

A RATIONAL APPROACH TO THE DESIGN OF A ROTATING DISC SYSTEM FOR THE TREATMENT OF BLACK LIQUOR

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ABSTRACT

The results of the treatability studies of black-liquor by RDS and evaluation of the applicability of biofilm kinetics into design methodology are presented. Theoretical evaluations verified by the experimental results showed that a bulk half-order and zero-order reaction rate expression could adequately define the overall removal process and provide the desired mechanistic explanation of the system. The experimental results were also used to calculate the kinetic parameters in order to provide design guidelines for practical application. It was determined that the transition from BOD rate limitation to oxygen rate limitation occurred at a BOD to oxygen concentration ratio of approx. 15 promoting the aeration of the RDS as a very important consideration for design and operation. The last part of the study was devoted to the possible calcium build-up in the biofilm. The findings indicated that the reaction products of $\text{Ca}(\text{HSO}_3)_2$ in black liquor had no appreciable effect on the removal rate.

KEYWORDS

Rotating disc system; biofilm kinetics; treatment of sulphide process black liquor.

INTRODUCTION

In recent studies, pulp and paper industry has been identified as the most important polluting source in Izmit Bay, Turkey. The sulphide process black liquor requires specific attention as it represents almost two-thirds of the pollutional load generated by the industry. The characteristics of black liquor are given in Table 1. This liquor is reused for lignin recovery and then ten-fold diluted by washing wastes and discharged to the Bay without any treatment.

TABLE 1 The Characteristics of Black Liquor (average values).

Waste	Flow rate m ³ /d	COD g/m ³	BOD g/m ³	TSS ₃ g/m ³	TKN ₃ g/m ³	pH -	Temp. °C
Concentrated black liquor	1000	170000	30000	700	100	1.0	100

In order to meet the discharge standards, various systems were suggested for treatment of the diluted black liquor. However, limited land and energy made conventionally prescribed treatment such as activated sludge and aerated lagoons unattractive and promoted rotating disc system (RDS) as a likely alternative. The RDS has been claimed to have several additional advantages such as more resistance to shock loads, better settling and dewatering

characteristics of secondary sludge and easier operation, etc. A review of the available literature on the RDS suggested that most widely used loading approach, which consists in relating percent purification or effluent concentration to organic or hydraulic loading, couldn't be used for design and operation since there was no experience with the RDS treating black liquor of the calcium sulphide process. It was therefore decided to conduct a study for providing design and operation guidelines on the system, and this study was devoted to process characterization both from a fundamental and practical standpoint. In this respect, pilot-plant studies were carried out: a) to identify the dominant mechanisms and phenomena responsible for removal efficiency; b) to describe these phenomena in terms of expressions readily applicable for design and operation; c) to determine kinetic constants and process parameters. This paper summarizes the results of these studies and evaluates the applicability of the basic principles of the biofilm kinetics into the design methodology.

THEORETICAL CONSIDERATIONS

The kinetic concepts related to biofilm reactors have been developed considerably within the last fifteen years (La Motta, 1974; Williamson and McCarty, 1976; Harremoës, 1978; Gujer, 1989). The dominating phenomena associated with substrate removal are:

- a) the bacteria are imbedded in the matrix of a biofilm,
- b) the substrates have to be transported into this matrix in order to be degraded and the reaction products have to be transported out again.

In all biofilm studies the transportation of the substrates and reaction products has been attributed to Fickian diffusion, whereas several proposals for the reaction rate inside the biofilm have been given (Harremoës and Göneç, 1983). However, it has been demonstrated that a zero-order intrinsic reaction rate, modified by diffusional resistance into a bulk zero or half-order rate equations with respect to the bulk concentration of the substrate considered, can adequately define the overall substrate removal process (Riemer, 1977; Göneç, 1982; Harremoës, 1982, 1989; Göneç and Harremoës, 1985; Jansen and Harremoës, 1985). The following equations summarize the results:

zero-order bulk reaction

$$r_a = k_{oa} = k_{of} L \quad \text{valid for } \beta = \sqrt{\frac{2DC^*}{k_{of}L^2}} \geq 1 \quad (1)$$

half-order bulk reaction

$$r_a = k_{1/2a} C^{*1/2} \quad \text{valid for } \beta < 1 \quad (2)$$

$$k_{1/2a} = \sqrt{2Dk_{of}}$$

where

r_a	is the removal rate ($\text{g/m}^2 \text{ d}$)
k_{oa}	is the zero-order removal rate ($\text{g/m}^2 \text{ d}$)
$k_{1/2a}$	is the half-order rate constant ($\text{g}^{1/2}/\text{m}^{1/2} \text{ d}$)
k_{of}	is the intrinsic zero-order reaction rate ($\text{g/m}^3 \text{ d}$)
L	is the thickness of the biofilm (m)
D	is the molecular diffusion coefficient in the biofilm (m^2/d)
C^*	is the bulk concentration at the surface of the biofilm (g/m^3)
β	is the penetration ratio (dimensionless).

The equations presented above are valid for both organic matter and oxygen in heterotrophic biofilms. The rate limiting substrate that penetrates the biofilm least may be determined by the following equation:

$$\frac{C_{org}^*}{C_{oxy}^*} > < \frac{D_{oxy}}{D_{org} \nu} \quad (3)$$

where ν is the stoichiometric coefficient (Owen and Williamson, 1976; Jansen and Harremoës,

1985). On the other hand, the removal rate is half-order in organic matter if the oxygen concentration is big enough. If it is not, the removal becomes independent of the organic matter concentration.

It has also been shown that the removal rate leads to bulk first-order reactions due to either liquid-film diffusion or first-order enzymatic reactions controlled by the half-saturation constant at very low organic matter concentrations as expressed below:

$$r_a = k_{1a} C^* \quad (4)$$

where k_{1a} is the first-order rate constant (m/d).

EXPERIMENTAL PROCEDURES

Pilot Plant

The pilot-plant system consisted of a 29.5 l semi-circular tank in which 0.3 m diameter twenty disc units were rotating, and a 7.25 l settling tank. The discs had 2.6 m² of surface area for microbial growth and were submerged in the tank to about 33% of the disc diameter. The rotating assembly consisted of a single shaft and was rotated by a 1/4 kW electric motor at 15 rpm. Flow rate was regulated by a pumping system. LiCl tracer studies indicated that there was no significant short circuiting through the tank and the system closely simulated the ideal characteristics of a completely mixed tank.

Wastewater Characteristics

The pilot plant was installed at the laboratory of TÜBİTAK (Turkish Scientific and Research Council) which is close to the pulp and paper industry. The effluent from the cooking unit of the sulphide process of the pulp and paper industry was used as a wastewater source. The characteristics of the effluent have been given in Table 1. This black liquor was first refrigerated at 4°C to prevent biodegradation, and then neutralized and diluted by tap-water daily before feeding the system. The dilution was made according to the influent BOD concentration considered and the BOD/COD ratio fixed as 0.2. Since the diluted black liquor didn't include the necessary nutrient for microbiological activity, a nutrient solution was added to the tank to achieve a BOD/N/P ratio of 100/5/1, continuously.

Sampling and Analytical Programs

The sampling points were chosen as the influent line to the system, six consequent sampling valves along the discs tank and the effluent and sludge line of the settling tank. The flow rate, pH, temperature and dissolved oxygen were continuously measured and recorded at these sampling points. The influent and effluent BOD, and total suspended and volatile solids at the sampling points were analysed, accordingly.

The total suspended solid mass (TSS) within the biofilm was determined at the end of the experimental period by weighing the biomass stripped from the discs after drying at 103°C for a minimum of 2 hr. Since the volume (V) and area (A₁) of the biomass was measured before, the TSS concentration (X) was calculated as TSS V⁻¹, and then the thickness (L) was determined from $L = \text{TSS} X^{-1} A_1^{-1}$. Consequently, the volatile suspended solids (VSS) was determined by weighing the biomass after burning at 550°C. The residue remaining after burning procedure (inert part) was used for Ca⁺⁺ analysis which was performed by the Hitachi AAS.

Experimental Planning

The experiments were planned to measure the effect of hydraulic and organic loading, to show the applicability of the biofilm kinetics, to determine the kinetic constants for design and operation. The biofilm characteristics and a possible calcium build-up in the biofilm were the other important issues considered for the experimental planning.

At the beginning of the experiments numerous preliminary runs were conducted to select the most suitable hydraulic and organic loading range for BOD removal and thus to optimize the running time of the experimental program.

RESULTS AND DISCUSSION

Organic Matter Removal Characteristics

As would be expected from the theoretical considerations, the system removed BOD in proportion to the hydraulic loading as can be seen in Fig.1. Analysis of variance calculations showed that the effect of influent BOD concentration on removal was not significant. Thus, the removal rates plotted against the organic loading in Fig.2 reflect the hydraulic loading effects rather than the increase of influent concentrations. It can be revealed that there is an upper limit so after that the removal rate doesn't increase with the increasing loading rate. This is the typical result of the rate limitation as discussed below.

Applicability of Biofilm Kinetics

According to the theory given before, a plot of BOD removal rate versus bulk BOD concentration should yield a curve as shown in Fig.3. The data correlate well with the theory. Although different hydraulic loadings were used, these data qualitatively indicate the tendency that there is a gradual transition from a first-order removal at low concentration of BOD to half-order removal and to a zero-order removal at higher concentrations.

These data were also used in Fig.4. which shows the removal rate as a function of the bulk BOD concentration plotted in log-log scale. Now it is obvious that the removal rate is first-order due to either liquid-film diffusion or first-order enzymatic reactions controlled by the half-saturation constant if the BOD concentration is less than approx. 20 g/m^3 . The first-order rate constant is calculated as 0.9 m/d . It is evident from the figure

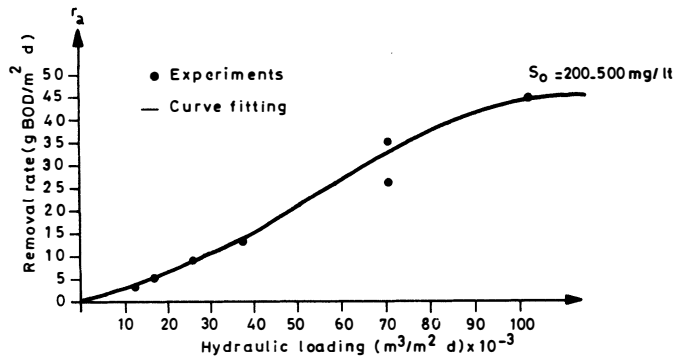


Fig.1 Hydraulic loading effect on the removal rate.

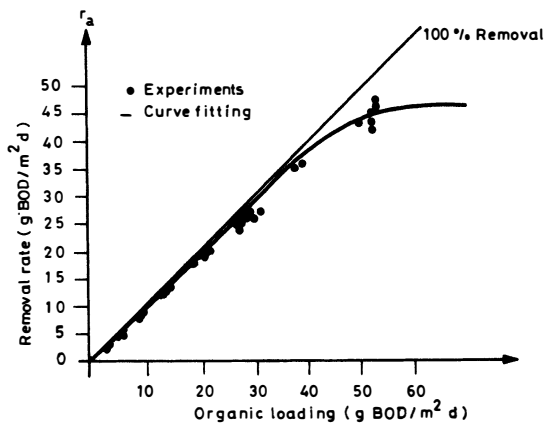


Fig. 2 Organic loading effect on the removal rate.

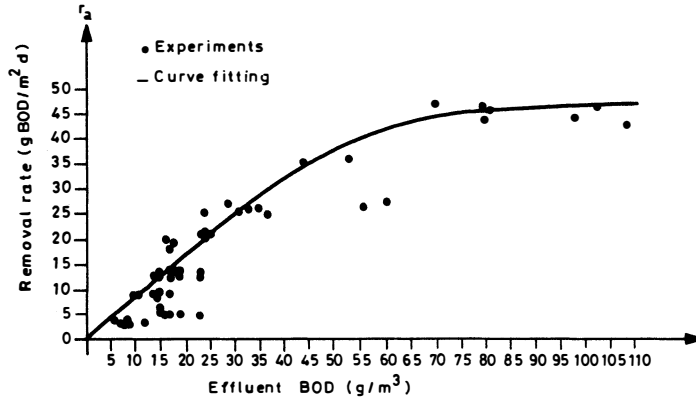


Fig. 3 Removal rate versus effluent BOD conc.

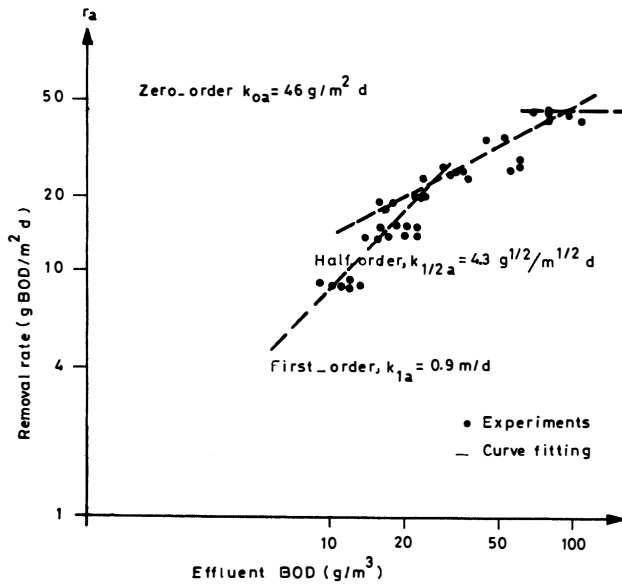


Fig. 4 Removal rates vs effluent BOD in log-log scale.

that the removal rate depends on the bulk BOD concentration according to half-order reaction with the rate constant of $4.3 \text{ g BOD}^{1/2}/(\text{m}^{1/2} \text{ d})$ if the bulk BOD concentrations are in the range of $20\text{--}100 \text{ g/m}^3$. If the BOD concentration is higher than approx. 100 g/m^3 , the removal rate becomes independent of the BOD concentration, i.e. it is a zero-order reaction in BOD with the rate of $46 \text{ g BOD/m}^2 \text{ d}$.

The theory described before predicts the criterion for transition from BOD rate limitation to oxygen rate limitation as follows:

$$\frac{C_{\text{org}}^*}{C_{\text{oxy}}^*} \geq \frac{D_{\text{oxy}}}{\nu D_{\text{org}}} \tag{5}$$

It is also interesting to evaluate this transition in numerical values using the diffusion coefficients and stoichiometric constants which are chosen from the literature (Table 2) and to compare with data:

$$\frac{C_{org}^*}{C_{oxy}^*} \approx \frac{21 \times 10^{-10}}{0.7 \times 2 \times 10^{-10}} = 15 \quad (6)$$

For an oxygen concentration of 6 g/m^3 the transition to oxygen rate limiting occurs for BOD concentration near 90 g/m^3 . The data are adequately represented by these calculated values. It should be indicated that the bulk oxygen concentration measured couldn't be used for a final interpretation of this study since the water film tended to be fully saturated with oxygen during the time of exposure - irrespective of the oxygen concentration in the bulk water (İlhan, 1985). Furthermore, turbulence generated at the water surface of the tank by the rotation of the discs was the reason of aeration in the system.

The kinetic parameters calculated according to equations 1 and 2 and available data collected from the literature are given in Table 2. These parameters are found to be comparable to findings in the literature and thus they can be used for design and operation. During the long-term experiments the thickness of the biofilm increased rapidly (to approx. 2 mm) probably without a corresponding increase in the number of bacteria and the removal rate decreased based on the total biofilm volume (İlhan, 1985). Furthermore, the half-order rate and diffusion coefficients increased as the film grew older and thicker. However most values given in Table 2 were derived from lab-scale reactors in which biofilm thickness is in the order of μm . This may lead to some inadequate variances from the literature.

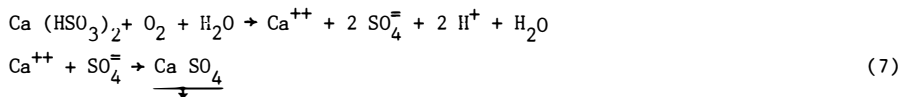
TABLE 2 Kinetic Parameters for Organic Matter Removal.

Substrate	Half-order Rate Const. $k_{1/2a}$ $\text{g}^{1/2}/\text{m}^{1/2} \text{ s}$	Zero-order Rate Const. k_{of} $\text{g}/\text{m}^3 \text{ s}$	Diffusion Coefficient D m^2/s	Source of Evaluation
Glucose	$3.3-4.4 \times 10^{-5}$	1.0-16.7	$1.0-2.8 \times 10^{-10}$	From a large number of sources
Acetate	4.0×10^{-5}	3.5	$2.3-9.5 \times 10^{-10}$	
Methanol	2.0×10^{-5}	1.3	$1.5-20.8 \times 10^{-10}$	
Starch	-	0.1-0.7	6.7×10^{-10}	
Propionate	-	-	8.3×10^{-10}	
Mixed	-	-	$5.0-9.6 \times 10^{-10}$	
Sewage	$2.4-2.7 \times 10^{-5}$	1.1-1.7	$0.1-5.0 \times 10^{-10}$	
Papermill effluent	-	0.7-2.5*	-	
Kraft mill effluent	-	0.4-0.6*	-	McAliley (1974)
Black liquor	5.0×10^{-5}	6.1	2.0×10^{-10}	This study
Oxygen	$2.4-4.9 \times 10^{-5}$	0.2-5.5	$0.4-35.0 \times 10^{-10}$	Literature
Oxygen	13.5×10^{-5}	7.6	21.0×10^{-10}	This study

Ca^{++} Build-up In The Biofilm

*predicted from the experimental results.

The distribution of possible Ca^{++} ions in skimmed-off biofilm from the disc plates was another interest of this study, because either $\text{Ca}(\text{HSO}_3)_2$ oxidation in the system or one of the end products, CO_2 , resulting from biological process can react with Ca^{++} ions according to the following reactions:



Eq.(7) and (8) show that calcium sulphate or calcium carbonate build-up in the biofilm mainly depends on pH, temperature and solubility of products. With these reaction conditions, a decrease in the removal rate should be expected; in other words, substrate and/or oxygen diffusion into the biofilm is limited.

From the above theoretical considerations, at the end of the experimental study phase, dry solids concentrations of skimmed biofilm from the disc plates were analyzed. The volatile and inert matter variation was determined to be 90 to 92% and 8 to 10%, respectively. The Ca^{++} ions level in the inert matter part was found to be as low as 2.7-6.6%.

CONCLUSION

It may be concluded that the RDS is capable of achieving at least 85% BOD removal of a black liquor at a hydraulic loading of $0.1 \text{ m}^3/\text{m}^2 \text{ d}$ or an organic loading of $50 \text{ g}/\text{m}^2 \text{ d}$. This is an upper limit to the removal induced by direct oxygen transfer from the air to the RDS. Oxygen cannot be supplied fast enough to meet the demand of the higher removal rates. This is an important conclusion of general applicability and it makes the aeration of the RDS a very important consideration for design and operation. Since the oxygenation capacity is inversely proportional to the radius of the discs, the max. loading rate will be lower for full-scale plants as compared to this study. Particular attention should be given to the first stages of the RDS because these stages will be exposed to the highest BOD concentration and loading.

Although the mat-like structure maybe accounted for the streaming of the filaments in the current, i.e. collapse of the mat when withdrawn from the water and resuspension when submerged, it is likely that the substrate removal is governed by the biofilm kinetics. It has been demonstrated that the BOD removal rates lead to bulk first-order reactions due to either liquid film diffusion or first-order enzymatic reactions at low BOD concentrations; to bulk half-order reactions at higher concentrations as a result of part penetration of BOD; and finally bulk zero-order reactions at high concentrations when the biofilm is fully penetrated. This final situation was reached when the BOD oxygen ratio was bigger than 15. Accordingly, the oxygen concentration has determined the removal rate and it has been rate limited by the oxygen concentration. This relationship can be applied to design.

The striking feature of the results obtained is the promotion of the biofilm kinetics as an equally significant tool for the design of the RDS, despite the complexity of the black liquor and of the removal processes involved.

It is also concluded that Ca^{++} ions build-up in biofilm was negligible compared with concentrated sulphite liquor inflow and $\text{Ca}(\text{HSO}_3)_2$ concentration used in the experimental study.

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