0\left(1 - \frac{\theta_H}{0.162 + 0.8786\ \theta_H}\right) \tag{18}$$

The observed value of k_s in the present study is lesser than the value of k_s reported in previous studies by Isik and Sponza [4] and Ubay [32]. This can be attributed to the fact that k_s highly depends on the initial substrate and microorganism concentration [4]. The initial substrate concentration in those previous studies was far greater than that of the present study and thereby resulted in the smaller k_s value.

4.3.3. Monod kinetic model

To determine the kinetic parameters of Monod, Eq. (13) has been plotted in Fig. 4. The values of Monod kinetic coefficients, Y and K_d, were calculated as 0.375 g VSS g COD^{-1}, and 0.0044 d^{-1}, respectively, from the intercept and slope of the straight line presented in Fig. 4.

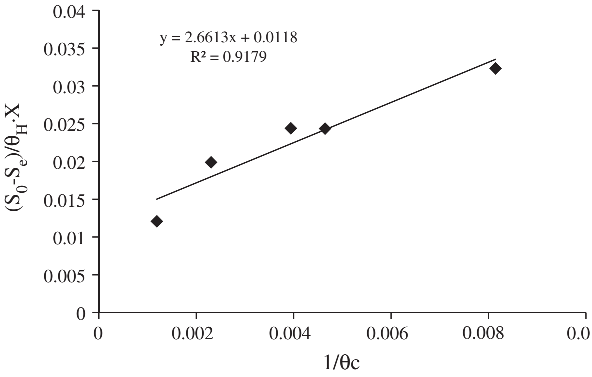

Fig. 4. Determination of yield coefficient (Y) and death rate constant (K_d) of Monod model.

The value of sludge yield Y was found to be higher than the reported value for the acetoclastic methanogens (0.01−0.05 g VSS g COD^{-1}) and acidogens (0.14−0.17 g VSS g COD^{-1}) [8,20,33]. The possible reason of this variation may be related to the determination of the overall yield for the mixed cultures in the present study. The endogenous decay coefficient was observed in the lower side of the range reported for the acetoclastic methanogens (0.004–0.037 d^{-1}) [20,33]. The slightly lesser value of the maximum specific growth rate constant in the present study as compared to the reported range for acetoclastic methanogens (0.041–0.912 d^{-1}) [20,34,35] may be related to the use of mixed cultures and comparatively reduced operating temperature of UASB reactor.

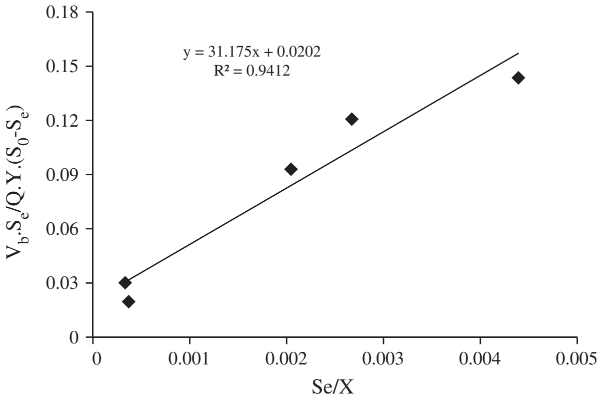

Fig. 5. Determination of maximum specific growth rate (μ_m) and kinetic coefficient (β) of Contois model.

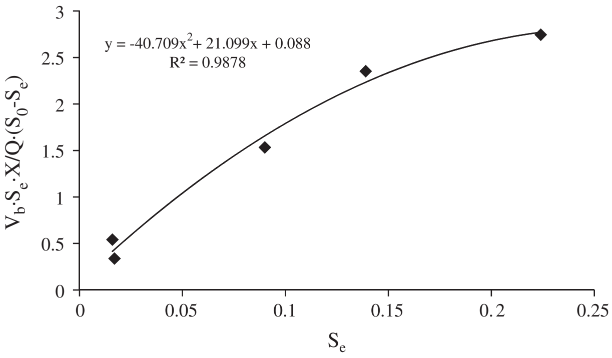

Fig. 6. Determination of kinetic coefficients for Haldane model.

Table 2
Comparison of kinetic coefficients as per the modified Stover Kincannon, Grau second-order, Monod, Contois and Haldane model

Model	Reactor type	Wastewater type	HRT (h)	OLR (kg COD m^{-3} d^{-1})	Kinetic parameters			References
					U_{max} L^{-1} d^{-1})	K_B L^{-1} d^{-1})		
Modified Stover Kincannon	Hybrid batch fed moving bed	Synthetic phenolic wastewater			1.0	1.4		[37]
	UASB	Synthetic textile wastewater	6–100	1.01–16.86	7.5	8.2		[4]
	UASB	Municipal wastewater	5–24	11.78–0.57	1.996	1.536		[31]
	Microaerophilic – aerobic hybrid	Real textile wastewater	55.2–218.4	16.4–2.6	212	22.89		[10]
	UAFB	Formaldehyde-containing wastewater	10–24	0.18–3.61	3.4	4.6		[38]
	UAF	Fruit canning wastewater	12	19	109.9	53.5		[39]
	BFFR	Distillery spent wash	432–480	5.0–20.0	2.0	1.69		[40]
	UASB	Physico-chemically pre-treated synthetic textile wastewater	8–30.8	0.62–2.4	4.84	4.27		Present Study
Grau second-order					k_s	a	b	
	Hybrid batch fed moving bed	Synthetic phenolic wastewater				2.39	1.114	[37]
	UASB	Synthetic textile wastewater	6–100	1.01–16.86	0.337	0.562	1.095	[4]
	Hybrid UASB	Synthetic coal wastewater	18–36	0.5–1.0	1.72	0.078	0.964	[41]
	UAFB	Formaldehyde-containing wastewater	10–24	0.18–3.61	0.133	0.64	9.36	[38]
	UASB	Physico-chemically pre-treated synthetic textile wastewater	8–30.8	0.62–2.4	0.1	0.162	0.8786	Present Study
Monod					Y	K_d		
	Anaerobic batch reactor	Synthetic textile wastewater	240		0.115 −3.174	0.000125 −0.006		[8]
	MSBR	Dairy wastewater			0.228	0.138		[42]
	UASB	Physico-chemically pre-treated synthetic textile wastewater	8–30.8	0.62–2.4	0.375	0.0044		Present study
Contois					μ_m	β		
	UASB	Synthetic textile wastewater	6–100	1.01–16.86	0.105	0.465		[4]
	UASB	Mixed industrial and municipal wastewater	21.6–345.6	0.848–0.44	0.013	0.021		[43]
	UASB	Physico-chemically pre-treated synthetic textile wastewater	8–30.8	0.62–2.4	0.032	0.65		Present study
Haldane					μ_m	K_s	K_i	
	Anaerobic batch reactor	Synthetic textile wastewater			0.0015–0.006	651.04–1372.88	5121.56–18727.59	[8]
	UASB	Synthetic wastewater (sucrose)	4–8	1.85–3.5	0.55	167.11	3636.36	[20]
	UASB	Physico-chemically pre-treated synthetic textile wastewater	8–30.8	0.62–2.4	0.047	4.17	523	Present Study

4.3.4. Contois model

Contois model is a modified form of Monod model. Eq. (15) was plotted in Fig. 5 to determine the value of kinetic parameters (β and μ_m). The values of μ_m, and β were calculated from the Fig. 5 as 0.032 d^{-1} and 0.65 mg COD mg VSS^{-1}, respectively.

In this study, the obtained value of the Contois coefficient (β) is lower than the value reported by few researchers [4,36]. Some of the possible reasons may be the difference in the reactor configuration, type of wastewaters, initial substrate concentration and type of anaerobic culture used for UASB operation.

4.3.5. Haldane model

To obtain the kinetic coefficients (k, K_s and K_i) of Haldane model, Fig. 6 was plotted as per the Eq. (17) using second-order polynomial regression method. The values of k, K_s and K_i were found to be 0.047 d^{-1}, 4.17 mg L^{-1} and 523 mg L^{-1}, respectively, with a very high correlation coefficient (R^2) of 0.987. Smaller value of K_i as compared to the influent COD indicates the minor inhibition effect inside the reactor for the influent COD concentration beyond 523 mg L^{-1}. This could be due to the presence of a small quantity of residual dyes in the influent after physico-chemical pre-treatment.

The values of kinetic parameters of the present study are smaller compared to the studies reported by Bhunia and Ghangrekar [20]. One of the likely reasons of this difference may be linked to the difference in the type of wastewater being treated in the UASB reactor and operating conditions.

4.4. Comparative evaluation of investigated kinetic models in the biological reactors

Kinetic parameters of different kinetic models in the present study were compared to the pre-investigated kinetic models in different bioreactors. As seen in Table 2, the presented kinetic data depict that the performance of different types of biological process can be assessed using different types of kinetic models.

A wide range of variation can be seen in the values of kinetic coefficient of different models summarised here (Table 2). Compared with the present study, the values of maximum removal rate constant (U_{max}) and saturation value constant (K_B) as per the modified Stover-Kincannon are higher than the values reported by few researchers [31,40] for the treatment of municipal wastewater and distillery spent wash using UASB reactor and BFFR, respectively. However, several researchers reported the higher values of these parameters for the treatment of different types of wastewater in the different reactors [10,39]. It is also important to note that, for similar organic loadings and operating conditions, the kinetic parameters obtained for formaldehyde-containing wastewater [38] are entirely different for pre-treated textile wastewater (present study), and cannot be correlated. Similarly, the kinetic coefficients obtained for Grau second-order, Monod, Contois and Haldane model were also found to be different in the pre-established studies. The reasons behind the observed variations in the values of the kinetic parameters may be attributed to the fact that substrate removal rates not only depend on the operating conditions but also on the reactor configuration, type of microorganism culture and the nature of substrate [39].

5. Conclusion

From the present study, it is concluded that carbonaceous organics could be removed effectively from physico-chemically (using composite coagulant) pre-treated textile wastewater using an UASB reactor operated at variable HRTs and organic loading rates. The observation of an increase in VFA and the decrease in the percentage methane content of the total biogas with a decrease in HRT (and increase in OLR) indicates an imbalance between acidogenesis and methanogenesis with a relatively higher rate of acidogenesis inside the UASB reactor. Out of different kinetic models investigated in the study, the modified Stover-Kincannon and Grau second-order kinetic models were observed to be the best fit for the carbonaceous substrate removal with a correlation coefficient close to 0.994. The microbial growth kinetics of UASB reactor could be better described by the Contois type kinetic model.

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Symbols

S_0 — influent substrate concentration (g L^{-1})
S_e — effluent substrate concentration (g L^{-1})
Q — inflow rate (L d^{-1})
V — reactor volume (L)
V_b — sludge bed volume (L)

K_B — saturation value constant ($g\,L^{-1}\,d^{-1}$)
U_{max} — maximum substrate utilisation rate ($g\,L^{-1}\,d^{-1}$)
k_s — Grau second-order substrate removal rate constant (d^{-1})
X_0 — biomass concentration in influent wastewater ($g\,L^{-1}$)
X — biomass concentration in reactor ($g\,L^{-1}$)
X_e — biomass concentration in effluent wastewater ($g\,L^{-1}$)
θ_H — hydraulic retention time (d^{-1})
a, b — kinetic constant for Grau second-order model
μ — specific growth rate (d^{-1})
μ_m — maximum specific growth rate (d^{-1})
K_s — half saturation constant ($g\,L^{-1}$)
K_i — inhibition constant ($g\,L^{-1}$or $mg\,L^{-1}$)
k — maximum specific substrate utilisation rate (d^{-1})
K_d — endogenous decay constant (d^{-1})
Y — Yield coefficient (g VSS g COD^{-1})
θ_c — mean cell residence time (d)
β — kinetic parameter for Contois model (g COD g VSS^{-1})

Abbreviations

LC_{50} — lethal concentration, resulting in 50% mortality
BDL — below detection level
UAFB — upflow anaerobic fixed film
BFFR — biphasic fixed film bioreactor
UAF — upflow anaerobic filter
MSBR — membrane sequencing batch reactor

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