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A kinetic study of a mesophilic aerobic moving bed biofilm reactor (MBBR) treating paper and pulp mill effluents: The impact of phenols on biodegradation rates

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ABSTRACT

This study investigated the impact that phenols have on the biodegradation rate of paper and pulp mill effluents in a bench-scale aerobic moving bed biofilm reactor (MBBR). Paper and pulp mill effluents were collected from recycle and neutral sulfite semi-chemical mills. The phenol concentrations of the four individual paper and pulp mill effluents were 4.61, 29.1, 42.65 and 60.6 mg/L. The removal of chemical oxygen demand (COD) was continuously monitored for individual effluents during the experiments. The hydraulic residence time (HRT) and organic loading rates (OLR) in the experiment were varied between 5 and 45 h and 2–6 kg COD/m^3.day, respectively. The biodegradable chemical oxygen demand (COD) removal efficiency at a hydraulic residence time (HRT) of 16 h was 86, 65, 60 and 46% for individual mill effluents. The Kincannon-Stover, first order and Grau second order kinetic models were evaluated to describe the removal of organics in a mesophilic aerobic MBBR. The highest correlation coefficients (r^2) were found for the Kincannon-Stover model. According to the Kincannon-Stover model, the maximum substrate removal rates were 11.14, 10.46, 5.31 and 4.63 gCOD/L.day for mill effluents containing 4.61, 29.1, 42.65 and 60.6 mg/L phenols, respectively. The trend indicated that phenols inhibited the biodegradation rates of paper and pulp mill effluents in a mesophilic aerobic MBBR. Additional intermediate or pre-treatment may be required to remove excessive phenols to ultimately increase the performance of MBBRs in the paper and pulp industry.

1. Introduction

The paper and pulp industry produces large volumes of organic-rich wastewater. These organic compounds can include cellulosic material, phenols, solvents, chlorinated complexes and sulfide complexes [1]. The direct discharge of mill effluents to the surrounding environment can negatively impact the terrestrial and aquatic ecosystems. The growth, maturation, mortality and metabolism of various fish species can be altered due to the direct discharge of mill effluents [2]. Excess nutrients and biodegradable organics in discharged mill effluents can deplete dissolved oxygen, and cause slime and scum growth in surrounding waterbodies [3,4]. To prevent this, the implementation of biological treatment systems is generally required to meet environmental discharge legislations.

Paper and pulp mill effluents often contain toxic and inhibitory constituents which can complicate the bioremediation process [5,6]. The inhibitory effect caused by some of the mill effluents can potentially be linked to the phenolic content. According to Hussain et al. [7], the growth rate of activated sludge (AS) can be severely inhibited by high phenol concentrations. Alkylphenols, such as cresols and xylenol present in mill effluents are considered to be 5–34 times more toxic to mixed bacterial cultures than pure phenol [8]. Bacterial cultures generally adapt and acclimatise in high phenolic wastewaters in order to increase specific growth and substrate removal rates [9,10]. However, the rate at which the effluent composition fluctuates within the paper and pulp industry often exceeds the rate of microbial adaptation [11].

Aerobic moving bed biofilm reactors (MBBR) yielded promising results for the treatment of paper and pulp mill effluents [12,13]. Various studies investigated the performance of aerobic moving bed biofilm reactors (MBBR) treating paper and pulp mill effluents [14,15]. However, there are a lack of studies investigating the kinetics and the potential impact of phenols on this bioremediation process. Kinetic models such as the Kincannon-Stover, Grau second order and first order models are frequently used to describe the substrate removal in MBBRs [16–18]. Consequently, the primary objectives of this study are to assess:

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Nomenclature

COD	Chemical oxygen demand, mg/L
TCOD	Total COD (sum of biodegradable and non-biodegradable fractions), mg/L
COD_{bd}	Biodegradable COD, mg/L
C_o	Initial chemical oxygen demand concentration, mg/L
C_F	Effluent chemical oxygen demand concentration, mg/L
sCOD	Soluble chemical oxygen demand, mg/L
OLR	Organic loading rates, kg COD m^{-3}. d
f_b	Biodegradable COD fraction
X	Biomass concentration, mg VSS/L
V	Reactor volume, m^3
Q	Volumetric flowrate, m^3/hr
HRT	Hydraulic residence time, hr
DO	Dissolved oxygen concentration, mg/L
VOA	Volatile organic acids, mg/L
BOD	Biological oxygen demand, mg/L
TDS	Total dissolved solids, mg/L
TSS	Total suspended solids, mg/L
VSS	Volatile suspended solids, mg/L
NSSC	Neutral sulfite semi chemical pulping process
RME	Recycle mill effluent
MBBR	Moving bed biofilm reactor
k	First order kinetic rate constant, L/mg VSS.day
k_1	Lumped first order rate constant, 1/hr
K_B	Saturation constant, g COD/L.d
U_{max}	Maximum substrate removal rate, g COD/L.d
a	Grau second order kinetic constants (hr)
b	Grau second order kinetic constants (dimensionless units)
t	Reaction time

(i) the applicability of different kinetic models to describe organic removal in a MBBR
(ii) the potential impact that phenols have on the biodegradation rate of paper and pulp mill effluents.

2. Materials and methods

2.1. Paper and pulp mill effluent characteristics

Clarified mill effluents were collected from two separate paper mills. Mill X utilised mainly recycled material as a feedstock whilst Mill Y used a combination of virgin fibre and recycled material as feed. Effluent A, was produced in Mill X while Effluent B and C were produced in Mill Y. Effluent D was a blend containing 57% (v/v) of Effluent B and 43% (v/v) of Effluent C. Effluent B and C were blended to evaluate the impact of lower COD and phenol loadings on the performance of the MBBR. The blending ratio was estimated with historical mill production data. The process characteristics of the individual mill effluents are presented in Table 1.

All the samples were collected from the supernatant stream exiting the primary clarifiers. After collection, all the samples were stored at 4 °C. The wastewater characteristics of the mill effluents are presented in Table 2.

The wastewater characteristics of Effluent D are expected to be a combination of Effluent B (57%) and C (43%). The various effluent samples were tested at an external lab for volatile and semi-volatile organics. The detected semi-volatile organic constituents for effluent A, B, C are presented in Table 3. These semi-volatile organic screening results indicate that phenols, organic acids and other solvents are present in the mill effluents.

2.2. Mesophilic aerobic moving bed biofilm reactor (MBBR)

A laboratory scale 10 L moving bed biofilm reactor (MBBR) was used in this study. The MBBR had a reactor carrier media filling ratio of 30% (v/v). The total surface area of the carrier media inside the reactor was 340 m^2/m^3. The density of the carriers was 0.95 g/cm^3. The dimensions of the carrier media are presented in Fig. 1(b). The temperature of the supernatant exiting the clarifiers at the mills was 35 °C. Consequently, the temperature inside the reactor was maintained at a constant 32 °C using a ViaAqua heater to try to reproduce field conditions. Two 2 L/min Sonic 9905 air pumps were used to supply air to the MBBR, where each airline was equipped with air stones. The dissolved oxygen (DO) concentrations inside the reactor ranged between 3.0–3.5 mg/L. A peristaltic pump (Watson Marlow 120S) was used to vary the feed flow rates according to need.

2.3. Reactor start-up period

The moving bed biofilm reactor (MBBR) was inoculated with activated sludge which was collected from a local wastewater treatment plant. Effluent A was used as a feedstock for the maturation of the reactor over a 30 day period. The concentration of the paper and pulp mill effluent was gradually increased during this maturation period to acclimatise it to full strength. The attached and suspended biomass had increased during the start-up period. The experiments were initiated after this 30 day maturation period.

2.4. Chemical analysis

The COD, VOA and phenolic measurements were determined with photometric methods and measured on a Merck Spectroquant®. A Merck COD cell test (100–1500 mg/L) (Code: 114539), volatile organic acid cell test (50–3000 mg/L) (Code: 101809) and phenol test (0.002–5 mg/L) (Code: 100856) were used to characterise the effluent. The modified Anthrone method was used to determine the carbohydrate content of the effluent [19]. The pH, conductivity and dissolved oxygen (DO) were monitored using a handheld IP67 Combo pH/COND/D.O. (8603) meter. The amount of suspended solids (SS) was measured according to standard methods described by Skrentner [20].

2.5. Mathematical models: biological kinetics

2.5.1. First order kinetic model

In well-agitated systems, the substrate (C_F) removal according to first order kinetics can be given by the following expression [18,19]:

$$\frac{dC_F}{dt} = \frac{Q.\,C_o}{V} - \frac{Q.\,C_F}{V} - k.\,X.\,C_F \tag{1}$$

The rate at which the substrate change (dC_F/dt) within the reactor at steady state conditions is considered to be insignificant and subsequently Eq. (1) can be simplified to yield Eq. (2).

$$\frac{C_o - C_F}{HRT} = k.\,X.\,C_F = k_1.\,C_F \tag{2}$$

Table 1
The process specifications for each mill effluent type.

Parameter	Effluent A	Effluent B	Effluent C
Recycle material (%)	95	50–55	25
Broke (%)	5	5–7	5
NSSC (%)	0	40–42	70
Hardwood (%)	–	60	100
Softwood (%)	–	40	–