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Decolourisation of dye and removal of COD from textile wastewater using biodegradation method

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A study has been conducted on the biodegradation of dye and removal of chemical oxygen demand (COD) from textile waste water using mixed microbial culture in batch mode process. The microbial consortium was isolated from textile dye wastewater. The effect of process parameters namely, pH, temperature and initial dye concentration on decolourisation and COD reduction of textile waste effluent were studied. The process parameters were optimised using response surface methodology (RSM) based on central composite design (CCD). The experimental results were analysed statistically to evaluate analysis of variance (ANOVA). The optimum values of pH, temperature and initial dye concentration were 7, 30°C and 327 mg/L, respectively. Under optimum process condition, the percent removal of dye and COD were 98.68 and 92.3, respectively. The experimental results were satisfied by the model.

Keywords: Dye, chemical oxygen demand, textile effluent, optimisation, central composite design, response surface methodology.

Introduction

Large amount of different reactive dyes are used for cloth dyeing in textile industry. Effluents from dye industry containing high concentration of biochemical oxygen demand (BOD), chemical oxygen demand (COD) and color that is very difficult to treat[1]. Numerous physical and chemical methods including adsorption, ion-exchange, flocculation/coagulation, precipitation, ozonation, membrane filtration and Fenton's oxidation have been reported for the treatment of dye wastewater[2]. But all the techniques are not widely used because of high operation cost and disposal problem of sludge[3,4].

Biological treatment of dye waste effluent using microorganisms is a cost-effective and environmental-friendly alternative technique compared to the physico-chemical process[5,6].

Optimizing the growth conditions of microbes is a necessary approach for the maximum removal of COD and color present in wastewater. Response surface methodology (RSM) based on central composite design (CCD) is a suitable modelling technique of a complex system to optimize the effects of the process parameters for desirable responses[7,8].

Under the present study, mixed microbial culture isolated from soil of textile dye wastewater was used for the removal of Remazol Brilliant Blue R dye and COD from synthetic dye wastewater in batch run experiments. RSM technique was used to optimize the process parameter such as pH, temperature and initial dye concentration for maximum reduction of responses namely, dye and COD.

Materials and methods

(A) Dye, chemicals and micro-organism:

Nutrient broth, nutrient agar and Remazol Brilliant Blue R dye were purchased from Merck, India. All chemicals used in the study were of analytical grade. The structure of Remazol Brilliant Blue R (RBB-R) dye is shown in Fig. 1. Stock solution of dye (1,000 mg/L) was prepared with distilled water. The required concentration of dye was obtained by dilution of stock solution.

Mixed bacterial strains were isolated from textile dye wastewater, Falta, West Bengal for the removal of dye and COD. Wastewater sample of small amount was spread on dye contained nutrient agar plate. At the end of the 24-h in-

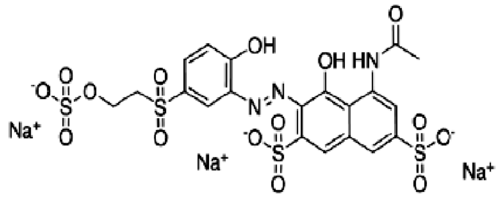

Fig. 1. Chemical structure of dye Remazol Brilliant Blue R (CAS: 70616-89-1; Mol. Wt. = 626.53 g-mol^{-1}; λ_{max} = 663 nm).

cubation period, the microorganisms present in the zone of decolorization were isolated and were grown in nutrient broth. The stock culture of the microbes was maintained as nutrient agar slant culture at 4°C. Dye solution mixing with nutrient medium was used as synthetic wastewater for decolorization and COD removal study.

(B) Batch experiments:

The experiments were conducted in 250 ml Erlenmeyer flasks with working volume of 100 ml. Bacterial consortium were grown in nutrient broth. The broth with different concentrations of dye was sterilized by an autoclave at 121°C for 20 min and was inoculated with 2% bacterial culture. After the 24-h incubation, the sample flasks were withdrawn at certain time interval and the mixed liquors were centrifuged at 5,000 rpm for 10 min to separate out cell. The supernatant was analyzed for the determination of residual dye and COD concentration. All the batch experiments were run in duplicate.

(C) Experimental design:

The RSM technique based on CCD was used to study the effects of independent process factors such as pH, temperature (°C) and initial dye concentration on responses namely, degradation of dye and removal of COD from textile wastewater. Three process variables were studied and their low and high levels are given in Table 1. The design was developed by Design Expert Version 10 (Stat Ease, USA).

The quadratic model equation to predict the optimal conditions of three factors can be expressed in the form of following equation:

$$Y_i = b_{0i} + b_{1i}x_1 + b_{2i}x_2 + b_{3i}x_3 + b_{11i}x_1^2 + b_{22i}x_2^2 + b_{33i}x_3^2 + b_{12}x_1x_2 + b_{23i}x_2x_3 + b_{13i}x_1x_3 + e$$

where i = 1 signifies for percent removal of dye and i = 2 signifies for percent removal of COD; Y is predicted response (dye or COD); b_0 is intercept, b_1, b_2, b_3 are linear coefficients; b_{11}, b_{22}, b_{33} are squared coefficients; b_{12}, b_{23}, b_{13} are interaction coefficients; x_1, x_2 and x_3 are pH, temperature and initial dye concentration respectively; e is error term[9].

(D) Analytical methods:

Dye RBB-R concentration was determined by a spectrophotometer (Varian, India) at a wavelength of 663 nm corresponding to maximum absorbance obtained. Standard curve was prepared by plotting absorbance versus dye concentration ranging from 10 mg/L to 100 mg/L. Sample of unknown dye concentration was measured by standard calibration plot. The COD measurement was done by closed reflux procedure according to the standard APHA method[10].

The percent removal of decolorization and COD was evaluated by following equation:

$$\%\ \text{Removal} = \frac{(C_0 - C)}{C_0} \times 100$$

where C_0 and C are initial and final concentrations of dye and COD in the synthetic wastewater.

(E) Batch process under optimized condition:

After the analysis of RSM technique, a set of batch run was carried out in similar Erlenmeyer flasks under optimized condition of pH, temperature and initial dye concentration. The study was conducted for 24-h and the flasks were withdrawn at certain interval for the determination of cell growth, residual dye and COD concentration.

Results and discussion

(A) Optimization of pH, temperature and initial dye concentration on the removal of dye and COD:

The 20 batch runs were carried out to represent experimental design and two responses namely percent removal of dye and COD as shown in Table 2. The relation among independent factors and responses obtained by the quadratic

Table 1. Experimental design levels of independent variables

Variables factors		Coded and actual levels				
		$-\alpha$	-1	0	+1	$+\alpha$
pH	X_1	2	4	7	10	12
Temperature (°C)	X_2	13	20	30	40	47
Initial dye conc. (mg/L)	X_3	103	50	275	500	653

Table 2. Experimental results of factorial design

Run	pH	Temperature (°C)	Initial dye conc. (mg/L)	(%) Removal of dye	(%) Removal of COD
1	4	40	500	52	46
2	10	20	500	48	47
3	4	20	50	64	42
4	7	30	275	98.84	89
5	12	30	275	42	36
6	7	30	275	98.4	92
7	7	30	653	92	87
8	7	30	275	96	88
9	7	47	275	47	42
10	2	30	275	28	24
11	7	30	275	97	90
12	10	20	50	28	26
13	7	13	275	22	20
14	10	40	500	24	23
15	7	30	103	94	91
16	4	40	50	21	19
17	7	30	275	97	90
18	7	30	275	97	91
19	4	20	500	26	24
20	10	40	50	23	21

model equations are given below:

(%) Removal of dye = 250.08 + 37.91×pH + 14.41× Temperature – 8.036E-003×Initial dye conc. – 0.05×pH×Temperature + 5.189E-003×pH×Initial dye conc. + 2.778E-003× Temperature×Initial dye conc. – 2.735×pH^2 – 0.24×Temperature^2 – 1.713E-004×Initial dye conc.^{2}.

(%) Removal of COD = 280.73 + 40.17×pH + 14.62×Temperature + 0.05×Initial dye conc. – 0.11×pH× Temperature + 2.599E-003×pH×Initial dye conc. + 1.44E-003×Temperature× Initial dye conc. – 2.63×pH^2 – 0.26×Temperature^2 – 1.63E-004×Initial dye conc.^{2}.

Three dimensional plots shown in Fig. 2 and Fig. 3 are the graphical relationship between responses (dye and COD removal) and independent factors (pH, temperature and initial dye concentration). The response surface plots depict that the maximum percent removal of dye and COD are 98.68 and 92.3 respectively. The optimum values of pH, temperature and initial dye concentration are 7, 30°C and 327 mg/L respectively. The validity of model was tested by the analy-

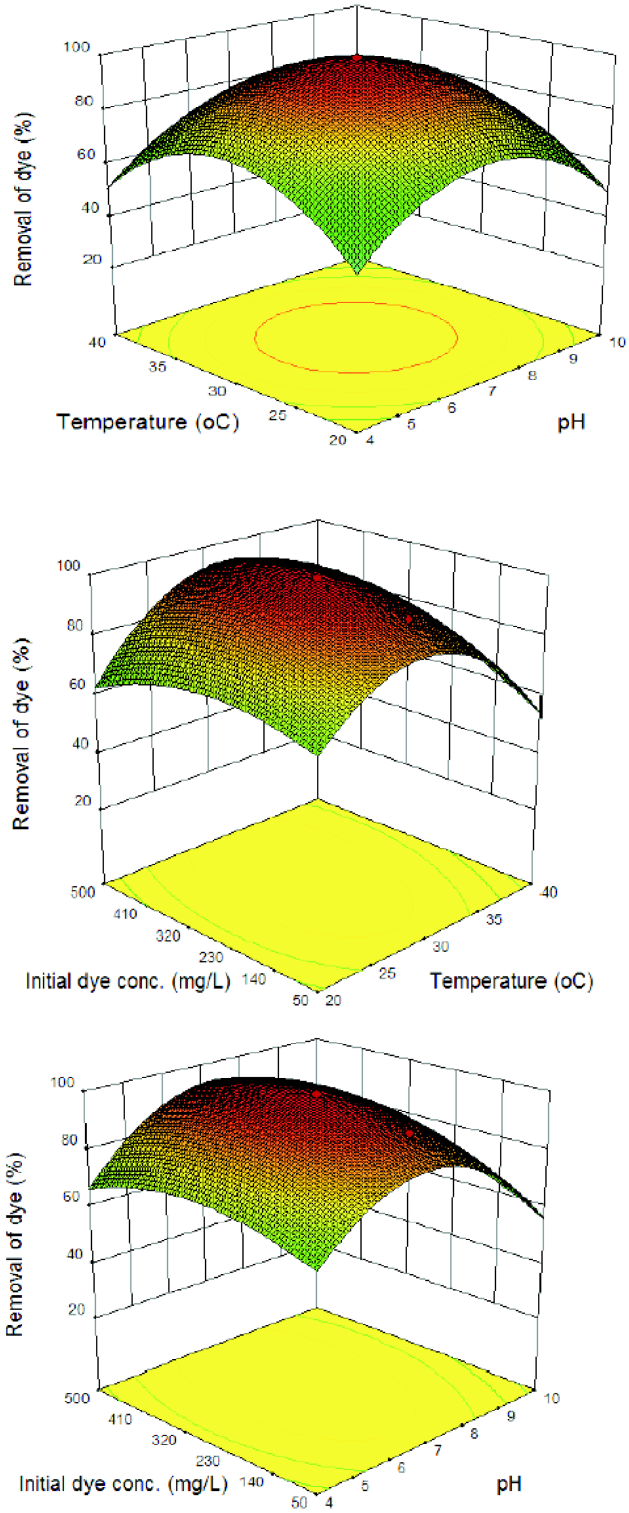

Fig. 2. Response surface and contour plots showing the effect of pH, temperature (°C) and initial dye concentration (mg/L) on removal of dye from textile effluent.

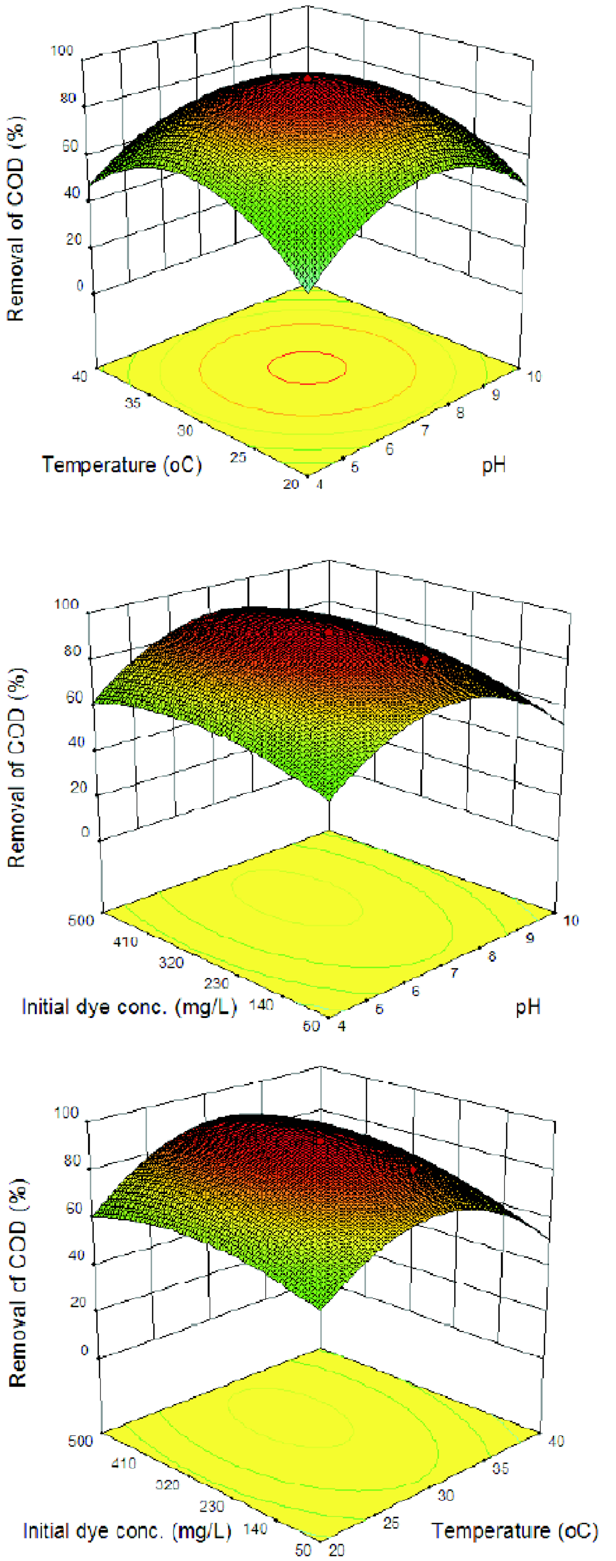

Fig. 3. Response surface and contour plots showing the effect of pH, temperature (°C) and initial dye concentration (mg/L) on removal of COD from textile effluent.

sis of variance (ANOVA). The ANOVA of percent removal of dye and COD by mixed bacterial consortium are given in Table 3 and Table 4. The significance of model was tested by Fischer's F-test. The model F-value of 84.44 for dye removal and 92.27 for COD removal indicates that the models are significant. The model P-value (< 0.0001) implies that the models are significant. R^2 values of 0.9837 and 0.9710 for two responses (dye and COD respectively) suggest a good matching between experimental results and predictions. A near value of R^2 and R_{adj}^2 indicates the adequacy of model. The correlation between experimental data and predicted values obtained from model equation are shown in Fig. 4 and Fig. 5. Optimization level of independent factors (pH, temperature and initial dye concentration) for maximum responses (dye and COD) using desirability function is shown in Fig. 6.

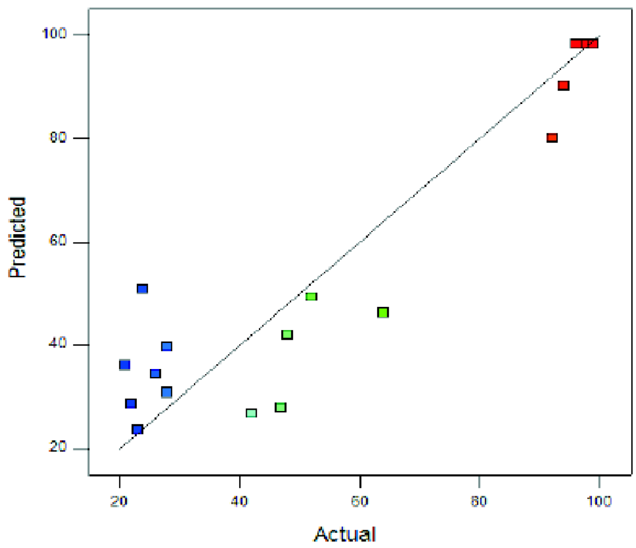

Fig. 4. Regression plot of predicted value against actual data from response surface models for dye removal.

(B) Batch process under optimum condition:

The behavior of optimally batch operating system was elucidated with respect to time history of cell growth, residual dye concentration and residual COD concentration as shown in Fig. 7. The increasing trend of cell growth has been observed with significant reduction of residual dye and COD concentration simultaneously during batch period.

Table 3. Analysis of variance fitted to the model for percent removal of dye

Source	Sum of squares	df[a]	Mean square	F-value	P-value	Prob > F
Model	17776.58	9	1975.18	84.44	< 0.0001	Significant
Residual	2339.39	10	233.94			
Lack of fit	2333.88	5	466.78	23.62	0.061	Not significant
Pure error	5.51	5	1.10			
R^2	0.9837					
R_{adj}^2	0.9790					
CV	25.59					

Note: df[a]: Degree of freedom.

Table 4. Analysis of variance fitted to the model for perfect removal of COD

Source	Sum of squares	df[a]	Mean square	F-value	P-value	Prob > F
Model	16487.89	9	1831.99	92.27	< 0.0001	Significant
Residual	1492.91	10	149.29			
Lack of fit	1482.91	5	296.58	18.29	0.074	Not significant
Pure error	10.00	5	2.00			
R^2	0.9710					
R_{adj}^2	0.9622					
CV	22.46					

Note: df[a]: Degree of freedom.

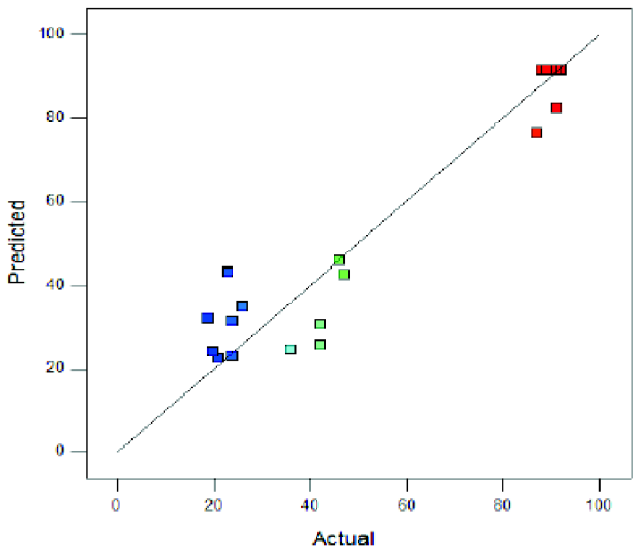

Fig. 5. Regression plot of predicted value against actual data from response surface models for COD removal.

(C) Kinetics:

Under the study, batch experimental results obtained from biodegradation of dye wastewater using mixed microbial culture was fitted to first order kinetic model equation. The first order kinetic equation is:

$$\ln\left(\frac{S_0}{S}\right) = kt$$

where S_0 is initial substrate (COD) concentration (mg/L) and S is final substrate (COD) concentration (mg/L), t is biodegradation time (h). k is the first-order rate constant (h^{-1}).

The batch experimental data was fitted to the first order equation is shown in Fig. 8. The value of rate constant k was 0.0484. The determination of coefficient (R^2) was 0.9114 that indicated the good fitness of the kinetic model for the biodegradation of dye wastewater.

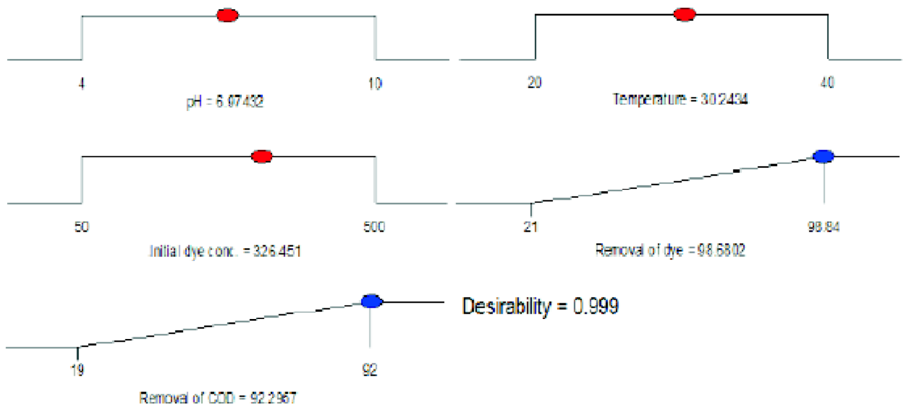

Fig. 6. Desirability ramp for pH, temperature, initial dye concentration, percent removal of dye and COD.

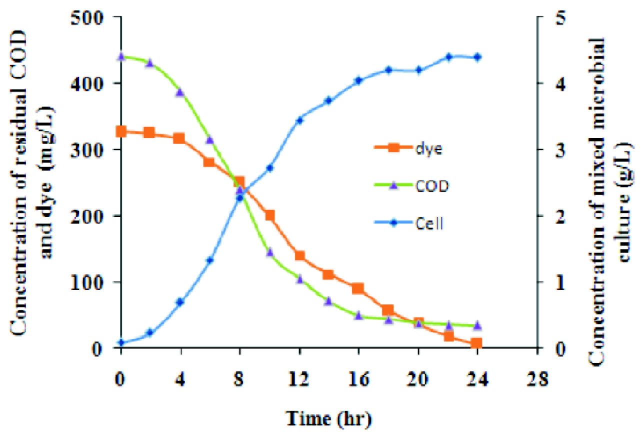

Fig. 7. Batch experiment of mixed microbial culture using dye wastewater with optimized values of pH (7), temperature (30°C) and initial dye concentration (327 mg/L); Cell growth; Residual dye: Residual COD. Means of two analytical replications.

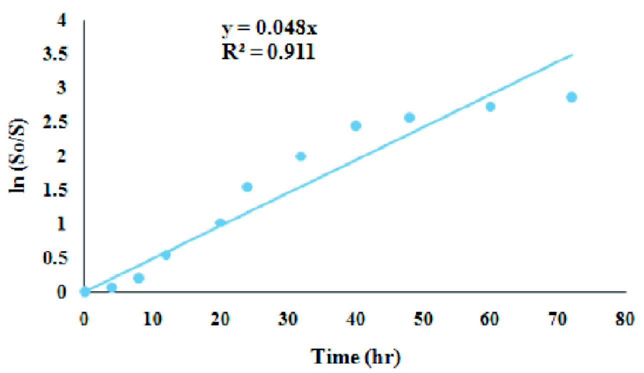

Fig. 8. First order kinetic plot for biodegradation of textile wastewater.

Conclusions

The present work investigated the percent decolorization of textile dye Remazol Brilliant Blue and reduction of COD during batch experiment using microbial consortium, isolated from textile dye wastewater. A five-level CCD design for RSM was used for the optimization of process parameters such as pH, temperature and initial dye concentration. The maximum percent removal of dye and COD were 98.68 and 92.3 respectively at the optimized condition of pH (7), temperature (30°C) and initial dye concentration (327 mg/L). Under optimum condition, identified by RSM technique, significant removal of dye and COD has been observed in batch mode operation. The first order model was well fitted with kinetics of dye degradation. It can be concluded that the outcome of the present investigation will be applicable for degradation of dye and COD reduction in large-scale.

References

1. S. C. R. Santos, V. J. P. Vilar and R. A. R. Boaventura, *J. Hazard. Mater.*, 2008, **153**, 999.
2. F. Deniz, *Mater. Sci. Eng.*, 2013, **C33**, 2821.
3. M. Jeckel, *Schriftenreihe Biologische Abwasserreinigung,* 1997, 3.
4. A. Bes-Piá, J. A. Mendoza-Roca, M. I. Alcaina-Miranda, A. Iborra-Clar and M. I. Iborra-Clar, *Desalination,* 2002, **149**, 169.
5. G. R. Gong, Y. Ding, L. Mei, C. Yang, H. Lio and Y. Sun, *Dyes Pigm.,* 2005, **64**, 187.
6. E. Ahmed, D. Ludo and B. Lorenzo, *Biofuels Bioproducts Biorefining,* 2014, **8**, 283.
7. R. H. Myers and D. C. Montegomery, John Wiley and Sons Inc., New York, 2002.
8. H. Lee, M. Song and S. Hwang, *Process Biochem.,* 2003, **38**, 1685.
9. S. Chattoraj, N. K. Mondal, B. Das, P. Roy and B. Sadhukhan, *Appl. Water Sci.,* 2014, **4**, 79.
10. APHA, *Water Environment Federation,* 1998.