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Full Length Research Paper

Determination of kinetic coefficients for the biological treatment of textile wastewater

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The objective of the research is to evaluate the performance of aerated lagoon for biological treatment of textile wastewater and to determine kinetic coefficients for the design of treatment facilities. For this purpose, a bench scale model of aerated lagoon was set up and was operated continuously for 92 days by varying aeration times from 5 to 15 days. Primary treated wastewater effluent collected from Nishat Textile Mills (Lahore, Pakistan) was fed as an influent to aerated lagoon. To evaluate the performance of aerated lagoon, the suspended solids (SS), biological oxygen demand (BOD) and chemical oxygen demand (COD) for both the influent and effluent were measured at each aeration time after ensuring steady state conditions. The influent BOD was observed to vary from 540 to 355 mg/L while the effluent BOD varied from 121 to 32 mg/L during the study period. The corresponding range of influent COD was between 1813 and 1116 mg/L and for effluent COD was between 592 and 224 mg/L. The results show that the average effluent BOD at aeration time of 7 days was lower than 80 mg/L. However, the effluent COD did not meet the National Environmental Quality Standards (NEQS) limit of 150 mg/L even at the aeration time of 15 days. This indicated the presence of large amount of chemicals in the textile wastewater, for instance bleaching agents like hydrogen peroxide and sodium hypochlorite; complex dyes and pigments like chromium based dyes used for imparting color to the fabric. The fate of these chemicals varies ranging from 100% retention on the fabric to 100% discharge with effluent. Chemical coagulation, prior to primary sedimentation, by coagulants like lime, aluminum salt (especially aluminum sulphate or alum), ferric chloride and ferrous sulphate, is most commonly employed for significant removal of COD. Overall removal rate constant (K) for the present study was calculated to have a mean value of 0.79 day^{-1} based on BOD. Based on COD, the overall removal rate constant (K) was found out to have a mean value of 0.39 day^{-1}.

Key words: Biological treatment, wastewater, kinetic coefficient, biological oxygen demand (BOD), chemical oxygen demand (COD).

INTRODUCTION

Textile is the largest industrial sector of Pakistan with respect to foreign exchange earnings and labor force employment. It alone accounts for 61% of the country export, 46% of industrial production, 38% of employed industrial work force and 8.5% of gross national product (GOP, 2006 to 2007). Textile industry could be termed as the back bone of Pakistan's economy. The number of industries working in this sector is estimated to be around 670. Karachi has the major share with almost 300 industries. Apart from Karachi, most industries are located in Punjab (Ara, 1999).

Wastewater is the major environmental issue of the textile industry besides other minor issues like solid waste, resource wastage and occupational health and safety. Pretreatment, coloration and post treatment of textile fibers usually require large amounts of water and variety of chemicals. Variations in the fabric quality and treatment process result into large fluctuation in daily flow rates and pollutants concentrations. Textile wastewater

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Figure 1. Laboratory bench scale model used for study.

pollutants are generally caustic soda, detergents, starch, wax, urea, ammonia, pigments and dyes that increase its biological oxygen demand (BOD), chemical oxygen demand (COD), solids contents and toxicity (ETPI, 2000). Textile processing industry is basically a water intensive sector, in which water is used mainly as a carrier for transporting a variety of chemicals to the fabric for washing purposes. Consequently, a typical textile processing unit is expected to generate various types of wastewater streams, differing in magnitude and quality.

Textile wastewater contains substantial pollution loads and the concentrations of various pollution parameters are very high as compared to the values prescribed by National Environmental Quality Standards (NEQS) set by the Government of Pakistan (CPP, 1999). Therefore, for effective water pollution control, there is an urgent need to treat textile wastewaters. To this end, it is essential to determine the kinetic coefficients for the textile wastewater to help in the design of effective treatment facilities.

Biological methods are invariably employed for the treatment of biodegradable wastewaters. Knowledge of the microbial kinetics and determination of the kinetic coefficients for a particular wastewater are, therefore, imperative for the rational design of treatment plants (Edgardo, 2001). In Pakistan, little effort has so far been made to determine the kinetic coefficients for wastewaters originating from different industrial sources. Instead, values for various kinetic parameters are assumed based upon designer's will or past experience for the design of the wastewater treatment facilities. This practice is equivalent to taking a leap in the dark.

MATERIALS AND METHODS

Completely mixed stirred tank reactor (CSTR) without recycle was used in this study, because the bench scale reactors operated with solid recycle are difficult to control (Metcalf and Eddy, 1991). A view of the bench scale aerated lagoon set up for this study is shown in Figure 1.

Operational parameters of various components are shown in Table 1 and the various components of the bench scale aerated lagoon model are as follows:

Table 1. Operational parameters of different components.

Parameter	Unit	Value
(a) Aeration tank		
L:W	-	1.1:1
Surface area	cm^2	935.7
Volume	Liter	25.45
Aeration time	Day	5 to 15
Inflow	Liter/day	5.1 to 1.7
(b) Final clarifier		
L:W	-	6.6 : 1
Surface area	cm^2	106.4
Volume	Liter	2.4
(c) Detention time in final clarifier at various aeration times of aeration tank		
Aeration time in aeration tank (days)	**Hydraulic detention time (h)**	
5	11.3	
7	15.8	
9	20.4	
12	27.2	
15	33.9	

(1) Influent bottle
(2) Peristaltic pump
(3) Air pump
(4) Aeration tank
(5) Secondary clarifier
(6) Effluent tank

Operational procedure

The research work was carried out for a period of 3 months. Initially, for 15 days, the aeration tank was seeded with the sludge obtained from the recirculation pit of the secondary treatment plant at Nishat Mills Limited and domestic wastewater from University hostels.

Bench scale aerated lagoon as shown in Figure 1 was run on a continuous basis for the aeration time ranging from 5 to 15 days till the end of the research work. Aeration time in the aeration tank was controlled by changing the flow rate by the peristaltic pump. Before collecting the data for a particular aeration time under study, sufficient time was given to obtain the steady state condition. Mixed liquor suspended solids (MLSS) content of the aeration tank was used to evaluate the steady state conditions. The MLSS and dissolved oxygen (DO) were the operating parameters for the bench scale aerated lagoon and were measured continuously throughout the study period. A system in a steady state has numerous properties that are unchanging in time; this implies that

Table 2. Details of operational plan of model.

No. of day	Aeration time (day)	Flow rate (L/day)
23	4	6.4
10	5	5.1
12	7	3.6
19	9	2.8
14	12	2.1
14	15	1.7

Table 3. Details of parameters.

S/N	Unit	Parameter	Frequency
1.	Aeration tank	pH, DO, temperature and suspended solids.	Daily basis
2.	Influent and effluent	BOD, COD, suspended solids, pH and temperature	These parameters were measured after establishing the steady state conditions at different aeration times. Five data sets for each of the parameter were obtained corresponding to each aeration time

for any property p of the system, the partial derivative with respect to time is zero. MLSS varied every time with a change in aeration time, however, the change was observed to vary for 4 to 5 days after when the value of MLSS became constant and the reactor was assumed to achieve a steady state condition. The readings of influent and effluent were taken after MLSS and became unchanged for a specific aeration time. As a single reading for each, parameter was taken per day during the course of the study therefore, X-axis was a more representative of number of readings rather than time in all illustrations. A complete operational plan of the bench scale aerated lagoon for the present study is shown in Table 2.

Bench scale aerated lagoon monitoring

Controlled environmental conditions are necessary for biological treatment. These include pH regulation, consistent temperature, nutrient and trace element addition, maintaining a desirable oxygen level and proper mixing in the aeration tank. Nutrient concentration and pH levels were controlled in the aeration tank by adding nutrient supplement salts and concentrated sulphuric acid. There was no mechanism to control temperature and DO levels in the aeration tank; however, these remained within the prescribed limits throughout the study. The detail of the parameters of each unit is shown in Table 3.

Analytical procedure

All tests performed on the wastewater were carried out according to the procedures laid down in “Standard Methods for the Examination of Water and Wastewater” (20th edition, 1998). Description of these tests is discussed.

Nitrogen and phosphorus

Nitrogen and phosphorus in the raw wastewater was determined twice during the course of the study. This was done to analyze the amount of nutrients present in the raw wastewater. The amount of nutrients present at the corresponding BOD and COD values for the raw wastewater is shown in the Table 4. In the present study, total Kjeldahl nitrogen (TKN) test was performed using the Kjeldahl apparatus.

Benefield and Randall (1980) pointed out that the nitrogen and phosphorus requirements are commonly based on the BOD of the wastewater, where a BOD:N:P of 100:5:1 is considered adequate. For this study, the average value of BOD of the wastewater sample fed to the bench scale aerated lagoon was approximately 460 mg/L. Thus, the BOD : N : P for this particular wastewater came out to be:

BOD : N : P; 460 : 27.35: 0.178, and 100 : 5.94 : 0.038

The calculations shown are based on average BOD value and show that amount of nitrogen present in the wastewater was almost on the borderline of the required nitrogen. But phosphorus was 0.038 as against the desirable value of 1. Hence, it was deficient. The deficiency was met by adding calculated amount of “potassium dihydrogen phosphate (KH_2PO_4)” salt. The amount for this average BOD value came out to be 0.04 gm of KH_2PO_4 per liter of wastewater. A nitrogen supplement was also added to meet the nitrogen requirement in case the BOD was higher than the average BOD which subsequently reduced the nitrogen less than the desired 5 value of nitrogen. To meet the nitrogen deficiency ferrous ammonium sulphate $\{(NH_4)_2\ Fe\ (SO_4)_2\}$ was used. An amount ranging from 0.05 to 0.1 g of $\{(NH_4)_2\ Fe\ (SO_4)_2$ per liter of wastewater was added to meet nitrogen deficiency. The amount was calculated on the weekly basis.

Temperature and pH

Temperature and pH of the aeration tank were measured on daily basis. The pH was measured with the help of Hach Sension 3 pH meter and following the procedure mentioned in “Standard Methods, (1998) (4500-H-B). The pH for the raw wastewater was highly alkaline which was reduced by using concentrated sulphuric

Table 4. Values of nitrogen and phosphorus in raw wastewater.

Parameter	Date	Result (mg/L)
TKN	04-07-2009	26.2
	22-08-2009	28.5
	Average	27.35
Phosphorus	04-07-2009	0.189
	22-08-2009	0.165
	Average	0.178
BOD	04-07-2009	470
	22-08-2009	450
	Average	460
COD	04-07-2009	1506
	22-08-2009	1435
	Average	1471

acid. The same method was used for measuring influent (inf) and effluent (eff.) pH.

Dissolved oxygen (DO)

DO within the aeration tank was measured on daily basis. Azide modification of Winkler test as mentioned in the “Standard Methods, (1998) (4500-O-C)” was used along with DO analyzer DO-20A “Standard Methods (1998) (4500-O-G) for the measurement of DO in the aeration tank.

Mixed liquor suspended solids (MLSS)

Suspended solids (SS) of the aeration tank were measured using a 0.45 μm glass fiber filter, vacuum pump, drying oven, desiccator and weighing balance according to the procedures laid down in the ‘Standard Methods (1998) (2540; D & F)”. The same method was used for the determination of influent and effluent SS.

BOD and COD

BOD of the influent and effluent were measured using 5 day BOD test according to the procedures laid down in the ‘Standard Methods (1998) (5210-B)”. COD of the influent and effluent were measured using open reflux method according to the procedures laid down in the ‘Standard Methods (1998) (5220-B)”.

RESULTS AND DISCUSSION

Aeration tank temperature

During the study, the temperature of the aeration tank varied from 26 to 31.6°C. There was no mechanism to control the temperature of the aeration tank and therefore it varied with the change in temperature of the surrounding environment. The temperature of the aeration tank followed a gradual decrease during the study period. The obvious reason for this was decrease in atmospheric temperature due to weather change from July to September. The temperature variations for the present study remained within the range prescribed in the literature for the bacterial growth. The variation of temperature is shown in Figure 2.

Aeration tank pH

The pH of the aeration tank ranged from 6.9 to 8.05. The pH of the aeration tank was regulated by adjusting the influent pH using concentrated sulphuric acid having molarity equal to ‘1’. The pH of the aeration tank during the study period remained in the range reported suitable in the literature for normal growth of bacteria. The pH variation observed during the study is shown in Figure 3.

Aeration tank dissolve oxygen (DO)

DO of the aeration tank varied between 2.2 and 3.5 mg/L during the course of the study. The DO levels used to fall as a result of the clogging of stone diffusers, which were employed for aeration. The problem was overcome by washing the diffuser stones with chromic acid. Figure 4 shows the variation of DO in the course of study.

Aeration tank suspended solids (SS)

MLSS represent the amount of biomass present in the aeration tank. Time course of MLSS is shown in Figure 5. Monitoring of MLSS served two purposes in this study. Firstly, it was used for the determination of kinetic coefficients and secondly, to assess the steady state conditions in the aeration tank. Various mathematical models used in the design of biological processes are based on the assumption that system is working under steady state conditions. Unfortunately, steady state can seldom be achieved under practical conditions in full-scale systems due to fluctuations in the influent BOD, COD and suspended solids. The bench scale aerated lagoon model in present study was operated close to the actual field conditions under which such treatment systems usually work. Hence, MLSS could not be expected to remain constant during the course of study. MLSS oscillated between 223 and 320 mg/L. MLSS varied with change in aeration time.

Performance of bench scale aerated lagoon

The performance studies of the bench scale aerated

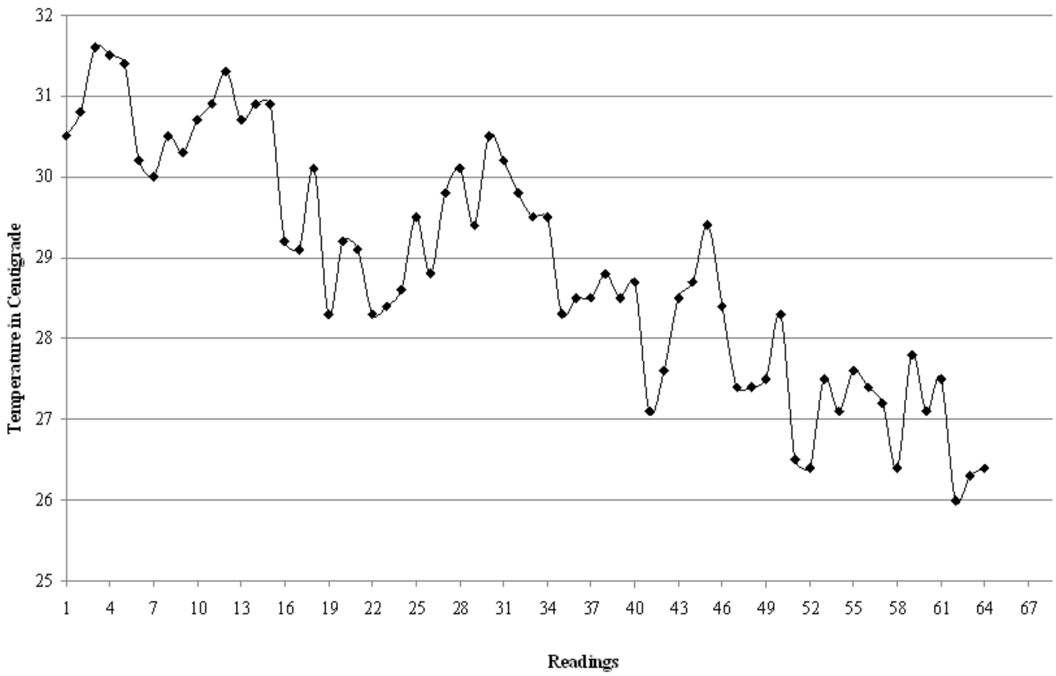

Figure 2. Time course of aeration tank temperature.

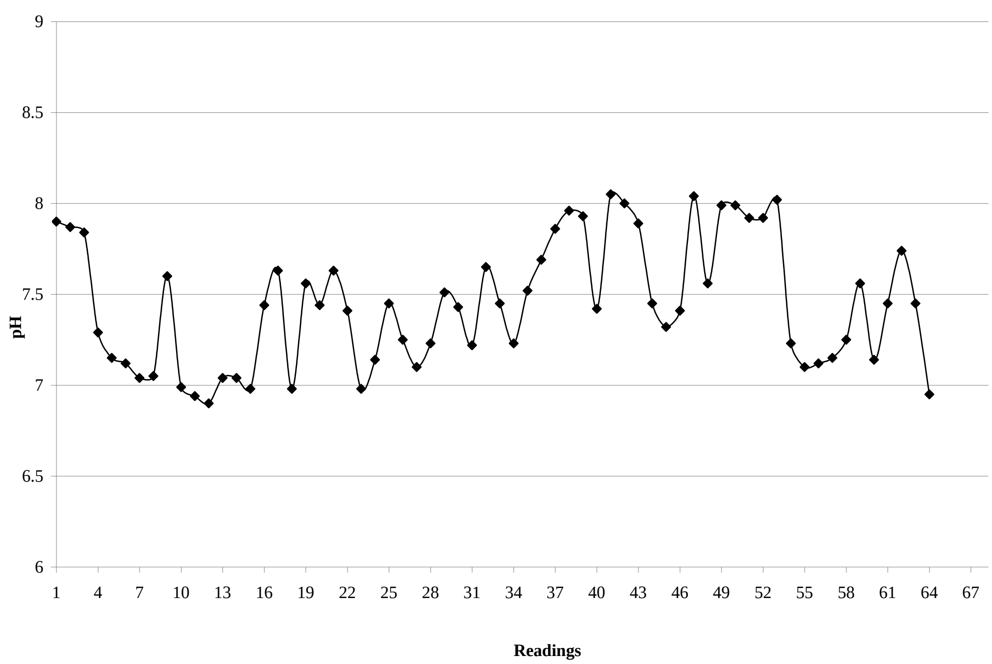

Figure 3. Time course of aeration tank pH.

lagoon were made by varying aeration time (θ) from 5 to 15 days and conducting tests on the selected influent and effluent parameters. Laboratory analysis was done for influent and effluent parameters like temperature, pH, SS, BOD and COD. The textile wastewater was highly alkaline in nature and concentrated sulfuric acid was used to reduce the pH before filling the influent bottle. The effluent pH was always less than influent pH and sometimes very close to influent pH due to the dilution factor of the tank aeration as the aeration tank itself was not

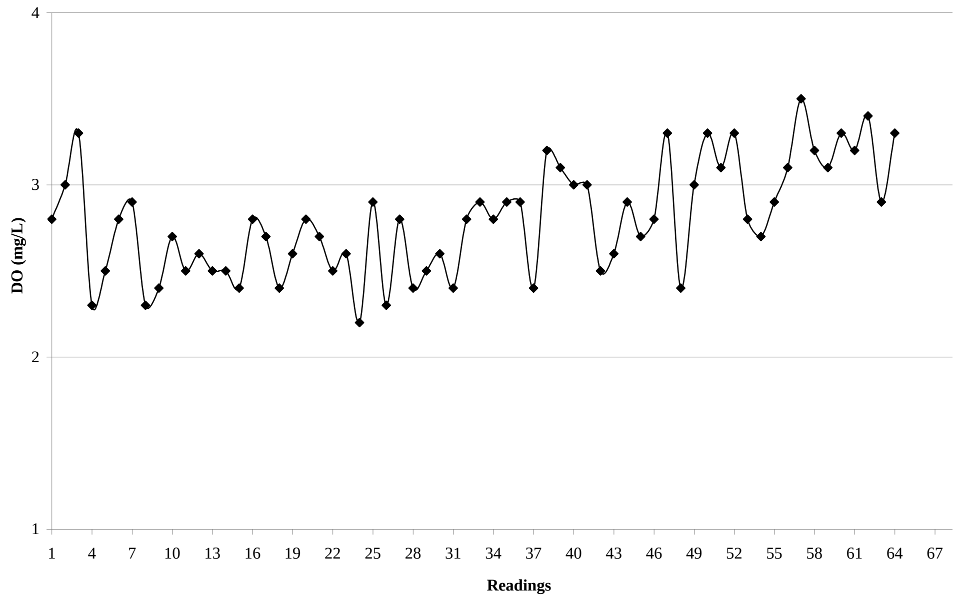

Figure 4. Time course of aeration tank DO.

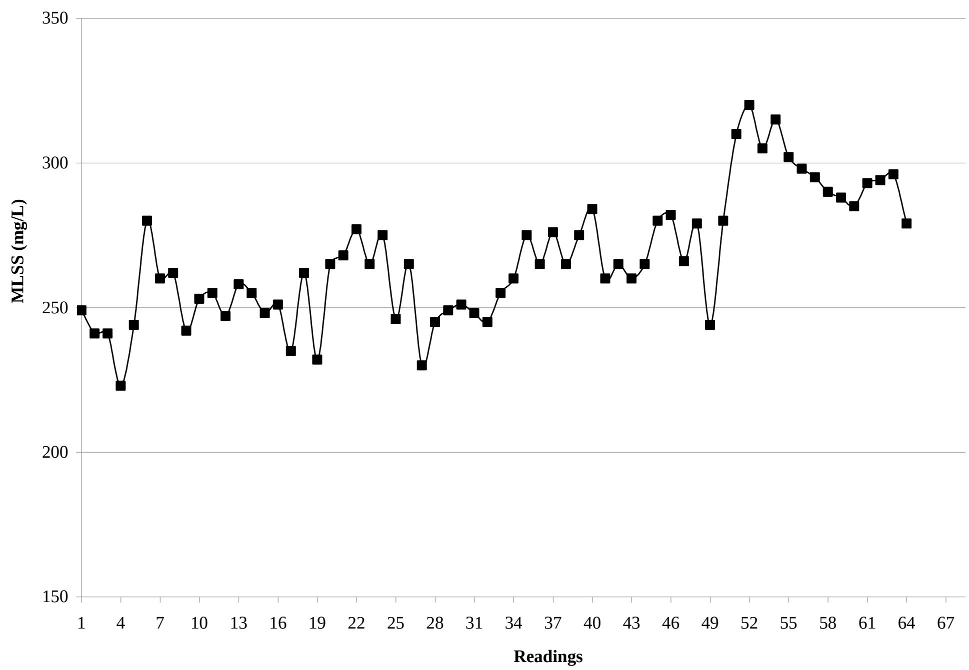

Figure 5. Time course of aeration tank suspended solids.

intended to reduce or increase the pH. For the purpose of performance evaluation of treatment system, three parameters that is, SS, BOD and COD were selected. The influent BOD was a representative of the characteristics of the processes used in the industry therefore sharp spikes are observed at some locations in the influent BOD graph. However, the effluent BOD graph was comparatively smooth due to steady state conditions and dilution factor of the aeration tank. A summary of the mean values of SS, BOD and COD at different aeration times along with their percentage removals is shown in Table 5.

Figures 6 to 10 show graphs for the influent and effluent pH, temperature, SS, BOD and COD.

Table 5. Summary of performance data on BOD, COD and SS with percent removal.

Aeration time (Day)	Average SS (mg/L)			Average BOD (mg/L)			Average COD (mg/L)			Aeration tank MLSS (mg/L)
	Inf.	Eff.	%	Inf.	Eff.	%	Inf.	Eff.	%	
5	104	50	52	506	115	77	1617	545	66	250
7	108	45	58	473	78	84	1560	416	73	268
9	81	28	65	385	47	88	1279	270	79	275
12	103	30	71	481	45	91	1569	275	82	284
15	110	27	75	479	36	92	1575	235	85	290

Inf., Influent; Eff., effluent

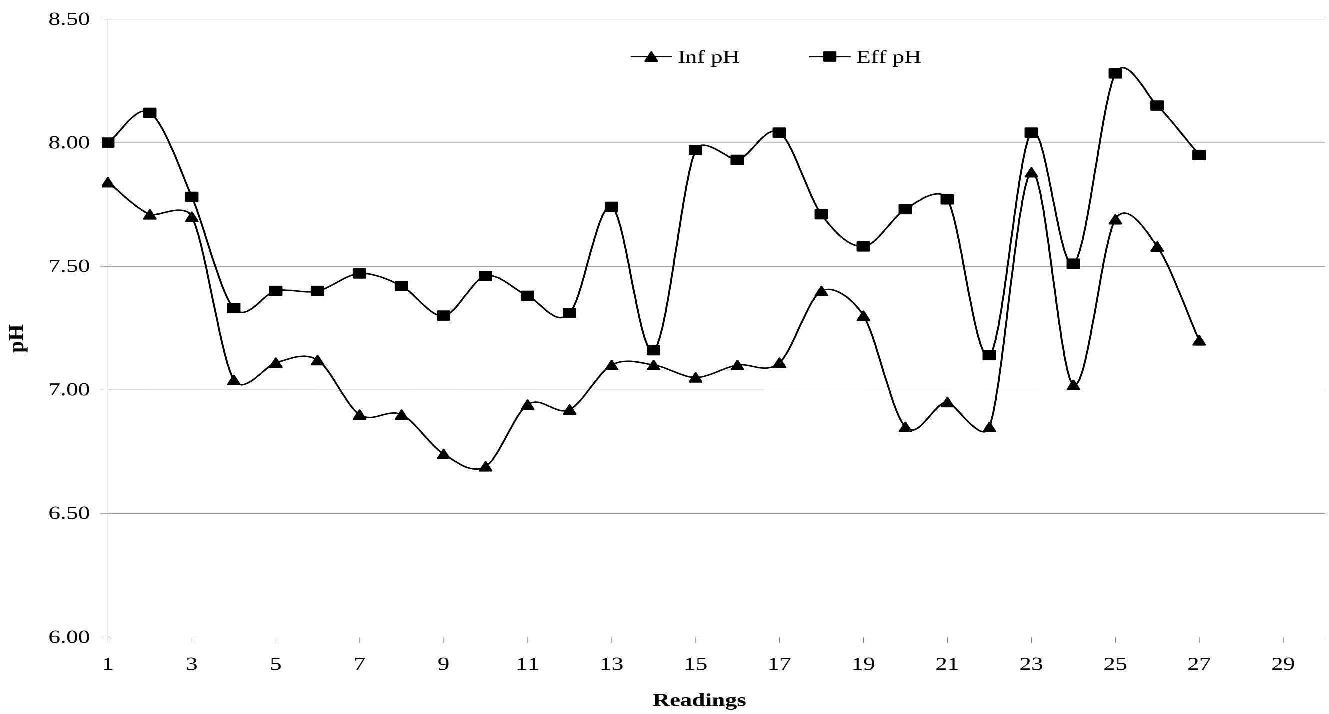

Figure 6. Time course of influent and effluent pH.

It is evident from Figure 6 that influent pH affects the effluent pH but not necessarily a rise or fall in the influent pH is immediately reflected in the effluent pH. It is also evident that the effluent pH always remained greater than the influent pH.

Figure 7 clearly indicates that both are related in the sense that a rise in influent temperature results in a rise of effluent temperature. During the course of the study the influent and effluent temperature remained in the range of 26 to 32.4°C. At the end of this study, the temperature decreased to 26.8°C. As the wastewater was stored in an incubator in the laboratory therefore, the influent temperature was observed to be less than the ambient room temperature soon after filling of the influent bottle. It gradually increased and came closer to the ambient room temperature afterwards.

The data shown in Table 5 show that at 5 days aeration time, the average value of percentage removal of suspended solids is 52% and it gradually rose to maximum value of 75% at 15 days aeration time. The SS of the influent already met NEQS limit of 150 mg/L as the influent introduced to the aeration tank was the settled and supernatant liquid of the collected sample. However, with the increase in aeration time, the removal efficiency of SS also increased. There could be two possible reasons to this effect. First, the longer detention times in the final clarifier and second, good settleability of sludge which was manifested by a thick sludge blanket at the bottom of final clarifier and clear supernatant above it. Figure 8 shows a time course of influent and effluent SS. The graph indicates frequent ups and downs in the influent SS as compared to effluent. As sampling was done after the primary sedimentation in the treatment plant at the factory, therefore, the influent SS was already

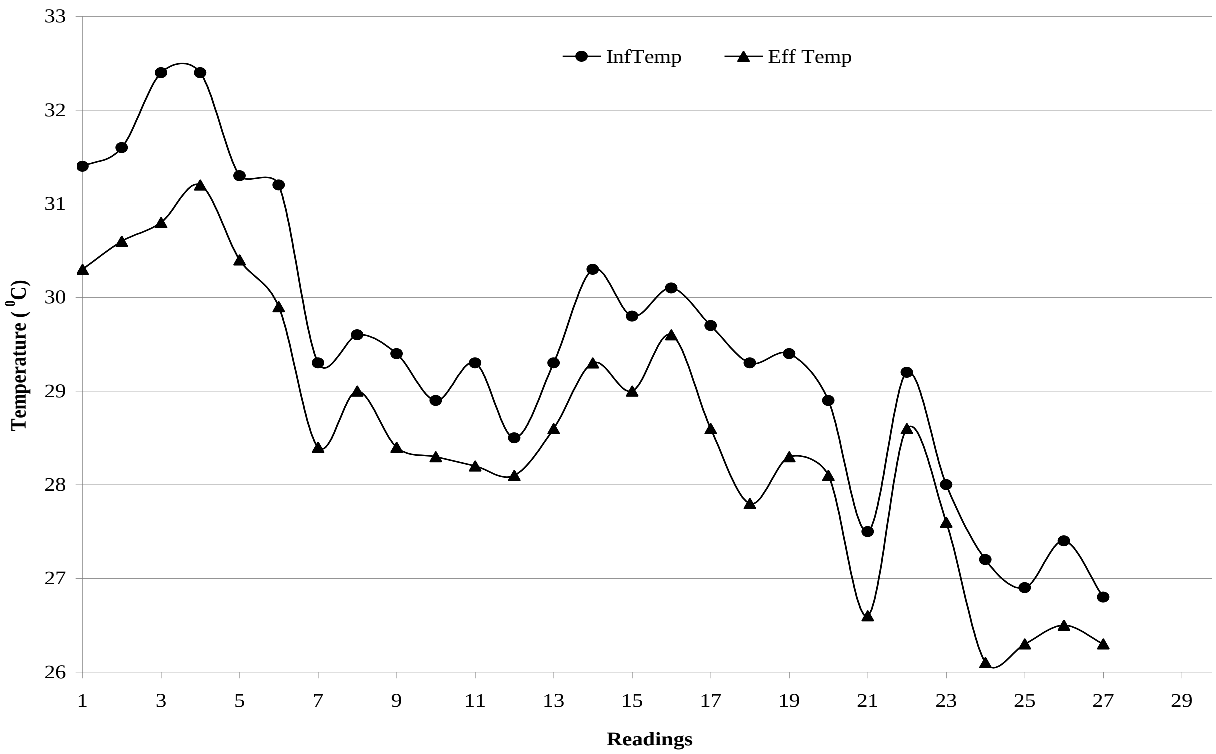

Figure 7. Time course of influent and effluent temperature.

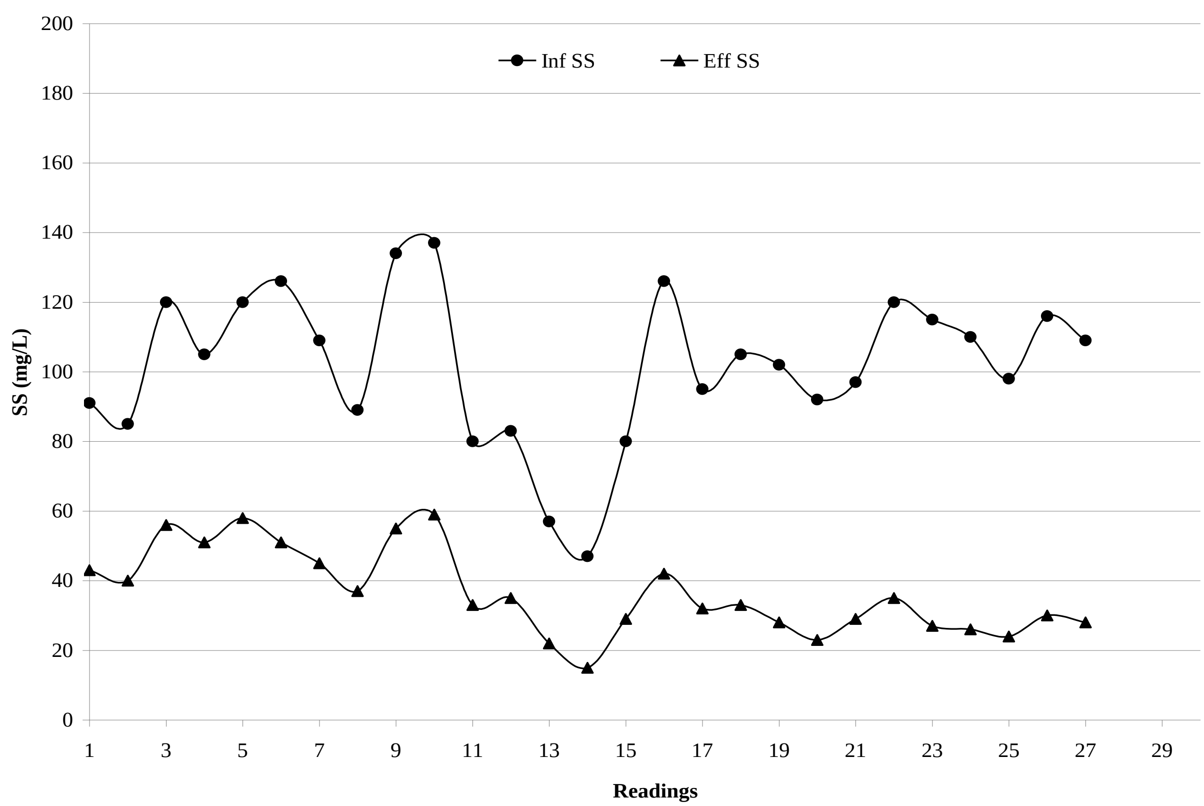

Figure 8. Time course of influent and effluent SS.

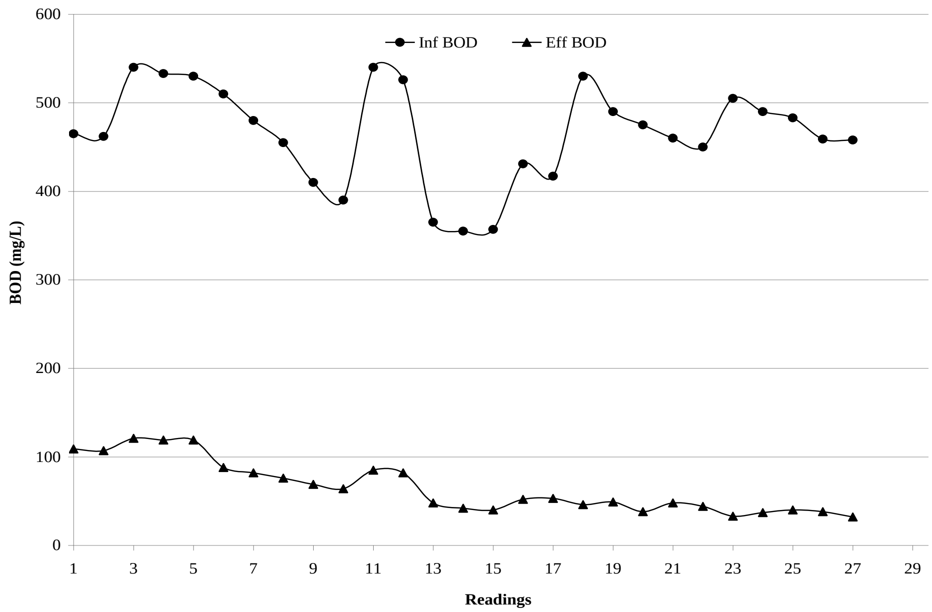

Figure 9. Time course of influent and effluent BOD.

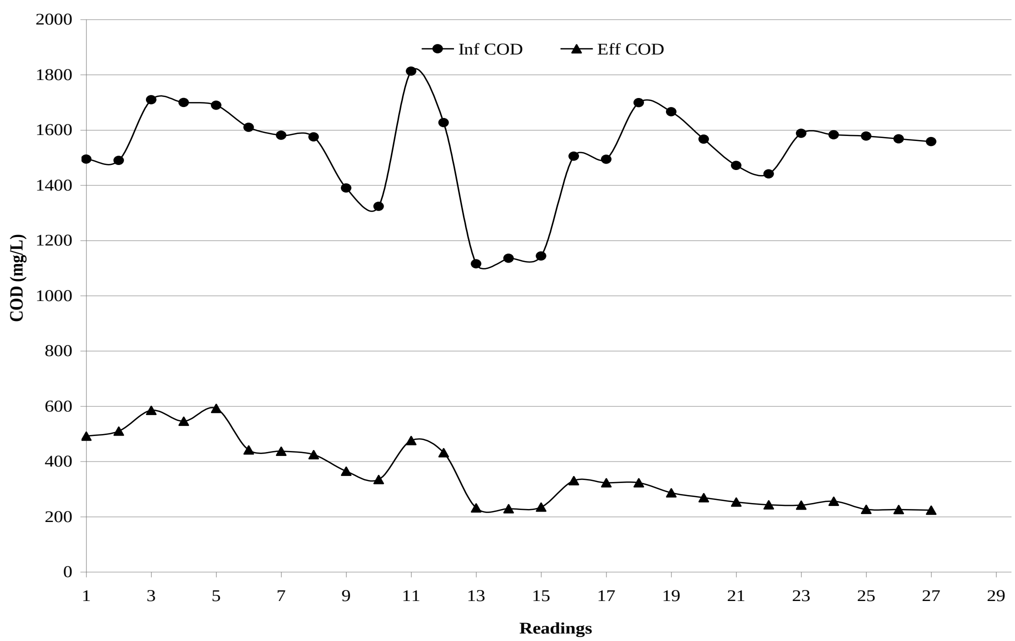

Figure 10. Time course of influent and effluent COD.

less than 150 mg/L and remained in a range of 50 to 120 mg/L. Effluent SS concentration consequently decreased with the increase in detention time in secondary clarifier.

BOD and COD food to mass ratio

Food to mass ratio (F:M) for BOD and COD in kgCOD/kgMLSS-d at various aeration times with corresponding percentage BOD and COD removal efficiencies are shown in Figures 11 and 12, respectively.

These values can help designers for the selection of an appropriate organic loading while targeting for particular removal efficiency. The data indicated that F:M ratio removal efficiency were inversely proportional to each other and hence, an increase in F:M resulted in a decrease in

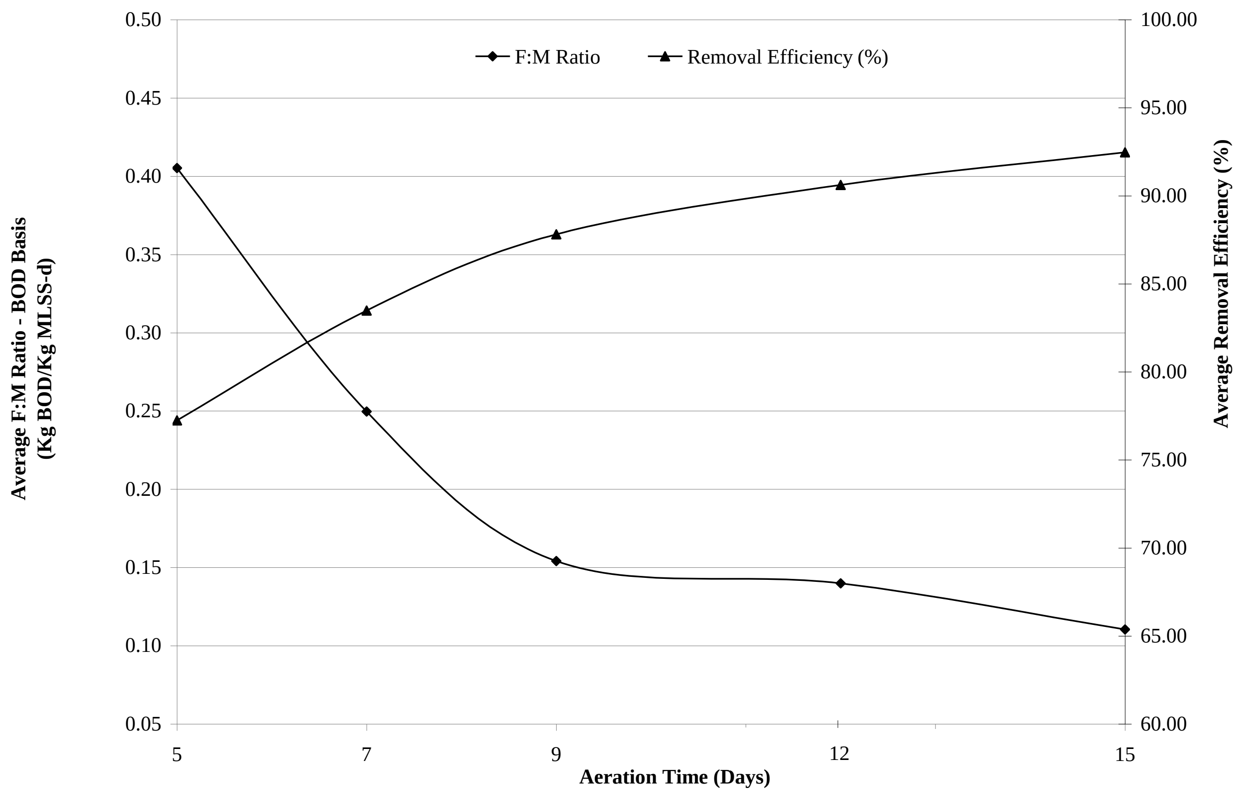

Figure 11. BOD F:M ratio and removal efficiency.

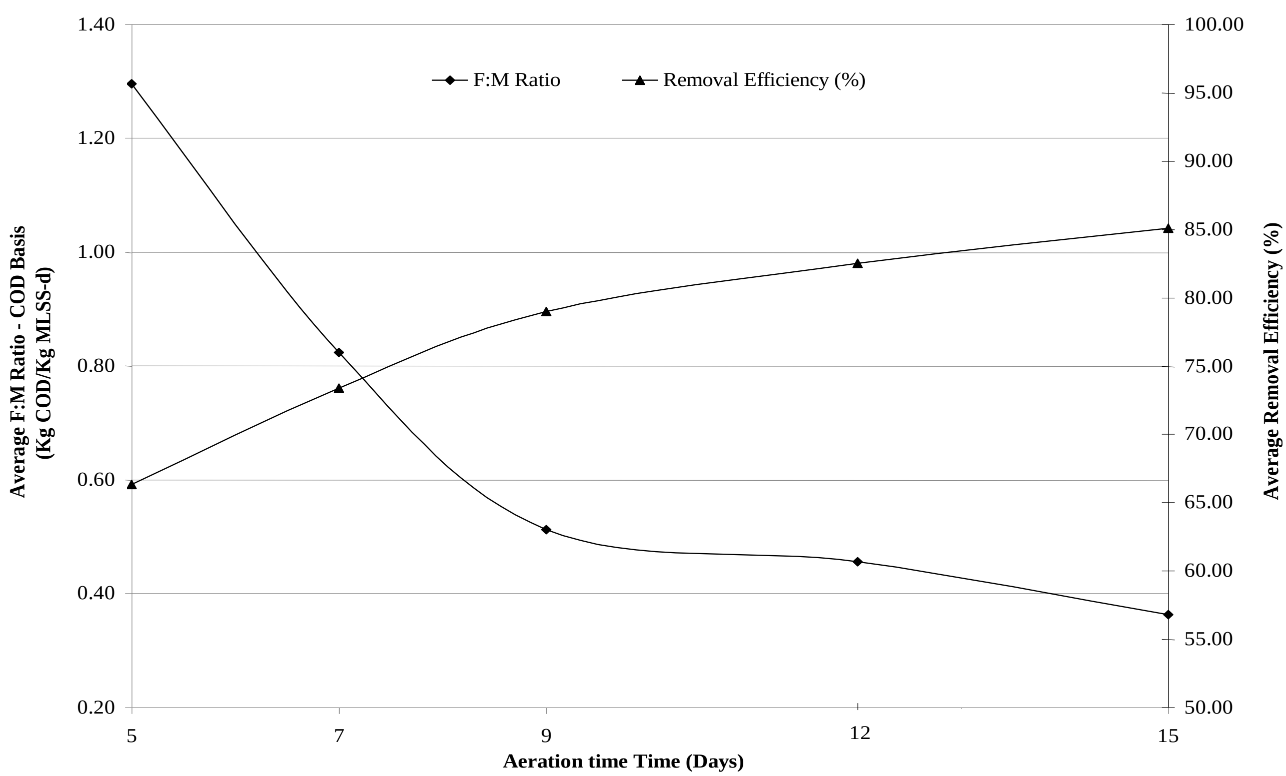

Figure 12. COD F:M ratio and removal efficiency.

Table 6. Summary table for mean values for kinetic coefficients on BOD basis.

Aeration time (Day)	S_o (mg/L)	S (mg/L)	X (mg MLSS/L)
5	506	115	250
7	473	78	268
9	385	47	275
12	481	45	284
15	479	36	290

Table 7. Summary table for mean values for kinetic coefficients on COD basis.

Aeration time (Day)	S_o (mg/L)	S (mg/L)	X (mg MLSS/L)
5	1617	545	250
7	1560	416	268
9	1279	270	275
12	1569	275	284
15	1575	235	290

efficiency. The F:M ratio is representative of the amount of food present on the tank to the number of microorganisms, an increase in this ratio means that the number of microorganisms present in the tank have been reduced therefore, decreasing the removal efficiency of the reactor. The statement is true vice versa. The range of F:M for BOD was 0.1 to 0.41 kgBOD/kgMLSS-d corresponding to an efficiency of 92 to 77%. Furthermore, the range of F:M for COD was 0.32 to 1.30 kgCOD/kgMLSS-d corresponding to an efficiency of 85 to 66%.

Kinetic coefficients

In order to determine the kinetic coefficients, the bench scale aerated lagoon was operated at 5, 7, 9, 12 and 15 days aeration times (θ). The aeration time is symbolically represented by θ. The reactor kinetics are based on mean cell residence time represented as θc, however, in a CSTR without recycle both values are same. At each aeration time minimum, five readings of Influent BOD and COD (S_o), effluent BOD and COD (S) and MLSS of aeration tank X were taken. Mean of these five readings was used for the calculation of the kinetic coefficient. These mean values are shown in Tables 6 and 7 for BOD and COD, respectively.

For k and K_s, a graph was plotted between $\frac{1}{S}$ along x-axis and $\frac{X\theta_c}{S_o - S}$ along y-axis and shown in Figures 13 and 14.

For K_d and Y, a plot was made between $\frac{S_o - S}{X\theta_c}$ along x-axis and $\frac{1}{\theta_c}$ and shown in Figures 15 and 16.

COD and BOD relationship

The correlation between the two parameters for influent was found out by plotting data for average influent COD and BOD as shown in Figure 17. The relation came out to be COD = 3.28 BOD.

First order model for aeration tank

It is quite common to design aerated lagoons using first order kinetics for BOD reaction. The resulting equation can be written as:

$$S = \frac{S_o}{1 + K\theta}$$

Overall BOD removal rate constant (K) was determined using McKinney's (1974) equation:

$$\frac{S_o}{S} - 1 = K\theta$$

where S_o is the influent BOD, mg/L; S is the effluent BOD, mg/L; K is the overall BOD removal rate constant, d^{-l}, and t is the aeration time, d.

From the study, the value of "k" came out to be 0.797 day^{-1} for BOD and 0.390 day^{-1} for COD and they are shown in Figures 18 and 19, respectively.

Conclusions

This paper deals with the determination of kinetic coefficients for biological treatment of wastewater from the textile industry. On the basis of research, the following major conclusions have been derived:

(1) An average value of 3.28 was recorded for COD/BOD ratio of the influent to the bench scale aerated lagoon. It clearly indicated that large portion of organic matter in textile wastewater is not easily biodegradable.
(2) The F:M ratio for BOD ranged between 0.1 and 0.41 kgBOD/kgMLSS-d corresponding to a removal efficiency of 92.47 to 77.24%. Furthermore, the range of F:M ratio

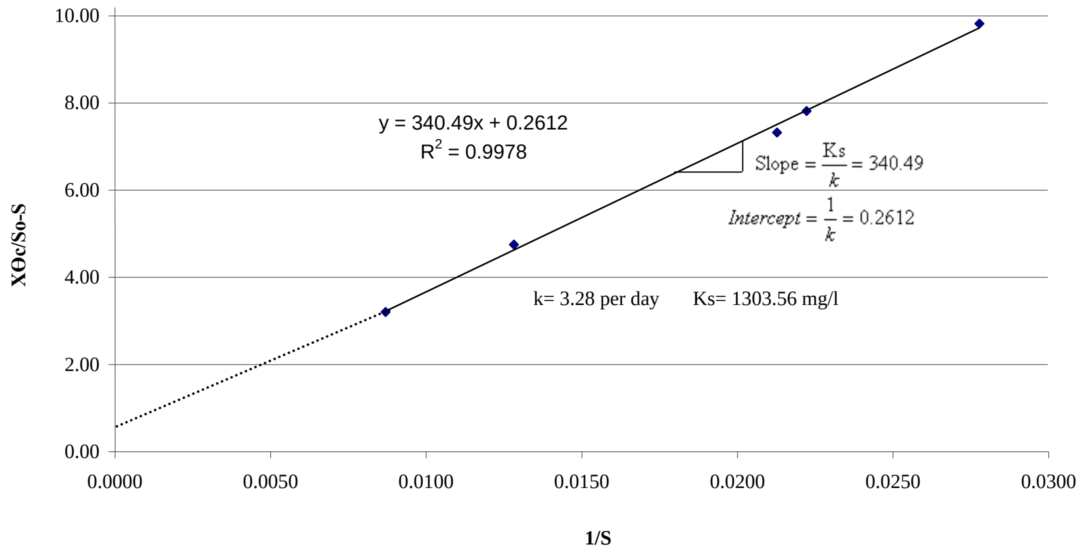

Figure 13. k and k_s on BOD basis.

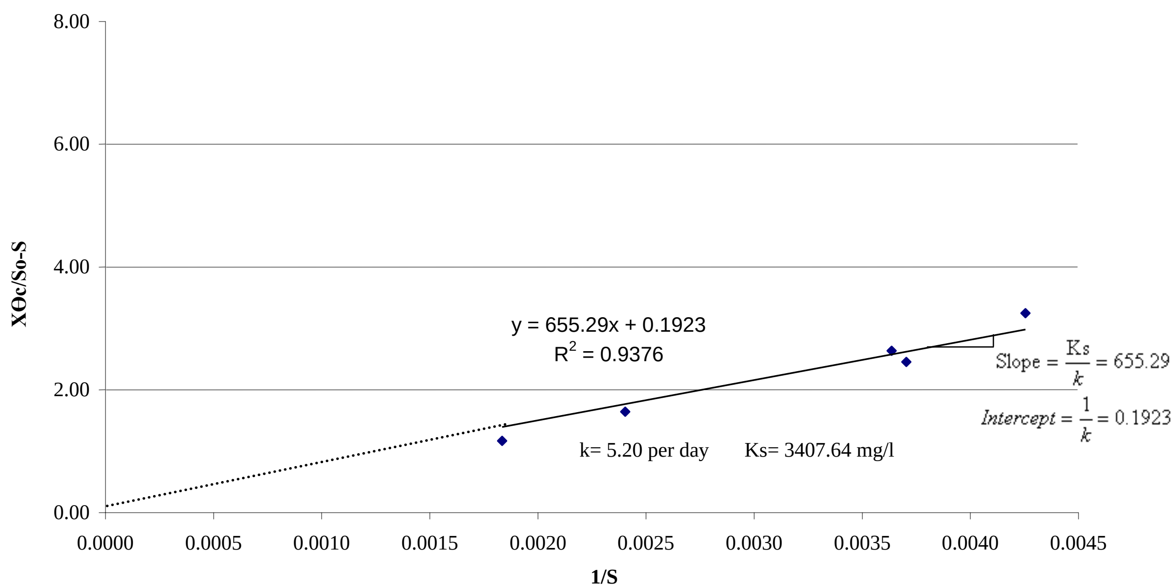

Figure 14. k and k_s on COD basis.

for COD varied between 0.36 and 1.30 kgCOD/kgMLSS-d corresponding to a removal efficiency of 85.08 to 66.30%.

(3) The kinetic coefficients k, K_s, Y and K_d determined were found to be 3.83 day^{-1}, 1303.56 mg/L, 0.70 and 0.01 day^{-1} on BOD basis and 5.20 day^{-1}, 3407.64 mg/L, 0.25 and 0.006 day^{-1} on COD basis.

(4) BOD removal followed a gradual rise with an increase in detention period and rose from 77% at 5 days aeration time to 92% at 15 days aeration time. The average effluent quality in terms of BOD at aeration time of 7 days met the NEQS requirements of 80 mg/L.

(5) The trend of COD removal also followed a gradual rise with an increase in detention period. The percentage COD removal observed at aeration times of 5 and 15 days were 66 and 85%, respectively. However, the effluent COD did not meet the NEQS Limit of 150 mg/L even at the aeration time of 15 days. The possible reason to this effect was the presence of non-biodegradable chemicals/dyes used during textile process in the factory.

(6) Overall removal rate constant (K) for wastewater of textile industry was calculated to have a mean value of 0.79 day^{-1} based on BOD. Based on COD, the overall removal rate constant (K) was found out to have a mean

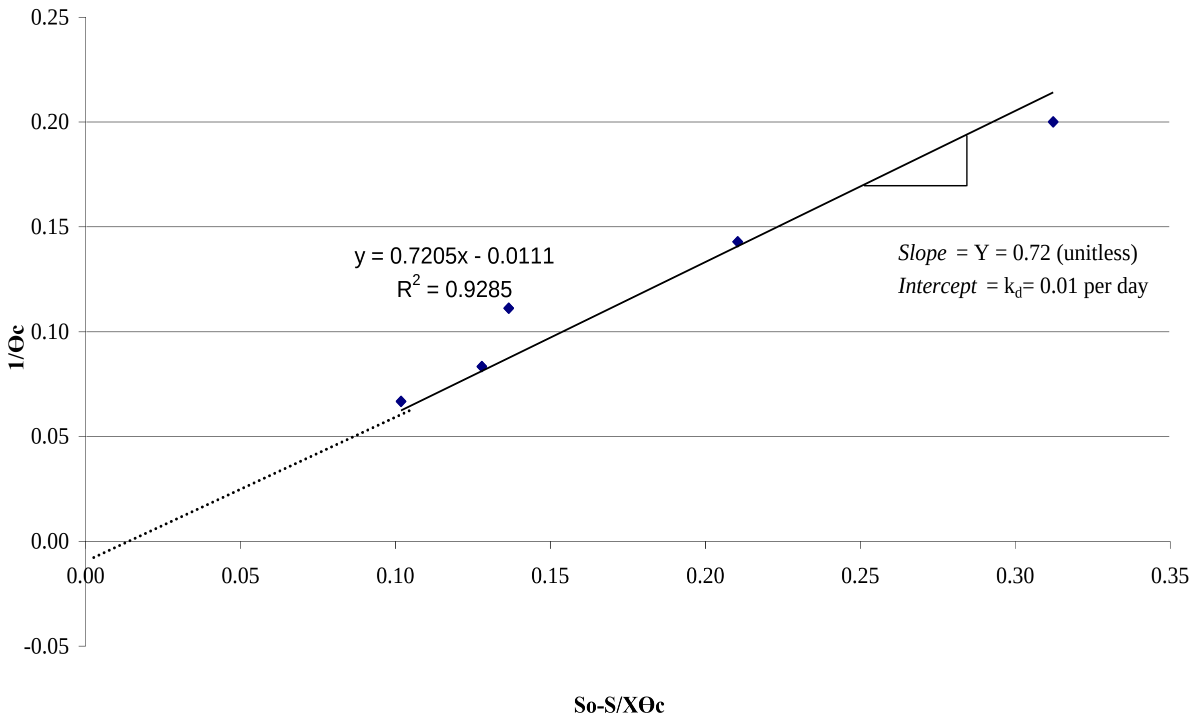

Figure 15. Y and k_d on BOD basis.

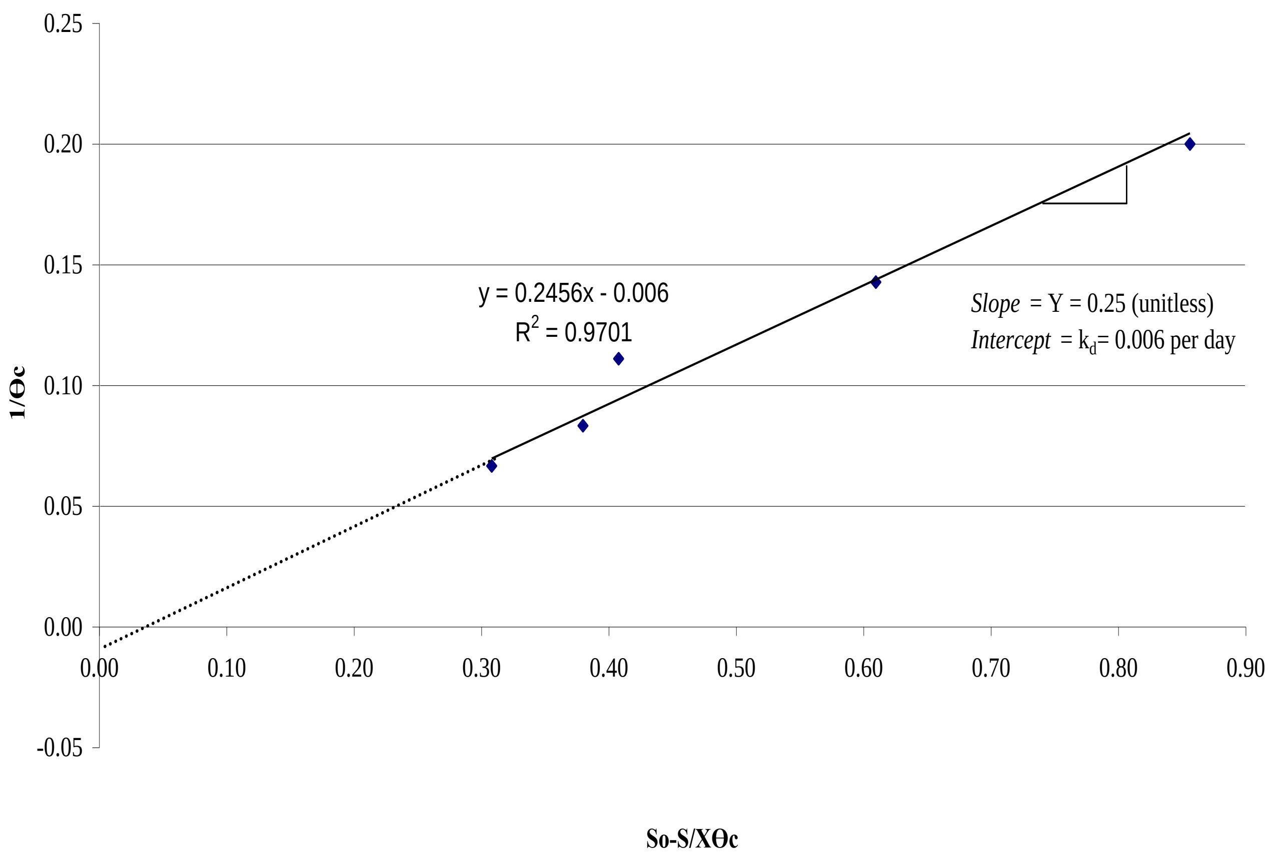

Figure 16. Y and k_d on COD basis.

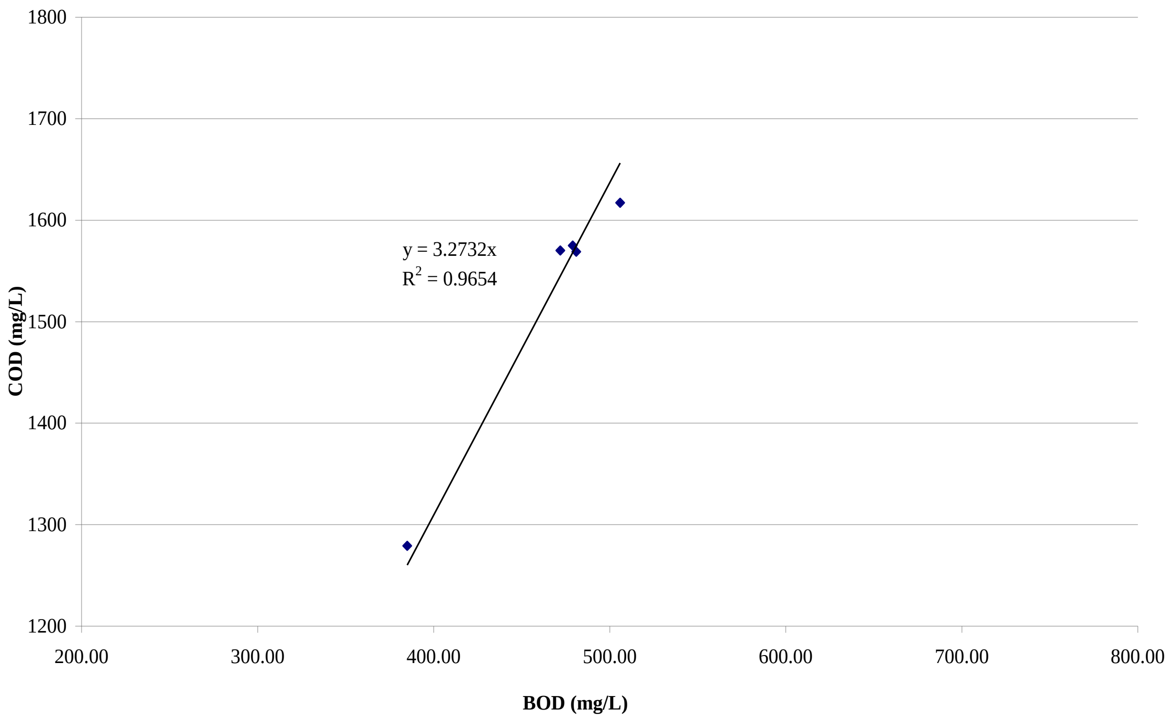

Figure 17. COD and BOD relation for influent.

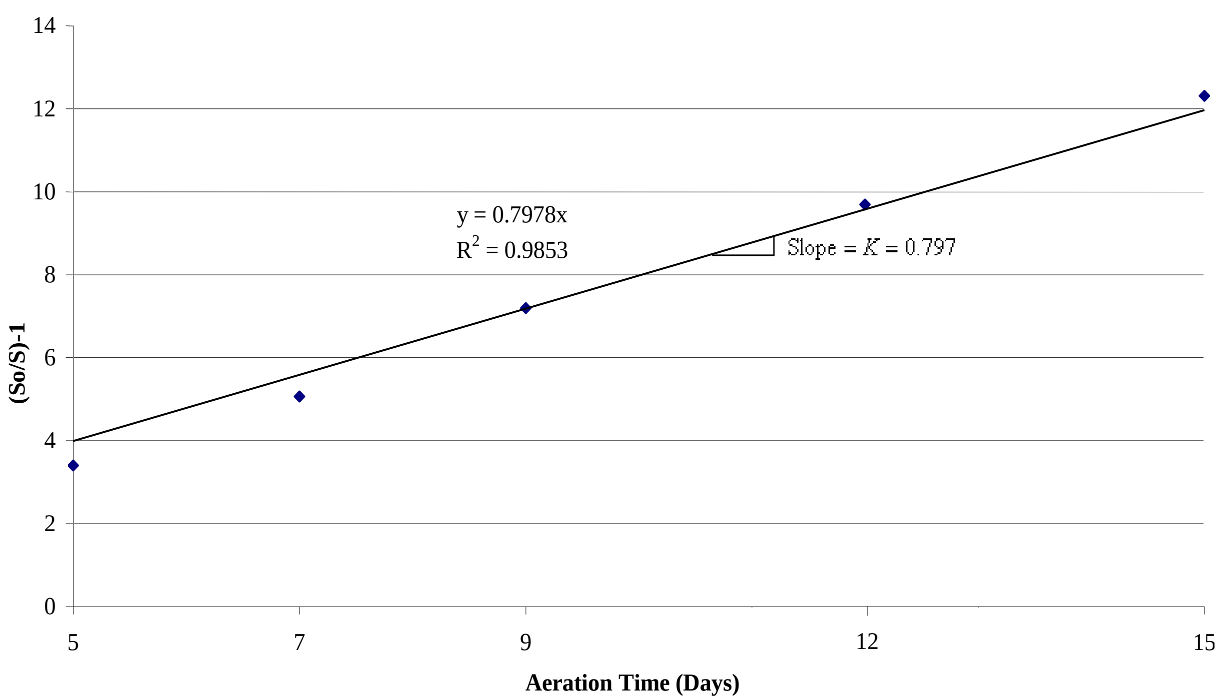

Figure 18. K value on the basis of BOD.

value of 0.39 day^{-1}.

(7) Average effluent BOD at 7 days aeration time revealed results conforming to NEQS in terms of BOD. Therefore, F:M ratio in the range 0.25 to 0.41 kgBOD/kgMLSS-d and

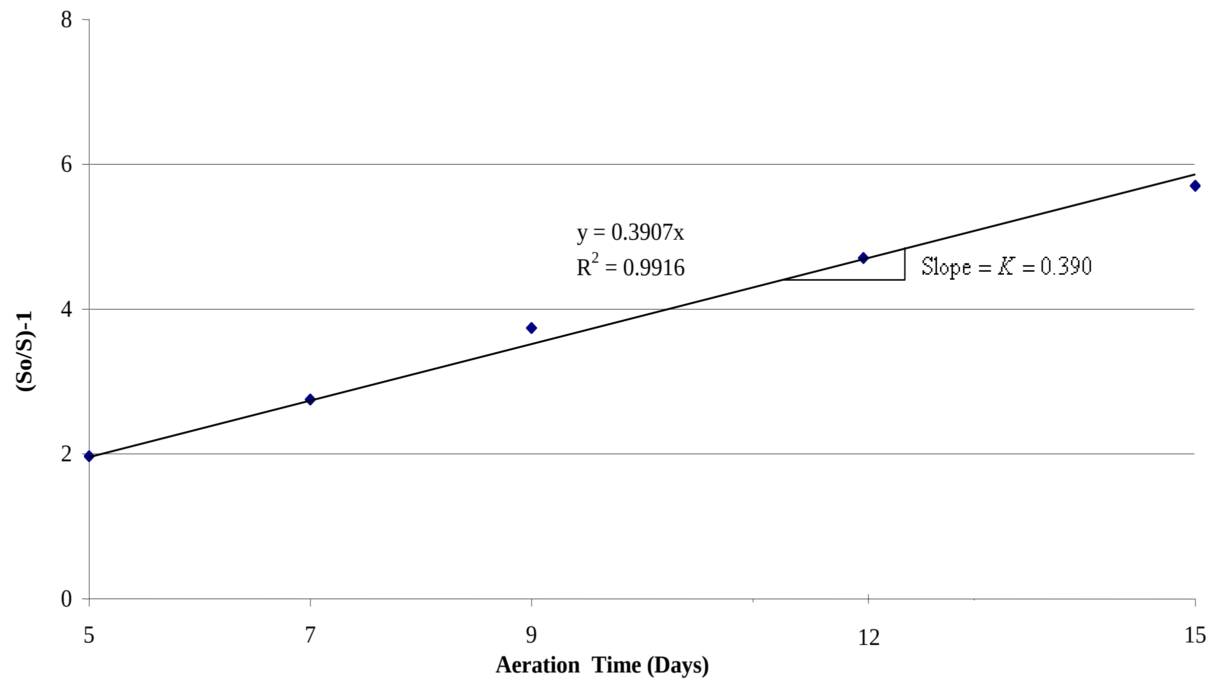

Figure 19. K value on the basis of COD.

a detention time of 7 days is recommended for textile wastewaters.

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