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Chloro-Organics in Papermill Effluent: Identification and Removal by Sequencing Batch Biofilm Reactor

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Abstract: Effluents from paper mills are among major sources of aquatic pollution and may be toxic since they contain chlorinated phenolic compounds which are measured as adsorbable organic halides (AOX). In this work, removal of chlorophenol was investigated using a Sequencing Batch Biofilm Reactor (SBBR) with Granular Activated Carbon (GAC) as a growth media. Wastewater for this study was obtained from treated effluent outlet of a papermill in Selangor. Treatment of the papermill secondary effluent shows that SBBR process, with a combination of adsorption and biodegradation, gave a good removal of pentachlorophenol (PCP), on average, about 70%. The growth kinetic parameters obtained were: $Y_{H=}$0.6504 mg biomass/mg PCP, $d_H = 6.50\times10^{-5}$ h^{-1}, $\mu_{h=}$0.00315 h^{-1} and $K_{s=}$5.82 mg PCP L^{-1}. These show that the SBBR system is suitable to be operated at long SRTs.

Key words: Chloroorganics, AOX, papermill, adsorption, biofilm

INTRODUCTION

Phenolic compounds are a group of organic pollutants present in the environment as a result of various processes such as industrial, biogeochemical and pesticide degradation. These compounds, especially chlorophenols are known for their toxicity and persistence in the environment. They are also accumulative, due to their oleophillicity. These are harmful to living beings, if present in low concentration.. For these reasons, some of them have been included in the list of priority pollutants of several countries and are subject to legislation (Penalver *et al*., 2002; Annachhatre and Gheewala, 1996). Toxicity and bioaccumulative potential of chlorophenols increase with the degree of chlorination (Loehr and Krishnamoorthy 1998), chlorophenol lipophilicity (Mohn and Kennedy, 1992) and the number of chlorine substituents on the phenolic ring (Annachhatre and Gheewala, 1996).

The toxic effects of chlorophenols seem to be linked to a chain reaction of their gradual dechlorination in body fluids and the formation of free radicals interfering with subcellular structures. The formation of peroxides and other products of lipid oxidation result in enzyme deactivation and liver dystrophy. Chronic toxicity studies on carcinogenic properties of some chlorophenols indicate that higher chlorophenols have immunosuppressive effects, are nephrotoxic and interfere with blood formation. Chlorophenols are excreted from the organism mainly in urine, partially free and partially in the form of their sulphate and glucuronide conjugates. Chlorophenols are known for their pronounced organoleptic characteristics, the taste threshold ranging between 0.040-30 μg L^{-1} and smell threshold between 30-1600 μg L^{-1} (Veningerová *et al*., 1997). The Granular Activated Carbon Sequencing Batch Biofilm Reactor (GAC-SBBR) combines technologies of adsorption and biodegradation, where the Sequencing Batch Reactor (SBR) is packed with GAC and the microorganisms grow in the reactor in the form of biofilms. From the literature on GAC-SBBR systems (Caldeira *et al*., 1999; Jaar and Wilderer, 1992), it can be summarized that the system can provide several advantages such as: the GAC is very adsorptive and has very high surface to volume ratio, due to its large number of internal pores and rough surface texture, which can be a good bacterial immobilization matrix to form the biofilm. The less biodegradable organics (mostly chlorinated organics) can be first adsorbed onto the GAC and are then slowly degraded by microorganisms. This can partially regenerate the activated carbon while the system is in operation. The GAC adsorption process can reduce the toxic effects of the pollutants and increase the stability of the system.

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The aim of the present work is to determine the presence, if any, of chlorophenol(s) in papermill treated (secondary) effluent and study their removal by using an SBBR system.

APPROACH AND METHODS

The SBBR reactor is a 1 lit glass reactor operated at room temperatures (25±2°C) and packed with 200g/l of 2-3mm Granular Activated Carbon (GAC) as a medium for biofilm growth. The acclimatized sludge used was taken from a pulp and paper mill wastewater treatment plant located in Sabah, Malaysia.

The waste water feed, or treated effluent, used for this study was taken from the wastewater treatment plant (WWTP) of a paper mill located in Selangor, Malaysia. The WWTP of the mill is shown in Fig. 1, which shows a secondary level process. The effluent meets the regulatory discharge limits; however there is yet no regulatory limit for chloroorganics. Typical analysis of the effluent was carried out immediately upon sampling, where samples were analysed for pH using a microprocessor pH meter (Model HI 931401, Hanna Instrument) before filtering using 0.45 μm nylon membrane filter (Whatman®). COD was measured using the Hach Reactor Digestion Method (EPA approved). Colour was determined using the APHA Platinum-Cobalt Standard Method. Typical parameters of this paper mill WWTP effluent is shown in Table 1.

Chlorophenols were analysed by using high performance liquid chromatography (HPLC) with UV detector (Agilent Series 1100, 2002), after extraction using ENV+ ISOLUTE® SPE column (IST). The HPLC was equipped with Zorbax SB-C18 column (150×4.6 mm, 5 μm). The mobile phase was 20% Acetonitrile (ACN)/80% 0.01 M H_3PO_4 to 45%ACN in 7.5 min, with gradient of 80% ACN in 2.0 min and UV detection at 254 nm (Agilent Technologies, Inc. 2002). Stock standard solution containing Pentachlorophenol (PCP), Tetrachlorophenol (TeCP), 2,4,6-Trichlorophenol (2,4,6-TCP), 2,4-Dichlorophenol (2,4-DCP), 2-Chlorophenol (CP) and phenol containing 2000 mg L^{-1} each in methanol were purchased from Supelco (Bellfonte, PA, USA). The retention times for Pentachlorophenol (PCP), Tetrachlorophenol (TeCP), 2,4,6-Trichlorophenol (2,4,6-TCP), 2,4-Dichlorophenol (2,4-DCP), 2-Chlorophenol (CP) and Phenol were 12.5, 11.8, 11.3, 10.5, 8.3 and 5.7±0.1 min, respectively.

Table 1: Papermill WWTP typical effluent characteristics

Parameter	Conc.
COD	49.3 ((mg L^{-1}))
Colour, PtCo	40.7
pH	7.66
Chloride, Cl^-	18.87 (mg L^{-1})
Nitrate-Nitrogen,NO_3-N	2.17 (mg L^{-1})
Ammonia-Nitrogen,NH_3-N	0.28 (mg L^{-1})
Suspended solids, SS	10.0 (mg L^{-1})

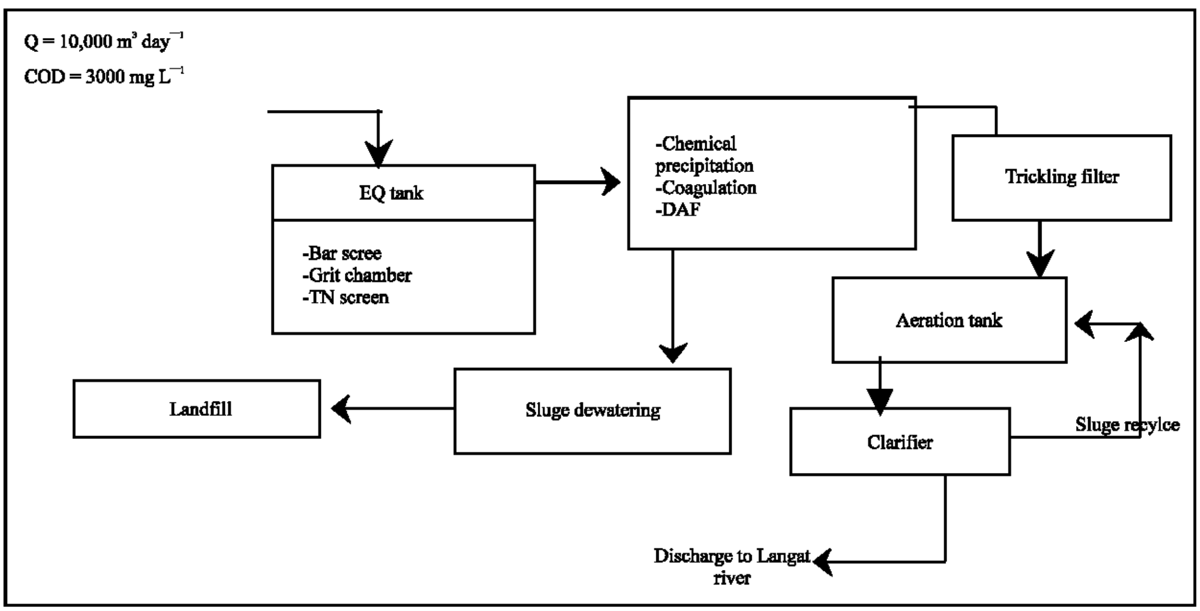

Fig. 1: Flow chart of the paper mill wastewater treatment plant

KINETICS FOR THE MICROBIAL GROWTH

Using the Monod equation and applying material balance for the substrate and biomass in SBBR, the equations for the microbial growth can be expressed as below:

$$V\frac{dX}{dt} = (QX_o) + (\mu XV) - (b_H XV) - (QX_e) \quad (1)$$

$$\frac{dS}{dt} = \frac{Q(S_o - S_e)}{V} - \frac{X}{Y_H}\left(b_H + \frac{1}{\Theta}\right) \quad (2)$$

Solving these equations at steady state and using the graphical solution method, the growth kinetic parameters Y_H, b_H, μ_h and K_s were determined.

RESULTS

Figure 2 shows the HPLC chromatograms for the SBBR's influent and effluent. Table 2 shows the peak heights for chlorophenol compounds in the HPLC chromatograms and the percentage removal obtained.

Table 2: Peak heights and percent removal of chlorophenol compounds

Chlorophenol compound	Peak Height, H (mAU) Influent	Effluent	Removal (%)
PCP	24.54	7.35	70.05
2,4-DCP	15.00	2.03	86.47
CP	15.89	-	100.00
Phenol	23.56	-	100.00

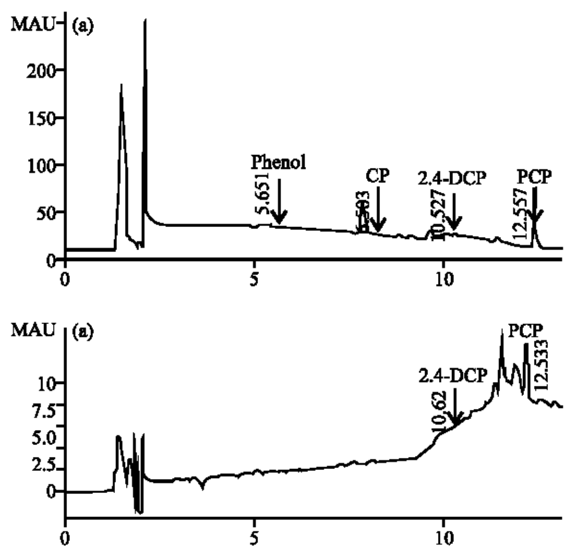

Fig. 2: HPLC chromatograms for SBBR's (a) influent and (b) effluent

DISCUSSIONS

PCP appears to be very resistant to microbial degradation due to its highly chlorinated phenolic nature. However, the ability to degrade this biocide has been demonstrated in this study's SBBR. Figure 2a and b show the HPLC chromatograms for the influent and effluent of SBBR for 2 days hydraulic residence time, HRT. From the SBBR influent chromatograph Fig. 2a, the PCP was detected at the residence time of 12.5 minutes. The HPLC chromatograms also showed presence of phenol, chlorophenol and 2,4-dichlorophenol in the papermill treated effluent. HPLC analysis of the SBBR effluent still showed traces of PCP and 2,4-DCP, but at much lower concentrations (Fig. 2b). CP and phenol were not detectable. Lower PCP concentration in the effluent than influent indicated that microorganisms in the SBBR have degraded the PCP compound. From the PCP standard curve, approximately 70% of PCP in the wastewater was removed by the SBBR system at HRT of one-day.

The results of HPLC analysis on SBBR's influent and effluent indicated that the reductive dechlorination process pathway might be carried out by the microorganisms in the reactor, by converting the PCP to chlorinated compounds (CP, DCP and Phenol) and gas CO_2. Reductive dechlorination, or removal of Cl atoms directly from the ring of aromatic compounds in a single step is a significant process because the dechlorinated products are less chlorinated and therefore less toxic and are more readily degraded either anaerobically or aerobically (Mikesell and Boyd, 1986; Tsuno *et al*., 1996) It is also part of the pathway towards cleavage of the phenol ring. Lower concentrations of PCP and 2,4-DCP, plus undetectable CP and phenol, showed that mineralization through phenol ring cleavage had occurred. The varied reactions of reductive dechlorination and oxidative phenol cleavage could be possible in a biofilm system as the biofilm harbours both anoxic and aerobic regions. COD removal by the SBBR was also studied; it showed that this system can still lower the effluent COD, in this case by about 53.4% COD from 58 mg L^{-1} (influent) to 27 mg L^{-1} (effluent).

Growth kinetics: Using the Monod equation and applying the material balance for substrate and biomass inside the reactor, the growth kinetic properties for the culture inside the SBBR were obtained by plotting the graph $(S_o\text{-}S_e)/(f_A.X_T.\tau)$ versus $1/\Theta c$ and the Hane plot (graph of $S_S/(1/\Theta c+b_H)$ versus S_s) (data not shown). The growth kinetic parameters (Y_H, b_H, μ_h and K_s) obtained are summarized in Table 3.

Table 3: Growth kinetic parameters for the SBBR

Growth kinetic parameters	Values
Specific growth rate coefficient, μ_h (h^{-1})	0.00315
Half saturation coefficient, K_s (mg PCP L^{-1})	5.82
Biomass yield, Y_H (mg biomass/mg PCP)	0.6504
Decay coefficient, b_H (h^{-1})	6.50×10^{-5}

According to Klecka and Maier (1985), organisms capable of high growth rates at high substrate concentrations typically grow less efficiently at lower concentrations due to low substrate affinities (high K_s). Alternatively, organisms that grow efficiently at low substrate concentrations generally exhibit low growth rates at high substrate affinities (low K_s). Grady *et al.* (1999) also noted that a system which have a higher value of μ_H and a lower value of K_s allowed the biomass to grow faster at a given substrate concentration, thereby giving a lower reactor substrate concentration for any given value of the SRT. All these means that the SBBR, whose acclimatized mixed culture has shown very low μ_h and high K_s values, has to be operated at a longer SRT, due the low PCP affinities and growth rate. A high b_H means that the bioreactor requires higher oxygen concentrations for oxidizing the substrate to carbon dioxide. On the other hand, a high yield system requires less oxygen because more electrons in the substrate will be retained in the biomass synthesized (Grady *et al.*, 1999). Considering these two parameters it can be deduced that the SBBR system imposes lower oxygen consumption and coupled with the low decay constant means that the system is stable and retains microorganisms longer.

CONCLUSION

This study revealed that treated paper mill effluents contained several types of chloroorganics; pentachlorophenol (PCP), chlorophenol and 2,4-dichlorophenol. These may be harmful over a long term as these pollutants are bioaccumulative. However, this study has shown that polishing treatment by a biofilm sequencing batch reactor is capable of removing the chloroorganics, leading to lowering of residual COD.

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