International Journal of Chemical Engineering and Applications, Vol. 2, No. 1, February 2011
ISSN: 2010-0221

Determination of Treatability Constant and Reaction-rate Constant for an Attached-Growth Upflow Fixed-Film Reactor on Pulp and Paper Wastewater Treatment

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***Abstract*— Pulp and paper industry generates large volumes of highly heterogeneous wastewaters containing compounds from wood or other raw material, process chemicals as well as compounds formed during processing. This study has designed a fixed film reactor which uses the concept of biological attached growth treatment to treat the pulp and paper wastewater. The laboratory-scale fixed film reactor is designed with a circular column of 120 cm height, 15 cm inner diameter and a total volume of 23000 cm^3. The column which constructed in PVC was packed with PVC plastic pipes which were cut into the size of 4.5 cm length and 3 cm diameter and had a specific surface area of 42 cm^2. An amount of 150 PVC plastic pipes were placed in the digester. The system was found could remove about 53% of BOD$_5$ and 89% COD. The treatability constant corresponding to the depth of the reactor, k in this study is found to be 0.038 gal/min$^{0.5}$ft and the observed reaction rate constant, K is 0.04 ft/d at 25°C. This fixed-film reactor could be operated as a trickling filter.**

***Index Terms*—pulping wastewater, treatability constant, reaction rate constant, COD, BOD$_5$.**

I. INTRODUCTION

Pulp and paper mill industry is a major consumer of water. Thus, it produces a large number of wastewater with high organic loading. The pollutants of wastewater from pulp and paper mill could be characterized as high content of biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (SS), toxicity and color will have great impact to the environment when untreated or poorly treated wastewater are discharged to receiving water. The wastewaters from the industry could cause slime growth, thermal impacts, scum formation, color problems and loss of aesthetic beauty in the environment [1]. Conventional treatment currently used in the industry is aerobic digestion which requires larger space and much ancillary equipments like aerator and agitator. This will increase the cost of operation and maintenance.

Pulping is the initial stage of the paper making industry. The wood chips are cooked with chemicals such as NaOH at high temperature (180°C) in a pressurized digester. After cooked, the pulp produced is washed with a large number of water and lastly, it will be gone through several processes such as screening, washing, bleaching and paper machine and coating operations. The contains of wastewater are wood debris, soluble wood materials, resins, fatty acids, color, BOD, COD, organic halides and volatile organic carbons [1,2,3,4]. According to [5], the characteristic of wastewater from pulp and paper mill are summarized in Table I. This shows that the wastewater from pulp and paper mill is very high strength and suitable for biological treatment because it has high BOD$_5$ value and organic compounds from wood which are food for microorganism.

In the conventional pulp and paper mill waste water treatment plant, water is screened with coarse filters, grit removal, and pH adjustment in the pre-treatment stage. The adjustment of pH is made by metering wastewaters from various parts of the mill together. The acid line from the chlorination stage raises the pH of other lines that tend to be alkaline. Washed grits from Kraft liquor recovery will be ground and used to raise the pH. In the primary treatment, solids are removed by settlement from the water using mechanical clarifier. The clarified wastewater is removed at the outer edge of the tank. Floating debris is collected by a surface skimmer.

The sludge is collected and dewatered. It is then disposed to landfill or incinerated or spread on agricultural fields. Air flotation also can be applied for solids removal and this method is more effective but expensive. Secondary treatment involves reaction of the wastewater with oxygen and microorganisms (bacteria and fungi) to remove oxygen-consuming materials [6]. The wastewater is prepared by pH balancing and addition of nutrients.

Manuscript received February 11, 2011. This work was supported by Research Management Institute of Universiti Teknologi MARA (UiTM) Malaysia and Faculty of Chemical Engineering, UiTM Pulau Pinang. Soo Kwan Leong is with the Faculty of Chemical Engineering, Universiti Teknologi MARA (UiTM) Malaysia, Permatang Pauh, Pulau Pinang, 13500 Malaysia. (phone: 604-382 3289; fax: 604-382 3292; e-mail: leong786@ppinang.uitm.edu.my).

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TABLE I. CHARACTERISTICS OF PAPERMILL WASTEWATER

Parameter	Concentration (mg/l)
COD	5020 – 27100
BOD_5	1600 – 13300
SS	16 – 6095

The BOD is typically reduced by 80-90% during secondary treatment [7]. Tertiary treatments are advanced treatment following secondary treatment. They are often considered for colour removal. The methods that could be applied are ultrafiltration, flocculation and carbon adsorption. Treatment with batch reactors seeded with a mixed culture of algae could reduce 84% of colour [4].

The presence of biodegradable components in the pulp and paper mill wastewater makes it suitable to be treated using biological digestion method. During the digestion in wastewater treatment process, biogas will be generated as by-product and this gas could be used as fuel.

The microorganism in the biological digestion system will convert the organic molecules into biogas. Fixed firm reactor is a digester with biofilm support structure like activated carbon, polyvinyl chloride (PVC) supports, hard rock particles or ceramic rings for biomass immobilization. The wastewater is distributed from below the column. The advantages of using this kind of reactor to treat wastewater from pulp and paper mill are simple to construct, economic, elimination of mechanical mixing, better stability at higher loading rate, able to withstand large toxic shock loads and organic shock loads [3,8,9].

Fixed film reactor could solve the problem of limited space because it utilizes lesser space compare to the activated sludge system which normally be used in conventional waste water treatment. Another advantage of anaerobic digestion is this system is simple and do not require many ancillary equipments like aerator and mixer. Anaerobic treatment which using biofilm reactor could achieve 90% removal of sulphur [10] and 80% removal of COD [2].

The wastewater from the pulp and paper mill should be well treated before discharge to the river to avoid any negative impacts to the environment. Aerobic digestion using activated sludge system is the conventional biological treatment in pulp and paper mill. But this system requires high energy to agitate and provide the oxygen into the wastewater and it also requires large space. Anaerobic system which using fixed film reactor could resolve these problems because it does not require any mixing agitator and aerator and also just need a small space. Besides these, anaerobic digestion could produce biogas as by-product and this gas could be used as fuel to save energy.

Membrane has been investigated to treat the pulp and paper mill wastewater for the purpose of reuse. The most important limitation appeared by membrane process is membrane fouling which will cause a rapid flux decline. Membrane selection and operation conditions are important to minimize the membrane fouling. Besides that, the cost of membrane also a great concern in selecting methods in treating the pulp and paper mill wastewater.

Biological treatment is ideally suited for the treatment of high-strength wastewaters that are typical of many industrial facilities including pulp and paper mills. The anaerobic process utilizes naturally-occurring bacteria to break down biodegradable material in the absence of oxygen. The factors such as pH, temperature and nutrient supply are the important requirement for the system to operate properly.

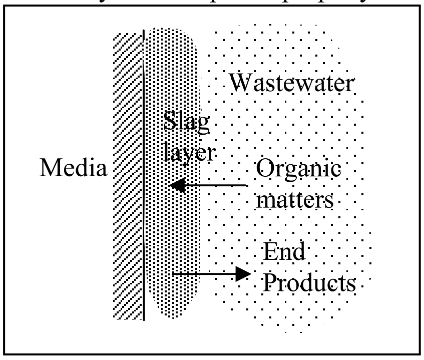

Figure 1. Schematic diagram of the phenomenon of degradation of organic matters on the surface of media

The trickling filter consists of a bed of highly permeable medium which could be constructed by rock, slag and a variety of plastic packing materials where the microorganisms will attach and grow as a bio-film. When the wastewater is percolated through the medium, the oganic materials from the wastewater will be adsorbed onto the biological film. These organic materials in the wastewater will be degraded by a population of microorganisms which attached onto the filter media.

A slime layer of the microorganisms will be formed on the surface of medium inside the bed. As the microorganisms grow, the thickness of the slime layer will also increase. The adsorbed organic matter is degraded before it can reach the microorganisms near the media face. The microorganisms near the media surface will be starved and enter into an endogenous phase of growth and lose the ability to cling onto the media surface due to the organic source could not reach to the inner part of the bio-film.The wastewater will wash the slime off the media, and a new slime layer will start to grow. This phenomenon of losing the slime layer is called "sloughing" and is primarily a function of the organic and hydraulic loading on the filter. The phenomenon of degradation of organic matters on the surface of media is shown in Fig. 1.

The objectives of this study were to reduce the COD and BOD_5 in the pulp and paper mill wastewater To achieve these objectives, experiments were conducted by using a fixed bed reactor which based on attached growth system. The principle of operation is that wastewater is passing through a column filled with an inert packing material which acts as a support surface for the growth of large amounts of attached microorganisms. Besides these, the results of the BOD_5 were used to determine the treatability constant, k and reaction rate constant, K corresponding to a filter of depth for the designed system.

TABLE II. CHARACTERISTICS OF WASTEWATER COLLECTED FROM PULP & PAPER MILL, NIBONG TEBAL, PENANG.

Parameter	Concentration (mg/l)
COD	2238 – 3567 (2903)

Parameter	Concentration (mg/l)
BOD_5	945 – 1530 (1237)
TSS	950 -3400 (2175)
pH	7.2 – 7.6 (7.4)

II. Material And Methods

A. Pulp and Paper Mill Wastewater

The wastewater was obtained from a local pulp and paper mill in the area of Nibong Tebal, Pulau Pinang. This pulp and paper mill is using recycled paper collected from various sources. Table II shows the basic characterization results of the real pulp and paper mill wastewater.

B. Fixed Film Reactor Operation

This study was performed on a laboratory-scale fixed bed reactor as designed in the schematic diagram shown in Fig. 2. The unit process is design based on an up-flow attached growth treatment process. Generally, this fixed bed reactor was made of a circular column of 120 cm height, 15 cm inner diameter and a total volume of 23000 cm^3.

The column which constructed in PVC was packed with PVC plastic pipes of 4.5 cm length and 3 cm diameter and had a specific surface area of 85 cm^2. An amount of 150 PVC plastic pipes were placed in the digester. The total surface area of the media is 12 750 cm^2. This reactor was instrumented with the devices including pump, heater, temperature controller, storage tank, main supply control valve and wastewater flow meter.

The seed sludge for the system was obtained from the paper mill in Nibong Tebal's wastewater treatment plant. The fixed film reactor was operated at the room temperature which is around 25°C. The feed, which was the real wastewater from paper mill, was pumped into the reactor. Initially the reactor was seeded with a mixture of sludge (20% v/v) and substrate and this mixture was recirculated for 2 days. The reactor was then fed continuously with various hydraulic retention time (HRT) 12 h, 24 h and 48h. The reactor operation conditions are given in Table III.

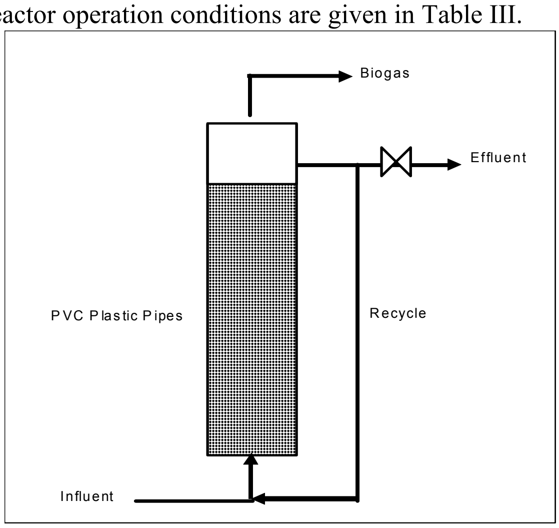

Figure 2. Schematic diagram of an Anaerobic Fixed Film Reactor

TABLE III. Reactor Operation Conditions

Phase	HRT (h)	OLR (kg $COD/m^3 \cdot d$)
I	12	1.21
II	24	0.67
III	48	0.43

C. Analytical Methods

The BOD_5 and COD were analyzed using the Standard Methods for the Examination of Water and Wastewater of the American Public Health Association (APHA) and is approved by the U.S. Environmental Protection Agency (USEPA); Dilution Method. The COD values were determined by HACH DR2010 spectrophotometer.

III. Result And Discussion

A. COD Removal

A decrease of COD removal efficiency occurred when the OLR in the fixed film reactor increased as shown in Fig. 3. When the OLR increased from 0.42 kg $COD/m^3 \cdot d$ to 1.21 kg $COD/m^3 \cdot d$, the COD removal efficiency decreased from averagely 89 % to 84%.

The results in this study were consistent with the investigation conducted by [11, 12, 13]. Reference [11] which using fixed film reactor to treat slaughterhouse wastewater, the researchers found that when the OLR increased from 8 kg $COD/m^3 \cdot d$ to 30 kg $COD/m^3 \cdot d$, the COD removal decreased from 85-95% to 55-75%. Reference [12] found that the increase in OLR has shown gradual increase in COD removal up to 10 kg $COD/m^3 \cdot d$ but after that the COD removal was decreased when using fixed film reactor to treat high suspended solids from a bulk drug industry.

The results from [13 also found the same trend when using fixed film reactor to treat the chess whey. It is concluded that the high OLR will inhibit the biomass activity and the designed reactor could be operated up to 1.21 kg $COD/m^3 \cdot d$ only.

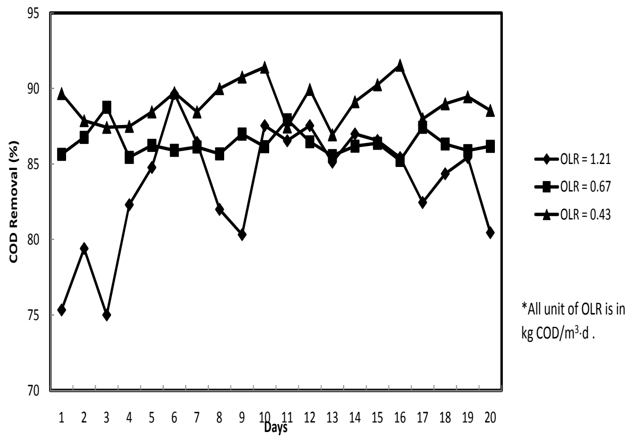

Figure 3. COD Removal

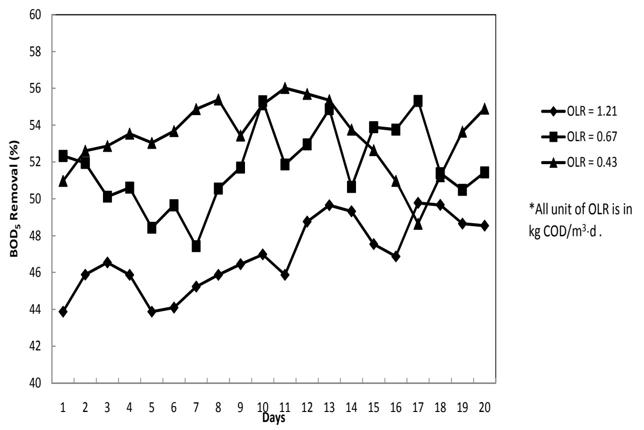

Figure 4. BOD_5 Removal

The results also shows that at the high OLR which is at 1.21 kg COD/m^3·day, the COD removal efficiency range is higher compare to lower OLR. The COD removal efficiency was range from 75% to 84% at the highest OLR while the COD removal efficiency only range from 87% to 92% at the lowest OLR. This shows that the COD removal efficiency was more reliable operated at lower OLR.

At the highest OLR, the COD removal could maintain above 85% from day 10 to 16 but it decreased after the day 14 until the last day operation. It evidences that the biomass activities were obstructed after the day 14.

B. BOD_5 Removal

The BOD_5 removal efficiency trend is similar to the COD removal efficiency. Fig. 4 shows that the BOD_5 removal efficiency is highest on the lowest OLR. Averagely, at OLR 0.43 kg COD/m^3·d, the BOD_5 removal efficiency could achieve 53.4% while at OLR 1.21 kg COD/m^3·d; the BOD_5 removal efficiency could achieve 43.9% only.

These results also consistent with the findings of [13] where the researchers studied the performance of anaerobic upflow fixed-film reactor on the acidic petrochemical wastewater and they found that the BOD_5 of reactor wastewater was increasing when the OLR was increased. The BOD_5 removal in this study was low compare to [12]. The highest removal could be achieved is only 53.4% but according to [12], the removal was around 90%. The BOD_5 removal efficiency also shows continuous increment from day to day.

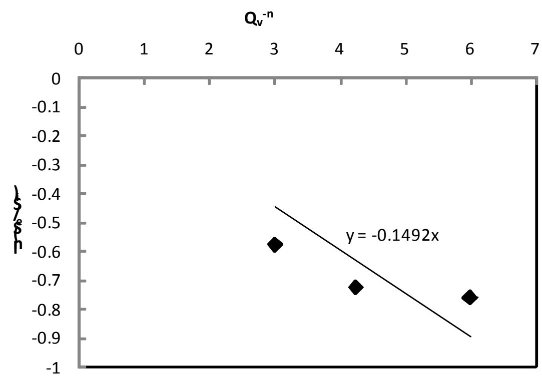

Figure 5. Graph of $\ln(S_e/S_i)$ versus $Q_v^{-0.5}$ for treatability constant determination

C. Treatability Constant

This fixed bed reactor was design according to the concept of trickling filter. A number of empirical relationships have been developed to predict the performance of the system with plastic media. One of the expressions which used most commonly to describe the observed performance of plastic packing are those proposed by [14] and [15] is shown in (1).

$$\frac{S_e}{S_i} = \exp\left[-kD(Q_v)^{-n}\right] \tag{1}$$

Where,

- S_e = Total BOD_5 of settled effluent from filter, mg/L
- S_i = Total BOD_5 of wastewater applied to the filter, mg/L
- k = treatability constant, (gal/min)^n·ft
- D = depth of filter, ft
- Q = volumetric flow rate, gal/min
- Q_v = volumetric flow rate applied per unit volume of filter,
  = Q/A, gal/ft^2·min
- A = cross-sectional area of filter, ft^2
- n = experimental constant, usually 0.5

The (1) could be rearranged to become:

$$\ln\left(\frac{S_e}{S_i}\right) = -kD(Q_v)^{-n} \tag{2}$$

The treatability constant corresponding to a filter of depth, k could be determined by using Fig. 5 which showed the graph of $\ln(S_e/S_i)$ versus Q_v^{-n}. The value of n was 0.5. The slope of the graph represents value of –kD. The diameter of this fixed film reactor is 120 cm (3.973 ft).

The k obtained from this study is 0.038 gal/min$^{0.5}$ft which is in the range of 0.02 – 0.04 gal/min$^{0.5}$ft proposed by [16]. This shows that the fixed bed reactor which designed in this study could be operated as a trickling filter.

The k could be used to design a filter with a different depth, the treatability constant must be corrected for the new depth using (3) [16].

$$k_2 = k_1\left(\frac{D_1}{D_2}\right)^x \tag{3}$$

Where,

- k_2 = treatability constant corresponding to a filter of depth D_2
- k_1 = treatability constant corresponding to a filter of depth D_1
- D_1 = depth of filter one, ft
- D_2 = depth of filter two, ft
- x = 0.5 for vertical and rock media filters
  = 0.3 for crossflow plastic medium filters

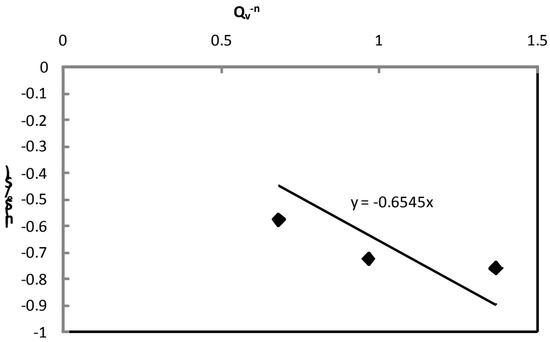

Figure 6. Graph of $\ln(S_e/S_i)$ versus $Q_v^{-0.5}$ reaction-rate constant determination

D. Reaction-rate Constant

The overall performance of trickling filters in terms of BOD_5 remaining was proposed by [17] could be represented by (4). Most of correlations describing the performance of trickling filters are based on the assumption that the rate of BOD_5 reduction at specific depths of medium can be represented by a first order reaction and plug flow is assumed in many cases [18].

$$\frac{S_e}{S_i} = \exp\left[-KS_a^m D(Q_v)^{-n}\right] \quad (4)$$

Where,

K = observed reaction-rate constant for a given depth of filter, ft/d

D = filter depth, ft

S_a = specific surface area of filter $= \dfrac{\text{surface area } A_s, \text{ft}}{\text{unit volume V, ft}^3}$

Q_v = volumetric flow rate applied to filter, $ft^3/ft^2 \cdot d$ = (Q/A)

Q = flow rate applied to filter, ft^3/d

A = cross-sectional area of filter, ft^2

m, n = empirical constant

As same as (2), the (4) could be rearranged become:

$$\ln\left(\frac{S_e}{S_i}\right) = -KS_a^m D(Q_v)^{-n} \quad (5)$$

The observed reaction-rate constant, K corresponding to a filter depth was determined by Fig. 6 which the slope of the graph represents the value of $-KS_a^m D$. The S_a is 16.8974 ft^2/ft^3 and the value of m is 0.5. The K obtained from Fig. 6 is 0.04 ft/d. The K value from this study is higher compared to [18] where the K obtained was 0.017 when treating municipal wastewater at 27°C. According to [18], the K is a function of the characteristics of the influent wastewater. The effect of temperature on the rate constant is expressed in (6) below.

$$K_T = K_{20}\theta \quad (6)$$

Where,

K = reaction-rate constant at temperature T

K_{20} = reaction-rate constant at 20°C

θ = temperature activity coefficient

Overall efficiency of a biological treatment process is very much depends on the temperature dependence of the biological reaction-rate constants. The temperature is not only influences the metabolic activities of the microbial population but also has a great impact on gas-transfer rate and the settling characteristic of the biological solids. The value of θ for trickling filters is in the range of 1.02 – 1.08 and the typical value is 1.035 [16].

IV. CONCLUSIONS

This study reveals the potentiality of using upflow fixed film reactor for wastewater from pulping and paper industry with high strength loading. The reactor could achieve 89% COD removal efficiency and 53% BOD_5 removal efficiency at OLR 0.42 kg $COD/m^3 \cdot d$. Besides these, the treatability constant corresponding to the filter depth, k obtained from this study is 0.038 $gal.min^{0.5}ft$ which means this fixed film reactor could be operated as a trickling filter. The observed reaction-rate constant corresponding to the filter depth, K is 0.04 ft/d at 25°C. The designed system has to be improved in removing the BOD_5 and the biogas production from the system has to be investigated in future.

ACKNOWLEDGMENT

We thank to Research Management Institute of Universiti Teknologi MARA (UiTM) particularly for their financial support and Faculty of Chemical Engineering, UiTM Pulau Pinang for providing the facility for developing this work.

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