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Kinetic modelling of hybrid upflow anaerobic sludge blanket reactor in treatment of pulp and paper mill wastewater

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Hybrid Upflow Anaerobic Sludge Blanket (HUASB) reactor filled with rumen liquid associated with cow-dung mixture (3:1) has been fabricated and tested for its performance on the removal of chemical oxygen demand (COD) with different operating conditions for the effluent of pulp and paper industry. The experimental procedure is carried out for a total period of 84 days by applying a COD (attained by trial and error method) range of 11312 kg COD/day in the influent with different Organic Loading Rate (OLR) and Hydraulic Loading Rate (HLR). To test the large scale application of the reactor, the initial COD concentration is not reduced from raw wastewater value. An efficiency of 85.6% was achieved with respect to COD removal during the study. Kinetic models are fitted to the data obtained and the best fit models are highlighted. Kinetic parameters like decay coefficient, first and second order rate constants, and yield coefficient are determined for the HUASB reactor.

Keywords: COD, HUASB reactor, Kinetic Modelling, Stover-Kicannon model, First order model, Monod model

The treatment of waste water using cost-effective and convenient technology includes developments of newly designed reactor and new operating systems are in emergent need in order to sustain the safe water disposal. Concerning these points in addition to the advanced removal and energy efficient, upflow anaerobic sludge blanket (UASB) reactors are being used often for wastewater treatment, recent past[1-4]. Earlier reports revealed its capability in removing COD, biological treatment ability, cost-effective nature and minimal sludge formation. There are tremendous reports available on the application of USAB in various industrial and municipal wastewater[1,6,7] treatments. The lack of static dynamic details and continuous online monitoring ways for anaerobic digestion are the current drawbacks in utilizing the UASB process. Even the sensors are prone to give stable and better precaution condition for the anaerobic reaction process, the activity of biosensor is affected as the long running time, which led to serious issues viz., corrosion of device, signal fuzzy and standard deviation in resulting data.

To date, only extremely limited work has been undertaken to review the UASB system's operating circumstances. Wastewater treatment plants are often accounted major points of antibiotic[5-8] discharge. High content of antibiotics are released into municipal wastewater due to the antibiotic abuse of human[9], which ultimately find their ways into natural environment. Another main source of antibiotics to the environment is antibiotic pharmaceutical industry. Literature proved that, the application of anaerobic treatment system is very effective for a large scale range of wastewaters includes antibiotics and pharmaceutical effluents[10].

The granular sludge placed in USAB acts as barrier towards the vulnerable microorganisms of toxic substrates, which enable high protection against wastewater containing biological toxic compounds. Jiang *et al*.[2] established that a microbial fuel cell treatment enhances the rate and extent of degradation of organic matter in the sludge, particularly when ultrasound is applied during sludge pretreatment. Process kinetics is being used for the mathematical description of both aerobic and anaerobic biological treatment processes. The understanding of process kinetics is essential for the design and operation of biological treatment systems, predicting system stability, effluent quality and waste stabilization.

Based on an extensive literature review and survey pertaining to the applications of HUASB for treating varieties of industrial wastewaters, an attempt was made to treat raw wastewater in this reactor. The sample analysis was carried over based on the American Public Health Association (APHA) standard procedures. The anaerobic hybrid reactor (AHR) is a combination of an anaerobic sludge blanket in the lower part and an anaerobic filter (AF) in the upper part has been designed in the present study. Since, this type of reactor combines a sus pended biomass and attached biomass, it is necessary to consider each region separately in order to calculate the kinetic coefficients of the reactor[12]. The Hybrid Upflow Anaerobic Sludge Blanket (HUASB) reactor is a latest design reactor which is the hybrid version of an UASB reactor with a random packing media at the top of the reactor. In such a reactor, the upper 50-70% is filled with either floating (or) stationary materials to retain some of the escaping biomass.

Experimental Section

Reactor setup

The HUASB reactor in laboratory scale grade has been designed and fabricated. It has the dimension of 10 cm diameter with 100 cm height having the capacity of 7.85 litres[14,15]. The reactor was designed using glass provided with three ports to collect samples at required time interval. The experimental arrangement of the HUASB reactor is shown in Fig. 1. There are three zones in the reactor. The bottom one of about 50 cm length collects the liquid, where the centre zone of about 25 cm height contains packing material which governs the solid residues and the top zone of about remaining cm (25 cm) is for collection of gaseous particles. Also, hoods are provided at top and bottom of the reactor for gas venting and probable sludge accumulation respectively. Plastic PVC tubes were connected to the ports to draw sample from it. In this study, polypropylene polyhedral spherical balls (heat and corrosion resistant) were used to pack the top 25 cm depth above the liquid portion in the reactor. The balls are white in colour with a diameter of 36 mm, height of 30 mm, weight of 4.41 g/piece, specific gravity of 0.92, total specific surface area of 388 m^2/m^3 .

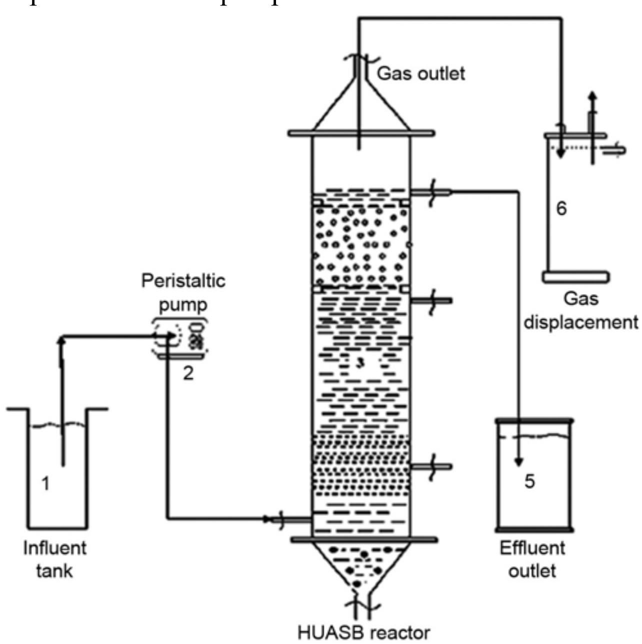

Fig. 1 — Experimental arrangement of HUASB reactor

Reactor operation

The HUASB reactor was started with an initial COD concentration of 11312 kg COD/day and with flow rate of 0.3 mL/min. With a view to provide inoculums to the anaerobic bacteria, one litre of rumen liquid and cow-dung mixture in the ratio of 3:1 was introduced into the reactor after sieving to remove the coarse particles. The rumen liquid was collected from the nearby veterinary hospital, Coimbatore. Then the reactor was allowed to stand for 28 days in unchanged condition to attain the steady state condition. After that, the performance of the reactor with different flow rates (0.4, 0.5, 0.7, and 0.9 mL/min) and HRTs of 16.2, 12.15, 9.72, 6.94, and 5.4 d were analysed.

Physicochemical properties of wastewater

The physico-chemical properties viz., chemical oxygen demand (COD), biochemical oxygen demand (BOD), conductivity, turbidity, total dissolved solids (TDS), total suspended solids (TSS), total hardness, chlorides, sulfates, oil and grease, colour and pH for the samples collected from various ports were calculated. All the parameters were calculated by standard APHA procedures.

Results and Discussion

Waste water dharacterisation

The chemical and biological parameters of raw wastewater collected from pulp and paper industry is shown in Table 1. It is observed from the Table 1 that, the wastewater seems to exceeds the limit of effluent standards with respect to solids, *p*H, Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), which requires meticulous treatment before discharging it into the water bodies and/or land applications[15]. Also, a typical COD/BOD ratio of 2.2 was noticed for the wastewater, on the basis of respective total values. Although the COD/BOD ratios vary between 3.5 and 8, for various Indian-based pulp and paper mill industries, the typical COD/BOD ratio for a particular wastewater originating from each unit may be less than the reported values. Hence, the COD/BOD ratio of 2.2 for this wastewater signifies the suitability of biological treatment.

COD removal efficiency

Performances of the HUASB reactor, based on COD removals (combined and separate variations), for all HRTs were carried out. The higher COD removal was obtained (about 87%) at reactor operation having a HRT and OLR of 16.2 d and 0.71 COD/m^3d, respectively. The maximum removal of COD of about 87% has been obtained in the last phase of the reactor operation. The decrease in TSS concentrations (at all the ports, as expected) has been observed from port 1 to port 3 under all HRTs. The results were shown in Table 2.

Kinetics of substrate removal

Kinetic studies play a vital role in industrial anaerobic reactor design. The bio-chemical process variables and kinetics of any waste water treatment can be evaluated only with the help of simulation and mathematical models. Process kinetics plays a significant role in the development and operation of any anaerobic treatment system. Based on the biochemistry and microbiology of the anaerobic process, kinetic studies provide a rational basis for process analysis, control and design. Besides the quantitative description of the rates of waste utilization, process kinetics also deals with operational and environmental factors[13,15]. Among the various available models proposed by the researchers, most reliable models like Monod kinetic model, First-order model, Grau Second order model and Stover-kicannon model were adopted to find the regression values for the reactor set up in the present study.

Table 1—Characteristics of raw wastewater from hardwood/Bagasse unit.

Sl. No.	Characteristics	Result*
I	*Chemical*	
1	*p*H	4.35
2	Acidity as $CaCO_3$, mg/L	1300
3	Alkalinity as $CaCO_3$, mg/L	Nil
4	Solids	
A	Total solids (TS), mg/L	5,790
B	Total non-volatile solids (TNVS), mg/L	1,850
C	Total volatile solids (TVS), mg/L	3,940
D	Total dissolved solids(TDS), mg/L	4,720
E	Total dissolved inorganic solids (TDIS), mg/L	4,010
F	Total dissolved volatile solids (TDVS), mg/L	710
I	Total suspended solids (TSS), mg/L	1,770
J	Settleable solids, mg/L	80
II	*Biological*	
1	BOD	
A	Total BOD_5 @ 20^0C, mg/lL	5,229
B	Soluble BOD_5 @ 20^0C, mg/L	4,840
2	COD	
A	Total COD, mg/L	11,312
B	Soluble COD, mg/L	9,884

First order kinetic model

The first order model states that, the rate of concentration variation of the substrate in a reactor with respect to time can be expressed as follows:

$$-\left(\frac{ds}{dt}\right) = \frac{Q}{V} \times S_o - \left(\frac{Q}{V}\right)S - K_1 S \quad \text{... (1)}$$

Under stable conditions, (*-ds/dt*) the rate of change in substrate concentration is negligible and the above equation gets reduced to Eq. 2, where, S_o and S are the substrate concentrations in the influent and effluent (mg COD/L), Q is the flow rate applied to the reactor (mL/min), V is the overall volume of the reactor (L), θ_H is the Hydraulic retention time in days and k_1 is the first order rate constant (d^{-1}).

$$\frac{S_o - S}{\theta_H} = K_1 S \quad \text{... (2)}$$

The value of k_1 is determined by plotting $(S_o - S/\theta_H)$ against the effluent substrate concentration S from the Eq. 2. The regression values and rate constant values were calculated from the plot of data acquired from reactor operation. Figure 2 shows the graph obtained by plotting the left hand side versus the right hand

Table 2 — Step-wise performance of HUASB reactor in COD removals.

Attribute phase	HRT, d	OLR, kg COD/m^3d	Steady state attainment, d	Maximum COD removal, %	Rate of COD removal, % per d
First (P1)	16.2	0.71	27	87	2.85
Second (P2)	12.15	0.58	12	2.7	0.25
Third (P3)	9.72	0.49	16	4.9	0.32
Fourth (P4)	6.94	0.35	12	2.5	0.22
Fifth (P5)	5.4	0.23	8	1	0.14

side portion of the Eq. 2. From the graph, it can be seen that the regression value (R^2) is 0.6339 and k_1 value obtained from the slope of the linear line of the graph is 0.1367 d^{-1}.

Stover and kicannon model

Stover and Kicannon have derived a kinetic model for bio film reactor based on total organic loading rate. The modified Stover-Kicannon model describes total organic loading rate as the main parameter to explain the kinetics of an anaerobic filter by means of organic matter removal and methane production[16-18]. Stover-Kicannon model was applied to analyse the removal efficiency of the reactor at the fixed bed region and the observations were made at five different OLR range.

The Stover-Kicannon equation can be given as:

$$\frac{ds}{dt} = \frac{Q}{V}(So - S) \qquad \text{...(3)}$$

$$\frac{ds}{dt} = U_{max}\left(\frac{QSo}{V}\right) \div \left(K_B + \left(\frac{QSo}{V}\right)\right) \qquad \text{...(4)}$$

The substrate removal rate (*ds/dt*) in Eq. 3 can be defined using Eq. 4 in which the U_{max} is the maximum substrate utilization rate (gL/d) and K_B, the saturation value constant (gL/d). By combining the Eqs 3 and 4, a modified Stover-Kicannon equation can be obtained as follows:

$$\left(\frac{ds}{dt}\right)^{-1} = \frac{V}{Q(S_o - S)} = \frac{K_B V}{Q U_{max} S_o} + \left(\frac{1}{U_{max}}\right) \qquad \text{...(5)}$$

U_{max} and K_B are obtained from the slope and intercept values of the plot. The calculations are carried out for the data obtained, in order to estimate the kinetic property of the Hybrid UASB reactor. Figure 3 showed the regression value, R^2 as 0.4994, the U_{max} value as 34.5 g/L and K_B value as 1043.41g/L d. The maximum utilization rate increases the reactor efficiency. Stover-Kicannon model suggested that, the substrate removal rates (COD) were affected by the organic loading rate entering the reactor.

Grau second order kinetic model

The kinetic performance of an anaerobic hybrid reactor could be evaluated by a Second order model[13]. The model was applied separately to the fixed bed region and the UASB region to evaluate the overall kinetic performance[17,18]. In this study, the same methodology is involved and the regression coefficient is estimated for the data at both fixed bed and UASB region of the Hybrid UASB reactor.

$$\frac{S_o \times HRT}{(S_o - S)} = HRT + \frac{S_o}{K_2 X} \qquad \text{...(6)}$$

The second order kinetic model is given by the Eq. 6, where, S_o and S are the influent and effluent concentration of the substrate (mg COD/L), X is the biomass concentration in the reactor (mg/L) and HRT is the hydraulic retention time (d) and K_2 is the second order rate constant (d^{-1}).

The term (S_o-S/S_o) expresses the substrate removal efficiency, E and the second term of the right side of the equation is accepted as a constant which results in Eq. 7

$$\frac{HRT}{E} = a + b \times HRT \qquad \text{...(7)}$$

In the Eq. 7, a = So/ (k_2(s) X) and b is a constant which are greater than unity. The plot between HRT/E and HRT for UASB region and fixed bed region of the reactor were drawn and the respective regression coefficients are 0.009 and 0.7305. The values of regression obtained in the present study are quite lesser compared to the literature data. Meanwhile,

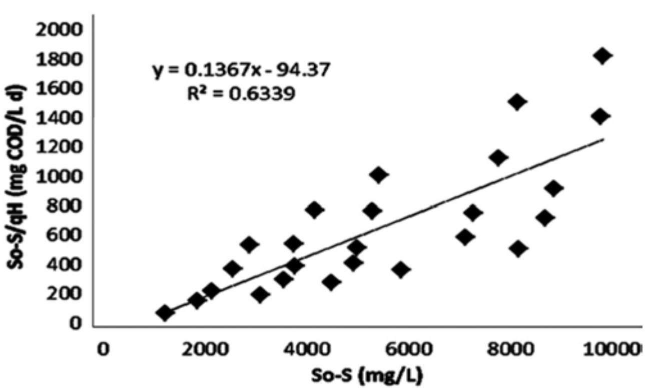

Fig. 2 — Regression graph for first order model

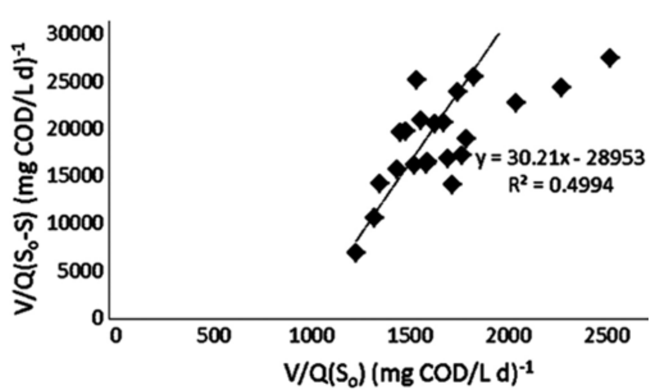

Fig. 3 — Regression graph for Stover-Kicannon model

comparing the regression value of overall reactor with the individual regression values of the fixed bed and UASB region separately, revealed that the Fixed bed reactor region attained high COD removal efficiency of about 87% and regression value as R^2=0.7305. The data used for analysing the second order kinetic model was obtained at the sample port at fixed bed region and sludge bed region of the reactor. As shown in Fig. 4, the regression value obtained for the second order kinetic model for the overall reactor (R^2=0.5818) is relatively lower than the values reported in the literature. The second order rate constant K_2 is obtained from the (*a*) value and evaluated as 0.0382 d^{-1}.

Monod Model

Monod model[19,20] was proposed based on the theory that concentration of substrate around micro-organisms is also a significantly consideration for evaluating kinetic parameters. In 1949, Monod proposed an equation for expressing the relationship between the specific growth rate and the rate limiting substrate concentration. The Monod equation is given,

$$\mu = \frac{\mu_{max} \times S}{K_s + s} \quad ...(8)$$

where,
μ = Specific growth rate per day,
S = Substrate concentration, mg/L,
μ_{max} = Maximum growth rate when the substrate is unlimited, d^{-1}
K_s = Half saturation constant, mg/L.

Under steady-state condition, it is assumed that the concentration of biomass in the influent can be negligible (dX/dt = 0 and –dS/dt = 0) and HRT (θ_H) is defined as the volume of the reactor divided by the flow rate of the influent.

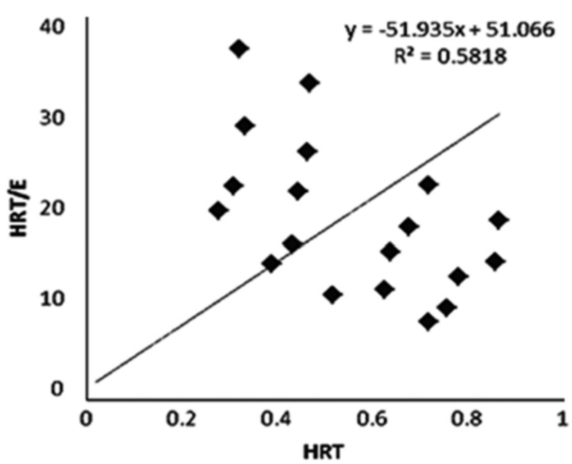

Fig. 4 — Regression graph for Second order kinetics of overall reactor

$$\mu = \frac{1}{\theta_c} + K_d \quad ...(9)$$

where, K_d is the decay coefficient and θ_C is the mean cell residence time which is the ratio of total biomass in the reactor to biomass wasted per given time represent the average time.

$$\theta_c = \frac{V \times X}{Q \times X_E} \quad ...(10)$$

By combining and rearranging Eqs 8 and 9, the kinetic parameters of the Y and K_d can be obtained from the following equation 11, where Y is the yield coefficient (mg VSS / mg COD).

$$\frac{S_o - S}{\theta_H \times X} = \frac{1}{Y} \times \left(\frac{1}{Q_c}\right) + \frac{1}{Y + k_d} \quad ...(11)$$

The regression coefficient and the kinetic parameters are obtained by plotting [(S_o-S)/(θ_H × X)] versus ($1/\theta_C$). The regression value obtained for the Monod model was negligible as it is obtained as very low (R^2= 0.013). Hence, the Monod model cannot be applied to design the HUASB reactor, while the kinetic coefficients K_d = 0.1615 d^{-1} and Y=0.0822 mg VSS mg COD^{-1} are obtained from the linear line of the graph. Figure 5 showed the regression graph for the Monod model. Similarly μ_{max} and K_s can be obtained by plotting $\theta_C/(1+\theta_C*K_d)$ against 1/S. From Fig. 6, values of kinetic constants μ_{max} = 0.0001 d^{-1}, K_s = -0.00008 d^{-1} are obtained with the low regression coefficient R^2= 0.1945. The negative values at rate constants and the substrate removal rates may indicate the maximum degree of degradation might have occurred in the reactor.

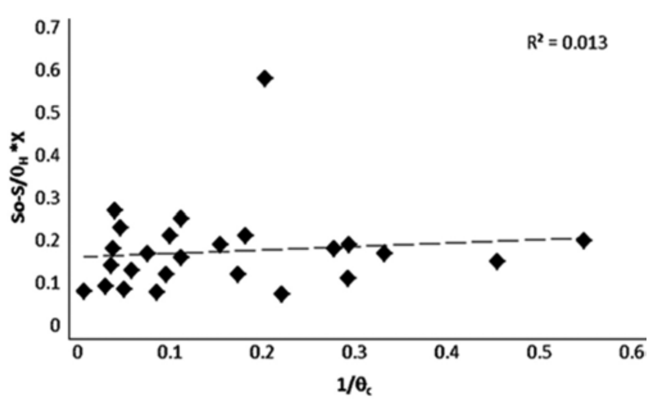

Fig. 5 — Regression graph for Monad kinetics to determine Y and K_d

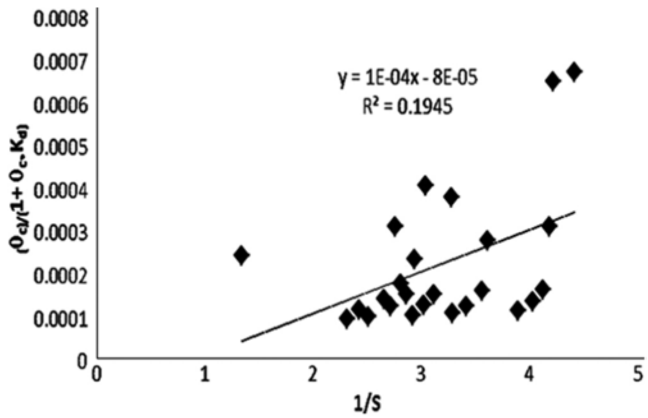

Fig. 6 — Regression graph for Monad kinetics to determine μ_{max} and K_s

Conclusion

At high HRT of 16.2 d, maximum COD removal efficiency of 86.5% is obtained and the optimized values are fitted in various kinetic models. The first order model showed a regression value of R^2 = 0.6339, second order model with 0.5818, whereas Stover- Kicannon model with R^2 = 0.4994. The observation of lesser regression values could be attributed to the real nature (industrial scale concentration) of collected samples. When second order model is applied to the attached bed region of the reactor, a regression coefficient of 0.7305 is obtained which indicates that the effectiveness of the packed media in substrate removal and TSS reduction. The observation of negative values is indicative of higher degree of degradation in the reactor. The validation of the reactor can be substantiated through this performance studies. Hence, it is clear from the results of the present study that the first order model and modified Stover-Ki cannon model are appropriate to design and operate the reactors for the treatment of wastewater.

References

1 Jia H, Yang G, Wang J, Hao Ngo H, Guo W, Zhang H & Zhang X, *Bioresour Technol*, 218 (2016) 286.

2 Jing Z, Hu Y, Niu Q, Liu Y, Li Y Y & Wang X C, *Bioresour Technol*, 137 (2013) 349.

3 Liu Z, Liu J, Zhang S, Xing X H & Su Z, *Bioresour Technol*, 102 (22) (2011) 10221.

4 Onodera T, Tandukar M, Sugiyana D, Uemura S, Ohashi A & Harada, H, *Bioresour Technol*, 152 (2014) 93.

5 Mohammadi A R, Mehrdadi N, Bidhendi G N & Torabian A, *Desalination,* 275 (2011) 67.

6 Qiu G, Song Y, Zeng P, Duan L & Xiao S, *J Hazard Mater* 246 (2013) 34.

7 Oktem Y A, Ince O, Sallis P, Donnelly T & Ince B K, *Bioresour Technol*, 99 (2008) 1089.

8 Sreekanth D, Sivaramakrishna D, Himabindu V & Anjaneyulu Y *Bioresour Technol*, 100 (2009) 2534.

9 Chen Z, Ren N, Wang A, Zhang Z & Shi Y, *Water Res*, 42 (2008) 3385.

10 Masud Hossain M K, Anantharaman N & Das M, *Indian J Chem Technol*, 16 (2009) 58.

11 Venkata Mohan S, Krishna Prasad A, Chandrasekhara Rao N, Vijiya bhaskar Y, Laith Babu V, Rajagopal D & Sharma P N, *Indian J Chem Technol*, 64 (2015)771.

12 Govindaradjane S & Sundararajan T, *Int J Eng Adv Technol,* 2 (4) (2013) 2249.

13 Jafarzadeh M T, Mehrdadi N & Hashemian S J, *Asian J Chem*, 21 (3) (2009) 1672.

14 Pandian M, Hao NGO H & Pazhaniappan S, *J Water Sustainability*, 1(3) (2011) 301.

15 Rizvi H, Yasar A, Ahmad N, Ali S, Abbas F, Hussain Bukhari I, Yasmeen T & Riaz M, *Arabian J Chem,* 8 (2015) 780.

16 Kreutz C, Passig Fernando, De Carvalho Karina Q, Mees Juliana B R & Gomes Simone D, 34 (2014) Doi.org/10.1590/S0100-691620140002000175.

17 Jijai Sunwanee, Srisuwan Galaya, O-thong Sompong, Ismail Norli & Siripatana Chairat, *Energy Procedia,* 79 (2015) 90.

18 Işik Mustafa & Teresa Sponza Delia, *Process Biochem,* 40 (2005) 1189.

19 Sniegowski Kristel, Mertens Jan, Diels Jan, Smolders Erik & Springael Dirk, *Chemosphere,* 75(6) (2009) 726.

20 Lee E, Cumberbatch J, Wang M & Zhang Q, *Bioresour Technol*, 23(2016).