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Kinetic analysis of treatment of textile wastewater in hybrid column upflow anaerobic fixed bed reactor

S. Sandhya*, K. Swaminathan

National Environmental Engineering Research Institute, CSIR-Complex, Chennai-600113, India

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Abstract

Treatment of textile wastewater is considered to be difficult by traditional systems. The present study is related to treatment of textile wastewater in an anaerobic reactor. The study showed the effectiveness of biological treatment of wastewater involving appropriate microorganism and suitable support media in a hybrid column, upflow anaerobic fixed bed (UAFB) reactor. COD and color were reduced to 84.80%, and 90% for textile wastewater. The reactor was operated at 1.038–8.21 g COD m^{-3} d^{-1} of loading and found that 81.58% COD and 86.22% color removal at the highest loading rate. At steady state under anaerobic condition, color was effectively removed. Biokinetic models were applied to data obtained from experimental studies in UAFB reactor. Treatment efficiencies of the reactor were investigated at different hydraulic retention times (9.6–23.76 h) and organic loading rates (1.038–8.21 g COD m^{-3} d^{-1}). Second-order and a Stover–Kincannon models were best fitted to the hybrid column reactor. The second-order substrate removal rate constant ($k_{2(S)}$) was found as 10.50 h^{-1} for UAFB. Applying the modified Stover–Kincannon model to the UAFB reactor, the maximum removal rate constant (U_{max}) and saturation value constant (K_B) were found to be 31.69 and 45.37 g d^{-1}, respectively.

Keywords: Textile wastewater; Anaerobic; Kinetic; Modeling

1. Introduction

The textile industry consumes large amount of water, energy and auxiliary chemicals. In India, an average mill producing 60×10^4 m of fabric per day is likely to discharge approximately 1.5 million liters per day of effluent [1] and the wastewater is drained into natural water bodies without proper treatment. Under typical reactive dyeing conditions, 20–50% of the dye remains in the spend dye bath in its unfixed hydrolyzed form, which has no affinity for fabric, resulting in colored effluents [2,3]. Untreated effluents from textile industries are usually highly colored and in particularly objectionable if discharged in open water. Stringent environmental regulation for the control of textile effluents is enforced in several countries [4,5]. The textile wastewater is of various color shades depending upon the demand of colored fabric. Important pollutants in textile effluent mainly are organics, color, toxicants and inhibitory compounds, surfactants, chlorinated compounds (AOX), pH and salts amongst which colored dyes are the most troublesome constituents of the wastewater. It is difficult to remove color from the effluents by conventional wastewater treatment systems. Considering both the volume generated and the effluent composition, the textile industry wastewater is rated as the most polluting amongst all industrial sectors. Previous studies showed that various combination of biological and physico-chemical treatment processes decolorize the wastewater but generate huge quantity of sludge [6,7]. Several emerging technologies such as electrochemical destruction [8] advanced oxidation [9] and sorption [10] have potential for decolorization. However, these approaches often involve complicated procedures or are not economically feasible. Recently reports are available for treatment of real textile wastewater in anaerobic treatment systems [11]. The traditional aerobic treatment system does not substantially decrease the coloration of these wastewaters [12], while a number of research reports demonstrated the effectiveness of anaerobic decolorization with digester sludge [13], anaerobic granular sludge [14] or sediments [15]. Anaerobic treatment alone has been shown to remove COD from textile effluents [16] and has the advantage of lower sludge formation and energy demand compared to aerobic treatment. Decolorization of textile dye stuffs have been carried out in UAFB reactor and high decolorization efficiencies were obtained [17,18]. Under anaer-

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* Corresponding author. Tel.: +91 44 22 541 964.
E-mail address: sswami_in@yahoo.com (S. Sandhya).

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obic conditions azo dyes are readily cleaved via a four-electron reduction at azo linkage generating aromatic amines. These steps remove color of the wastewater; however, do not completely mineralize the aromatic amines generated [19,20] with a few exception [14]. In the present study, UAFB was used in the treatment of textile wastewater and different operational parameters were evaluated including hydraulic retention time, initial organic loading. Determination of kinetic constants of a bioprocess is a useful tool to describe and to predict the performance of the system. UAFB reactor was operated continuously at different COD loading rates in order to evaluate the decolorization performance and to determine kinetic constants. Different mathematical models, including Monod model, second-order kinetic model, Stover–Kincannon model, were applied to the reactor and kinetic coefficient for the reactors were calculated.

2. Materials and methods

2.1. Set up and operational details of experimental system

The continuous experiments were conducted for treatment of textile wastewater in two-bench scale columnar UAFB reactor connected in series with the total void volume of to 0.5 l. The two similar reactors of 47 cm length and 2.35 cm diameter were connected in series and maintained at room temperature (30 °C). Insulated beads of 2.5 mm diameter were used as immobilization support matrix as they are chemically inert. The out let of the reactor was connected to U tube for gas and liquid separation. Microorganisms were immobilized on the matrix by circulating treated sewage along with the wastewater. The reactors were loaded several times with the fresh media till sufficient growth was achieved. The fixed bed reactors were connected in series and were immobilized with bacterial cells from sewage. Diluted (10%) textile wastewater was fed to reactors. The concentration of COD increased step wise with continuous monitoring of decolorization. The effluent was collected from second reactor and analyzed. Performance of the reactor was assessed by evaluating decolorization and COD removal. During the first 15 days COD removal efficiency was very less but it has improved gradually. Fig. 1 represents the schematic of model reactors.

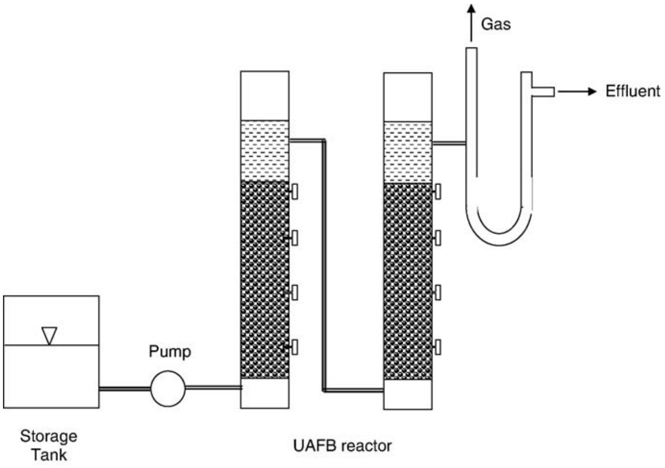

Fig. 1. Schematic diagram of hybrid column UAFB reactor.

2.2. Basal medium

The textile wastewater was always supplemented with nutrients g l^{-1} $NaHCO_3$, 5000; NH_4Cl 280; $CaCl_22H_2O$ 10; K_2HPO_4, 250; $MgSO_4{\cdot}7H_2O$, 100; yeast extract 200; trace element 1 ml l^{-1}. Starch was used as co-substrate (500 mg l^{-1}) [21].

2.3. Analytical methods

Color measurements in clarified (centrifuged) samples of effluents from UAFB were performed in UV–vis 160 Å, Shimadzu spectrophotometer. Absorbance of the samples was measured at the maximum (λ_{max}) wavelength each time for wastewater. The pH, chemical oxygen demand (COD), ammonia and total dissolved solids were determined according to standard procedure [22].

3. Results and discussion

3.1. Characterization of wastewater

Scouring and desizing effluents is the major contributor to the organic load in textile effluents. Textile wastewater used in this study was collected from fabric dying industry situated in Tamilnadu. The industry dyes about 10 t of hosiery and woven material per day, respectively. The general physico-chemical characterization of the wastewater is given in Table 1. The pH of the wastewater was always alkaline, reddish brown with adsorption maxima of 0.9 OD at 360 nm. The wastewater showed high concentration of COD and TDS with 3 mg l^{-1} of ammonia.

3.2. Effect of hydraulic retention time on decolorization and COD removal in UAFB

After initial acclimatization of biofilm growth on support media, constant decolorization was obtained at hydraulic retention time (HRT) of 23 h. The wastewater was fed along with nutrients after pH adjustment to 7.0. The reactor was continuously operated at different HRT and at different initial COD loadings. Fig. 2 depicts the variation in decolorization efficiency in UAFB with variation in HRT. Initial wastewater loading

Table 1
Characteristics of textile wastewater

Parameters	Concentration range	Average concentration
PH	9.6–12.5	12.5
Color, A_{340}, OD	0.5–1.4	0.9
Suspended solids	60–416	416
Total dissolved solids	4500–12800	12800
Total organic carbon	263.90–731.90	639.90
Chemical oxygen demand	1834.60–3828.0	3828.0
Biochemical oxygen demand	25.0–433.30	433.30
Aromatic amines	20–75	75.0
Ammonia	2.0–3.0	3.0
Chloride	1200–1375	1375
Sulphate	700–2400	1000

All the parameters expressed in mg l^{-1}except pH.

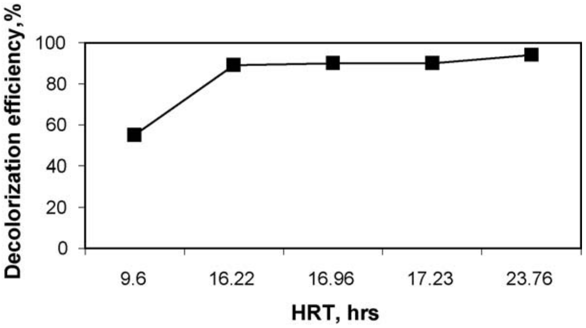

Fig. 2. Variation of decolorization efficiency in UAFB at different HRTs.

and COD were 6.34 g COD m^{-3} d^{-1}, 1880 mg l^{-1}, respectively. Decolorization efficiency decrease with decrease in HRT. When HRT was decreased from 23.76 to 9.6 h, the decrease in efficiency was from 94% to 55%. No significant increase was observed in decolorization efficiency for higher HRTs of 16 to 23 h. It remained constant and was around 90–94%. Accordingly it can be concluded that 16 h HRT can be considered optimum with 90% decolorization efficiency. The effluent from dye manufacturing industry containing 1200 mg l^{-1} and color of 500 degrees (dilution factor) has been treated in sequential anaerobic–aerobic condition and could achieved 83% and 90% removal, respectively [23]. It was concluded from these studies that anaerobic stage of the combined system removes both color and COD. In addition, it also improves the biodegradability of dyes from further aerobic treatment. This is in agreement with other published data on recalcitrance of azo dyes in aerobic sludge environment [6,24]. The color removal under anaerobic condition is mainly due to azo dye reduction.

The effect of HRT on COD removal was also investigated (Fig. 3). Initial COD concentration was 1880 mg l^{-1}. The COD of UAFB treated effluent was observed to be 420–190 mg l^{-1} for HRT of 9.6–23.76 h with approximately 74.44–89.36% COD removal efficiency.

3.3. Effect of initial COD concentration on decolorization and COD removal in UAFB

The reactor was operated at optimum HRT (16 h) with influent COD concentrations ranging from 243–1973 mg l^{-1}. The wastewater was diluted so as to get required COD. At each loading, the reactor was given stabilization time to get optimum COD removal. Fig. 4 depicts the variation in decolorization efficiency in UAFB reactor with different influent COD concentration. Decolorization efficiency in the reactor was nearly 90% for COD concentration of 1002–1973 mg l^{-1}. However, the efficiency increased with decreasing COD concentration from 1973 to 243 mg l^{-1} resulting in color removal efficiency to 94%. The COD removal efficiency in UAFB did not show significant change with varying initial COD concentration (Fig. 4). The COD removal efficiencies for 1002–1973 mg l^{-1} were nearly 76–81%. The average gas production was only 340 ml in 48 h, which was very low (data not shown). Isik and Sponza [25] have obtained 47% COD removal at 14 h HRT with 94.3% decolorization in UASB reactors treating simulated textile wastewater. In order to improve COD removal, the system can be operated at longer hydraulic retention time or an aerobic unit after anaerobic unit can be used as a polishing step. The performance of UAFB was evaluated for various organic loading rates. The results of COD removal efficiencies at different organic loading rates ranging between 1.038 mg l^{-1} and 8.21 g COD m^{-3} d^{-1} during experimental study are given in Table 2. Buyukkamaci and Filibeli [26] have obtained 77–90% COD removal efficiencies for anaerobic hybrid reactor treating synthetic wastewater.

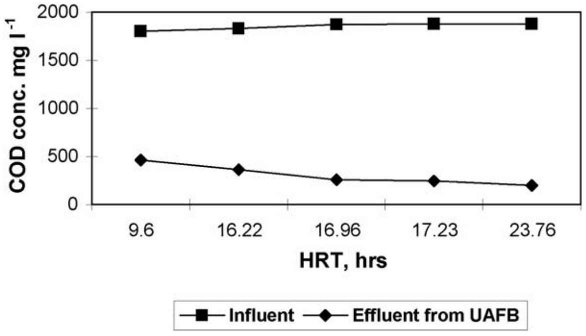

Fig. 3. Variation of effluent COD removal efficiency in UAFB at different HRTs.

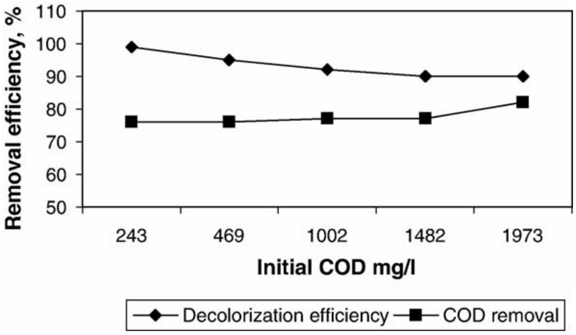

Fig. 4. Variation of decolorization and COD removal efficiency at different initial COD loading in UAFB.

3.4. Second-order kinetic application to the UAFB

The second-order model was applied to experimental results for UAFB treating textile wastewater. The general equation of a

Table 2
Performance of model reactor during the experimental study

HRT, h	C_0, mg l^{-1}	OLR, kg COD m^{-3} d^{-1}	COD removal efficiency, %
9.6	1800	4.52	74.44
14.88	243	1.038	75.78
15.21	469	1.99	75.20
15.38	1002	3.88	76.80
15.43	1482	6.11	77.43
15.98	1973	8.21	81.58
16.22	1828	6.16	80.30
16.96	1870	6.31	86.36
17.23	1880	6.34	86.96
23.76	1880	6.34	89.36

Table 3
Data for second-order kinetics model for UAFB

HRT, h	S_0, mg l^{-1}	S, mg l^{-1}	E, %	θ/E	X, mg VSS l^{-1}	$K_{2(\mathrm{s})}$, h^{-1}
9.6	1800	460	74.44	12.97	150	13.11
14.88	243	58	75.78	19.65	150	1.77
15.21	469	113	75.20	20.09	150	3.41
15.38	1002	229	76.80	20.02	150	7.30
15.43	1482	331	77.43	19.93	150	10.79
15.98	1973	369	81.58	19.58	150	14.37
16.22	1828	360	80.30	20.27	150	13.31
16.96	1870	255	86.36	19.72	150	13.62
17.23	1880	245	86.96	19.80	150	13.69
23.76	1880	200	89.36	26.69	150	13.69
Avg.						10.50

second-order kinetic model is given below [27,28]:

$$\frac{-\mathrm{d}s}{\mathrm{d}t} = k_{2(S)}X\left(\frac{S}{S_o}\right)^2 \tag{1}$$

If Eq. (1) is integrated and then linearilized, this equation will be obtained:

$$\frac{S_o\theta}{S_o - S} = \theta + \frac{S_o}{k_{2(S)}X_0} \tag{2}$$

If the second term of the right part of this equation is accepted as a constant, equation given below will be obtained:

$$\frac{S_o\theta}{S_o - S} = a + b\theta \tag{3}$$

where $a = S_o/(k_{2(S)}X)$ and b is a constant greater than unity. $(S_o - S)/S_o$ expresses the substrate removal efficiency and is symbolized as E. Therefore, the last equation can be written as follows:

$$\frac{\theta}{E} = a + b\theta \tag{4}$$

where S and S_o are the effluent and influent substrate concentration (mg COD l^{-1}); X, the average biomass concentration in the reactor (mg VSS l^{-1}); θ, hydraulic retention time (h), and $k_{2(S)}$ is the second-order substrate removal rate constant (d^{-1}).

It is very difficulty to calculate the biomass concentration on support matrix in anaerobic reactor. In this study, biomass concentration in UAFB was estimated from maximum specific substrate utilization rate (k) values, which were found by applying Monod model. Data used for a second-order kinetic model are given in Table 3 and (a) and (b) values are obtained using Fig. 5 for UAFB reactor. From Fig. 5, (a) and (b) values were found as 0.9151 and 5.1386, respectively, with correlation coefficient of 0.94. Second-order substrate removal rate constants ($k_{2(\mathrm{s})}$), which were calculated are given in Table 3. The formula for predicting effluent substrate concentration for the UAFB is given by

$$S = S_o\left(1 - \frac{\theta}{0.1 + 2.1093\theta}\right)$$

3.5. Modified Stover–Kincannon model for UAFB reactor

Monod type kinetic analysis based on cell mass and COD loading in continuous operation for decolorization purpose have been used [29,30]. In addition, there are kinetic models developed for organic substance removal in continuously operated anaerobic reactors [31,32]. Stover–Kincannon is one of the most widely used mathematical model for determining the kinetic constants in immobilized systems. The model has been applied to continuously operated mesophilic and thermophilic upflow anaerobic filters for the treatment of paper-pulp liquors [33] and simulated starch wastewater [34], anaerobic filter for soybean wastewater treatment [35], anaerobic hybrid reactor [26]. However, this model has not been applied for determination of COD reduction from textile wastewater treatment kinetic constants. Therefore, the Stover–Kincannon model was used for the kinetic analysis of COD and dyestuff removal in UAFB reactor in this study. This relationship can be seen from Fig. 5 according to the experimental studies, showing that the substrate removal rate increased with increase in substrate concentration.

The Stover–Kincannon model considers the organic substance removal rate as a function of organic loading rate at steady state as in Eq. (1).

Equations of the modified Stover–Kincannon model are as follows (2):

$$\frac{\mathrm{d}s}{\mathrm{d}t} = \frac{Q}{V}(S_\mathrm{i} - S_\mathrm{e})$$

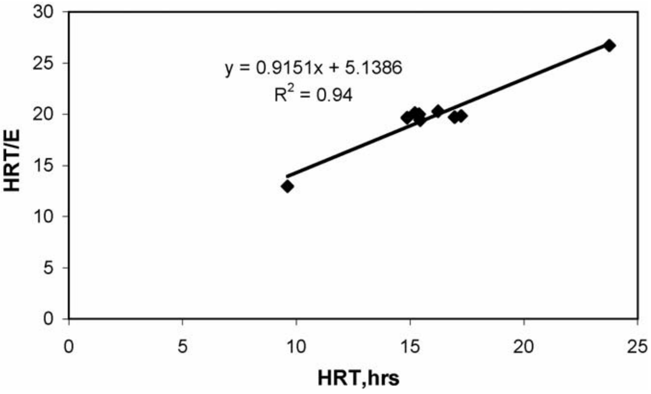

Fig. 5. Second-order kinetic model application for UAFB.

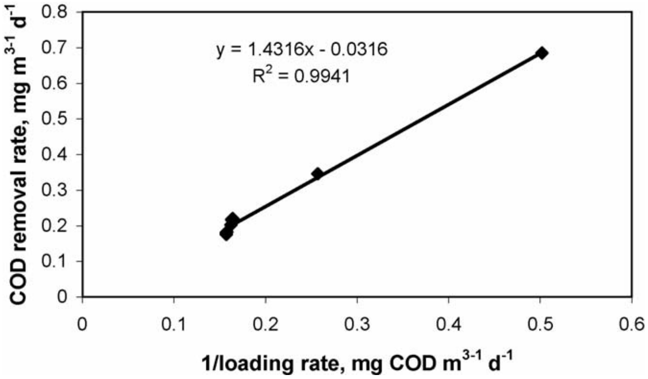

Fig. 6. Stover–Kincannon model application for UAFB.

where dS/dt is defined in two ways as follows:

$$\frac{ds}{dt} = \frac{U_{\max}(QS_i/V)}{K_B + (QS_i/V)} \quad (6)$$

$$\frac{ds}{dt} = \frac{kXS_e}{K_s + S_e} \quad (7)$$

$$\left(\frac{ds}{dt}\right)^{-1} = \frac{V}{Q(S_i - S_e)} = \frac{K_B}{U_{\max}}\frac{V}{QS_i} + \frac{1}{U_{\max}} \quad (8)$$

where dS/dt, substrate removal rate ($\mathrm{g\,l^{-1}\,d^{-1}}$); $U_{\max}$ the maximum utilization rate constant ($\mathrm{g\,l^{-1}\,d^{-1}}$); K_B the saturation value constant ($\mathrm{g\,l^{-1}\,d^{-1}}$); k the maximum rate of substrate removal ($\mathrm{l^{-1}\,d^{-1}}$); X the microorganism concentration (VSS) in the UAFB ($\mathrm{g\,l^{-1}}$); K_S the half-velocity constant ($\mathrm{g\,l^{-1}}$) and V is the clean-bed volume of the UAFB (l).

If $(dS/dt)^{-1}$ is taken as $V/[Q(S_i - S_e)]$, which is the inverse of the loading removal rate and this is plotted against the inverse of the total loading rate $V/(QS_i)$, a straight line portion of intercept $1/U_{\max}$ and a slope of $K_B/U_{\max}$ results. Experimental data was applied at high correlation ($R^2 = 0.99$) to the model (Fig. 6). From Fig. 6, ($K_B/U_{\max}$) and $1/U_{\max}$ were 1.4316 and 0.0316, respectively. The maximum removal rate constant ($U_{\max}$) is $31.69\,\mathrm{g\,l^{-1}\,d^{-1}}$ and the saturation value constant (K_B) is $45.37\,\mathrm{g\,l^{-1}\,d^{-1}}$, for UAFB reactor. The values of saturation constant K_B and $U_{\max}$ are comparable with Yu et al. [29] and Buyukkamaci and Filibeli [26].

From mass balance of substrate into and out of the volume, this equation can be obtained:

$$S_e = S_i - \frac{U_{\max} S_i}{K_B + (QS_i/V)} \quad (9)$$

4. Conclusions

Treatment performance of the UAFB model reactor was evaluated at different organic loading rates and hydraulic retention times using textile wastewater and kinetic analyses of the reactor were carried out according to the experimental results. After obtaining steady-state conditions, organic loading rate was increased from 1.038 to 8.21 g COD $\mathrm{l^{-1}\,d^{-1}}$ and hydraulic retention time was decreased step wise from 23.76 to 9.6 h, stepwise. COD removal efficiencies ranging from 78% to 94% were achieved during the experimental studies. The percentage of decolorization was about 94.0%.

Biokinetic models such as Monod model, second-order, Stover–Kincannon model, etc. were applied for the UAFB reactor. Second-order model and Stover–Kincannon model gave higher correlation coefficients, which was 99%. Therefore, these models could be used in the design of the UAFB reactor.

Second-order substrate removal rate constant ($k_{2(S)}$) was $10.50\,\mathrm{h^{-1}}$ for UAFB reactor. In previous studies, 1.655 and $13.6\,\mathrm{d^{-1}}$ for glucose waste, $0.217\,\mathrm{d^{-1}}$ for municipal wastewater, and $38.5\,\mathrm{d^{-1}}$ for landfill leachate waste [36] have been reported.

Applying a modified Stover–Kincannon model to UAFB reactor, maximum removal rate constant ($U_{\max}$) and saturation value constant (K_B) were 31.69 and $45.37\,\mathrm{g\,l^{-1}\,d^{-1}}$, respectively, with high correlation coefficient ($R^2 = 0.99$). Yu et al. [34] obtained value very similar, which are $U_{\max} = 83.3\,\mathrm{g\,l^{-1}\,d^{-1}}$ and $K_B = 85.5\,\mathrm{g\,l^{-1}\,d^{-1}}$. Kapdon et al. [37] has obtained $K_B = 37.9\,\mathrm{g\,l^{-1}\,d^{-1}}$, $U_{\max} = 12.9\,\mathrm{g\,l^{-1}\,d^{-1}}$ for synthetic wastewater in an anaerobic batch column reactor. The results of kinetic studies obtained from lab-scale experiments can be used for estimating treatment efficiency of full-scale reactors with the same operational conditions.

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