Modern Applied Science
www.ccsenet.org/journal.html
Vol. 2, No. 5
September 2008

Removal of Adsorbable Organic Halides (AOX) from Recycled Pulp and Paper (P&P) Mill Effluent Using Granular Activated Carbon–Sequencing Batch Biofilm Reactor (GAC-SBBR)

Abu Bakar Mohamad
Department of Chemical & Process Engineering, Faculty of Engineering
Universiti Kebangsaan Malaysia (UKM), 43600 Bangi, Selangor, Malaysia
Tel: 6-038-921-6406 E-mail: drab@vlsi.eng.ukm.my

Rakmi Abd Rahman
Department of Chemical & Process Engineering, Faculty of Engineering
Universiti Kebangsaan Malaysia (UKM), 43600 Bangi, Selangor, Malaysia
E-mail: rakmi@vlsi.eng.ukm.my

Abdul Amir Hassan Kadhum
Department of Chemical & Process Engineering, Faculty of Engineering
Universiti Kebangsaan Malaysia (UKM), 43600 Bangi, Selangor, Malaysia
E-mail: amir@vlsi.eng.ukm.my

Siti Rozaimah Sheikh Abdullah
Department of Chemical & Process Engineering, Faculty of Engineering
Universiti Kebangsaan Malaysia (UKM), 43600 Bangi, Selangor, Malaysia

Zakiah Wan Sudin
Department of Chemical & Process Engineering, Faculty of Engineering
Universiti Kebangsaan Malaysia (UKM), 43600 Bangi, Selangor, Malaysia
Tel: 6-038-921-6428 E-mail: zakiah_sudin@yahoo.com

Safura Shaari
Department of Chemical & Process Engineering, Faculty of Engineering
Universiti Kebangsaan Malaysia (UKM), 43600 Bangi, Selangor, Malaysia

The research was financed by Swedish International Development Agency under the Asian Regional Research on Environment and Technology Programme (SIDA-ARRPET) Phase II.

Abstract

Paper mills generate varieties of pollutants depending upon the type of the pulping process. The wastewaters discharged from these mills have high chemical oxygen demand (COD) and colour, in which indicating high concentrations of recalcitrant organics. This study was conducted using a Granular Activated Carbon – Sequencing Batch Biofilm Reactor (GAC-SBBR) of 3.0 L working volume, operated in an aerobic condition and packed with 200 gL^{-1} of 2-3 mm granular activated carbon (coconut shells) as a medium for the biofilm growth. For the six of months, the hydraulic retention time (HRT) was set at 36 hours and later it was adjusted to 24 hours in order to evaluate the performance of the system. The treated wastewater samples for these studies were taken from a recycled pulp and paper mill factory in Pahang, Malaysia with 4 different batch characteristics. The adsorbable organic halides (AOX) that had been determined and treated were pentachlorophenol (PCP), 2,3,4,5-tetrachlorophenol (2,3,4,5-TeCP), 2,4,6-trichlorophenol (2,4,6-TCP), 2,4-dichlorophenol (2,4-DCP), 2-chlorophenol (CP) and phenol at various concentration ranges. The Monod growth kinetic parameters for the process specific growth rate coefficient (μ_h), half saturation coefficient (K_s), endogenous decay coefficient (D_H) and Yield coefficient (Y_H) obtained were 0.0037 hr^{-1}, 65.23 mgL^{-1}, $4x10^{-5}$ hr^{-1} and 0.36 mg/mg, respectively. Analysis of the growth kinetic parameters in GAC-SBBR had deduced that the system was suitable to operate on long biomass retention time (BRT) under anoxic condition. The results also indicated that the biofilm attached onto granular activated carbon (GAC) can substantially remove these recalcitrant organics in the wastewater, within the range of 10 – 100% AOX removal depending on the selected HRTs.

Keywords: Adsorbable organohalides, Recalcitrant organics, Paper mill effluent, Biofilm, Sequencing batch reactor

1. Introduction

Chloroorganic compounds such as phenol and chlorophenol have become a major concern to public health due to their toxicological and recalcitrant characteristics. In order to remove these recalcitrant organics from industrial wastewater, the high costs activated carbon (AC) adsorption, as final treatment step is indispensable. This normal conventional adsorption technique has the disadvantages of inadequate exploitation of the adsorptive capacity, high cost of conventional thermal or chemical regeneration process for spent AC as well as decreasing adsorptive capacity of the AC, ultimate disposal problem, and toxic products such as chlorodibezodioxins might be generated in the thermal oxidation process (Kolb and Wilderer, 1997; Jaar and Wilderer, 1992). To solve most of these problems, the idea of using combined biofilm and granular activated carbon (GAC) adsorption were undertaken.

Granular Activated Carbon Sequencing Batch Biofilm Reactor (GAC-SBBR) was a technology system that was earlier developed by Wilderer (1992). It is a discontinuous technology where the sequencing batch reactor (SBR) was packed with GAC and the microorganisms were allowed to grow in the reactor by clinging onto suspended plastic media which later form the biofilm layer. Jaar and Wilderer (1992) had conducted the GAC-SBBR to study the removal of problematic wastewater containing 3-chlorobenzoate and thioglycolic acid. They had found that by adding the GAC inside the SBR, the system indicated high substrate removal efficiency with high process stability under various shock loading conditions. Furthermore, the study also found that the activated carbon had maintained approximately 90% of its adsorption capacity over a continuous operation period of 14 months. In addition, by introducing GAC inside the SBR, the GAC adsorption process was able to reduce the toxic effects of the pollutants and also increase the stability of the pollutant removing system (Xiaojian et al., 1991; Caldeira et al., 1999; Jaar and Wilderer, 1992).

Therefore the aim of this research is to investigate the performance and the effectiveness of the GAC-SBBR process in the removal of adsorbable organohalides (AOXs) and COD found to contain in the recycled paper mill effluent.

2. Approach and Methods

2.1 Effluents

The bleached effluent samples were collected from a recycled pulp and paper mill effluent in Pahang, Malaysia and it was taken after the second clarifier of the wastewater treatment plant. Samples were stored in 20-L plastic containers, kept at 4 $^{\circ}$C and transported back to our laboratory. The left over collected effluent was kept in the cold room for later use.

2.2 Inoculums

The original inoculums were a mixture obtained from a sewage oxidation pond in Kuala Lumpur and from the garden soils. The inoculums used in this experiment were procured from a batch anaerobic reactor located in the laboratory which has been maintained at ambient temperature condition.

2.3 GAC – SBBR

A reactor with 3 L working volume was used in this study. It was operated at room temperature and packed with 200 g/L of 2-3 mm granular activated carbon (coconut shells) as a medium for the biofilm growth as presented in Figure 1. The reactor was earlier operated at hydraulic retention time (HRT) of 36 hours for the six months and later was adjusted to HRT of 24 hours in order to make the performance comparison of the biofilm between both the HRTs. The samples were analyzed for COD, AOXs and the amount of biomass washout before being fed into the reactor.

2.4 Experimental Method

The overall methodology of this study is as illustrated in Figure 2. The GAC-SBBR system was initiated with the characterization of the influent and effluent samples and these were followed by the kinetic studies of the microorganism growth and the optimization of reactor operating parameters. The COD and biomass parameters were analyzed using the standard methods with the respective instruments as listed in Table 1. The AOXs were extracted using the solid phase extraction (SPE) technique and later analyzed using the HPLC instrument.

3. Results and Discussion

The characteristics of four batches of samples from recycled paper mill factory were determined and the results were as indicated in Table 2. Figure 3 showed that the maximum influent concentrations obtained for COD on all four samples were below 250 mgL^{-1} while the COD values on the effluent were below 100 mgL^{-1}. The removal ranges for COD at HRTs of 36 hours and 24 hours were 50–80% and 50–66%, respectively. As was previously observed by the study of Barr et al. (1996), the removal of COD was found to decrease with the decreasing of the HRT. It was also observed that at the initial stage of the study (approximately within the first 20 days), the COD removal was higher even though the biomass concentration was below 2000 mgL^{-1}. This was most probably due to the adsorption of the COD onto the freshly introduced GAC.

The concentrations of the compounds as identified in the paper mill effluent with their percentage removals were as shown in Figures 4 – 9. In Figure 4, the concentrations of phenol were found to be very low and could hardly be detected. However, in the third and fourth samples the concentrations of phenol started to appear as these samples have undergone almost 100% phenol removal after its treatment in the GAC-SBBR process.

The concentrations of chlorophenol (Figure 5) only exist in the first sample batch and 40-70% was removed after treatment at HRT of 36 hours. For dichlorophenol, 2,4-DCP, as shown in Figure 6, only in the first and third batch samples were detected with 60–100% and 30-80% dichlorophenol removal at HRTs of 36 hours and 24 hours, respectively, after treatment with GAC-SBBR. The percentages removal for trichlorophenol, 2,3,4-TCP, as depicted in Figure 7 at HRT of 36 hours were in range of 20–80% while at HRT of 24 hours its percentage removal was found to decrease in the range of 10–40%. Tetrachlorophenol, 2,4,5,6-TeCP, as shown in Figure 8 have the percentage removal in the range of 30–50% at HRT of 36 hours, and dropped below 20% at HRT of 24 hours. The concentration of pentachlorophenol, PCP, was found to be very low (Figure 9) and only exists in the first batch of samples with removal after treatment of 60–80% in the GAC-SBBR system.

Based on these results, it was observed that the removal of PCP was much higher than the removal of 2,4,5,6-TeCP but was comparable to 2,3,4-TCP and 2,4-DCP under the two selected HRTs. Based on earlier study by Annachhatre and Gheewala (1996), for the anaerobic environment, PCP degradation rate was slower than that of phenol or 2-CP but comparable to 2,4,6-TCP and 2,4-DCP, suggesting that increased chlorination of the aromatic ring does not necessarily have direct correlation with resistance to biodegrade. However, the chlorine positions in the phenolic ring also had significant effects on the biodegradability of the compound as have been indicated by earlier studies (Boyd & Shelton, 1984; Knoll & Winter, 1987).

The percentage removal of chlorophenols for this GAC-SBBR process was also dependent on the selected HRT. Longer HRT has indicated improved biodegradation process while at the reduced expense of GAC adsorption. The longer HRT would mean a much longer period for the microbe to react with chlorophenol in the reactor thus giving rise to more biomass in order to continue with the biodegradation process. Barr et al. (1996) had also confirmed the earlier presumption that an increased HRT could improve AOXs removal and decreasing HRTs would result in a decrease in the toxicity removal. It is thus indicated that as the HRT decreases, a greater proportion of the more recalcitrant compounds will resist to biodegradation.

The efficiency of a system is also very dependent on the characteristics of the microbe population in the reactor. The Monod growth kinetic parameters, namely, μ_h, K_s, D_H and Y_H, obtained for this process were 0.0037 hr^{-1}, 65.23 mgL^{-1}, $4x10^{-5}$ hr^{-1} and 0.36 mg/mg, respectively. Comparisons of these kinetic values from other similar studies for AOX and other persistent organic removals were as indicated in Table 3. Analysis of the growth kinetic parameters in GAC-SBBR had deduced that the system is capable to operate a long biomass retention time under anoxic condition (or less oxygen). Anderson et al. (1996) have reported that the consumption of non-biodegradable substrate would lower the specific growth rate, μ_h.

4. Conclusions

This study has shown that selection of a suitable HRT plays an important role in the COD as well as in the AOXs removal. For long HRT of 36 hours, the percentage removals of COD and AOX were much higher as compared to shorter HRT (24 hours) where their percentage removals were slightly lower. The individual AOX removable varies in ranges according to the specific HRTs being applied with no obvious trend patterns. The results of this initial study thus reaffirm the fact that GAC – SBBR system treatment of recycled pulp and paper mill effluents could be considered as an alternative option not only for energy cogeneration but also as a means of significantly reducing some of the more important, albeit organic recalcitrant, objectionable parameters.

References

Anderson, G.K., Kasapgil, B. & Ince, O. (1996). Microbial Kinetics of A Membrane Anaerobic Reactor System. *Environmental Technology*. 17: 449-464.

Annachhatre, A. P. & Gheewala, S. H. (1996) Biodegradation of Chlorinated Phenolic Compunds. *Biotechnology Advances*. 14(1): 35-56.

Barr, T. A., Taylor., J. M. & Duff., S. J. B. (1996). Effect of HRT, BRT and Temperature on The Performance of Activated Sludge Reactors Treating Bleached Kraft Mill Effluent. *Water Research*. 30: 799-810.

Boyd, S. A & Shelton, D. R. (1984). Anaerobic biodegradation of chlorophenols in fresh and acclimated sludge. *Application Environmental Microbiology.* 47: 272-277.

Caldeira, M., Heald, S.C., Carvalho, M.F., Vasconcelos, L., Bull, A.T., Castro, P.M.L. (1999). 4-Chlorophenol degradation by a bacterial consortium: development of a granular activated carbon biofilm reactor. *Application Microbial Biotechnology*. 52: 722-729.

Hess, T.F. (1990). Supplemental substrate enhancement of 2,4-Dinitrophenol mineralization by a bacterial consortium. *Applied and Environmental Microbiology*. 56:1551-1558.

Jaar, M.A.A. and Wilderer, P.A. (1992). Granular activated carbon sequencing batch biofilm reactor to treat problematic wastewaters. *Water Science and technology*. 26 (5-6): 1195-1203

Jacobsen, B.N. & Arvin, E. (1996). Biodegradation kinetics and fate modeling of pentachlorophenol in bioaugmented activated sludge reactors. *Water Research*. 30 (5): 1184-1194.

Klecka, G.M. & Maier, W.J. (1985). Kinetics of microbial Growth on Pentachlorophenol. *Applied and Environmental Microbiology*. 49: 46-53.

Knoll, G. & Winter, J. (1987). Anaerobic degradation of phenol in sewage sludge. *Application Microbiology Biotechnology.* 25: 384-391

Kolb, F.R. and Wilderer, P.A. (1997). Activated carbon sequencing batch biofilm reactor to treat industrial wastewater. *Water Science Technology*. 35 (1): 169-176.

Wilderer, P.A. (1992). Sequencing batch biofilm reactor technology . Harnessing biotechnology for the 21st century, Ladisch, MR. And Bose (Eds), American Cehnical Socity: 475-479.

Xiaojian, Z. et al. (1991). Simple combination of biodegradation and carbon adsorption – the mechanism of the biological activated carbon process. *Water Research*. 25(2): 165-172.

Table 1. Methods and instruments used to analyze stated parameters

Parameter	Instruments	Method	References
Chemical oxygen demand (COD)	HACH DR/2010 Spectrophotometer	Digestion Method	EPA
Adsorbable organohalides (AOX)	(HPLC) with UV detector (Agilent Series 1100)	Zorbax SB-C18 column (150 mm x 4.6 mm, 5µm) Mobile Phase: 20% Aceton Nitril (ACN)/80% 0.01M H_3PO_4 to 45% CAN in 7.5 min with gradient of 80% ACN in 2.0 min and UV detection at 254 nm	This study Agilent Technologies (2002)
Biomass	Filtration Unit	Mass Liquid Suspended Solids	APHA (1992)
Kinetics Growth	-	Monod Equation	Monod (1949)

Table 2. Characteristics of the four batches of samples taken from recycled pulp and paper mill factory effluents in Pahang

Parameter (unit)	P&P Mill Effluent			
	Batch 1	Batch 2	Batch 3	Batch 4
COD, (mgL^{-1})	184	93	118	177
OLR, (g COD $[Lday]^{-1}$)	0.123	0.062	0.079	0.177
Colour (Pt-Co)	66	59	60	63
pH	7.16	7.3	7.25	7.21
Suspended Solids, SS, (mgL^{-1})	10.5	10	10	10.5
Phenol, (ugL^{-1})	ND	ND	ND	74
Chlorophenol, (ugL^{-1})	13	ND	ND	ND
Dichlorophenol, (ugL^{-1})	35	ND	ND	151
Trichlorophenol, (ugL^{-1})	332	197	176	372
Tetrachlorophenol, (ugL^{-1})	ND	26	30	ND
Pentachlorophenol, (ugL^{-1})	15	ND	ND	ND

ND = Not Detected.

Table 3. Growth kinetic parameters in this study and by other previous researches

Reference	System	Subtract	HRT (hrs)	Growth kinetic parameters			
				Y_H (mg/mg)	D_H ($hour^{-1}$)	μ_h ($hour^{-1}$)	K_s (mgL^{-1})
This study	GAC-SBBR	AOX	24	0.36	$4x10^{-5}$	0.0037	65.23
Jaar & Wilderer (1992)	GAC-SBBR	3-Chlorobenzoat	-	0.45	-	0.40	13
Hess et al. (1993)	SBR	2,4-DNP	79-230	0.41±0.15	-	-	1.12±0.5
Jacobsen & Arvin (1996)	SBR	PCP	4.3-13.9	0.4	-	0.05	-
Klecka & Maier (1985)	Batch	PCP	312-348	0.136	-	0.074	$60x10^{-3}$

*AOX: Adsorbable organic halides; PCP: Pentachlorophenol; DNP: 2,4-Dinitrophenylhydrazine

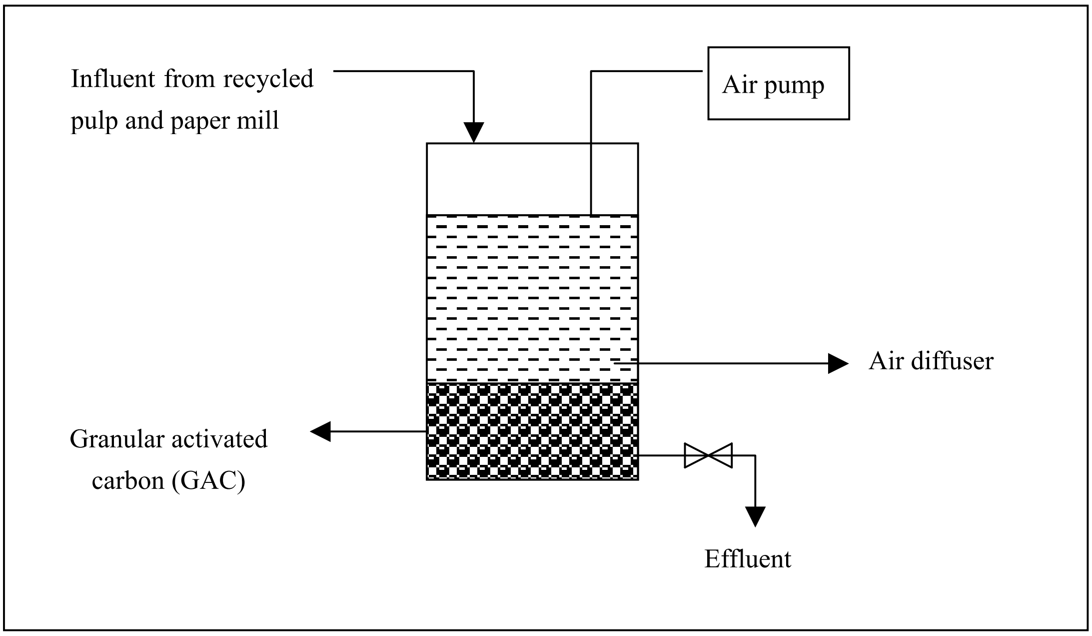

Figure 1. Schematic Diagram of the Granular Activated Carbon-Sequencing Batch Biofilm reactor (GAC-SBBR)

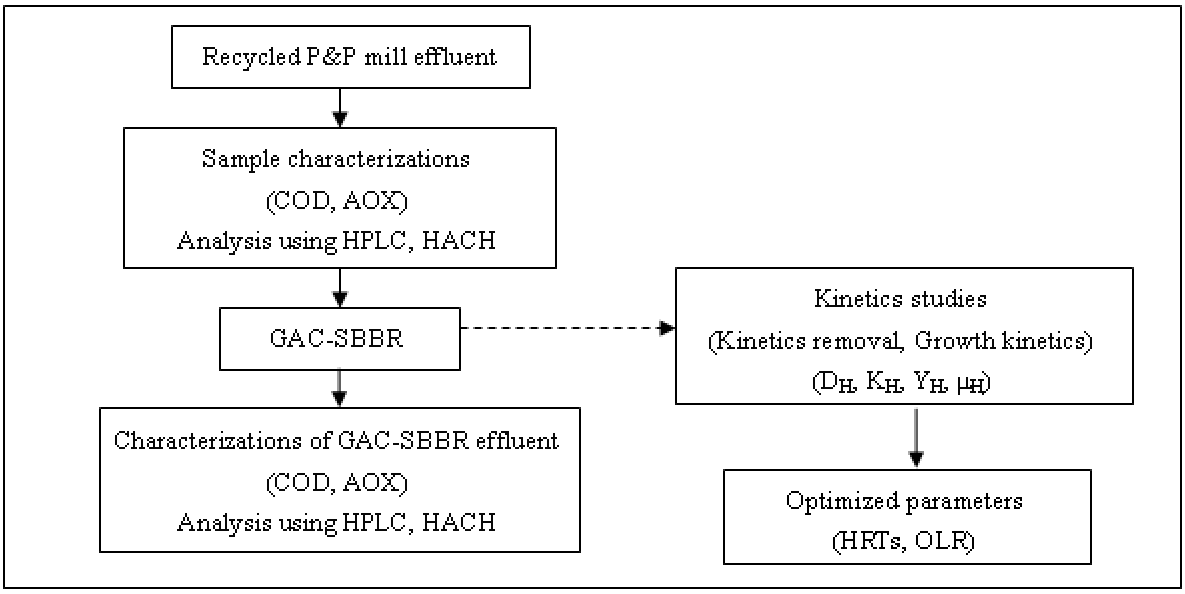

Figure 2. Overall methodology summary

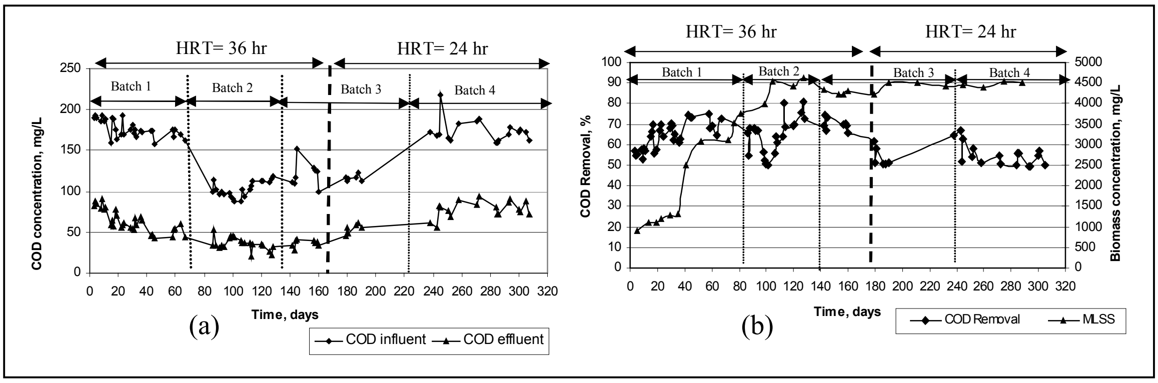

Figure 3. (a) Influent and effluent concentrations of COD and (b) Relation between COD percentage removal with biomass concentrations with both taken at HRTs of 36 hours and 24 hours

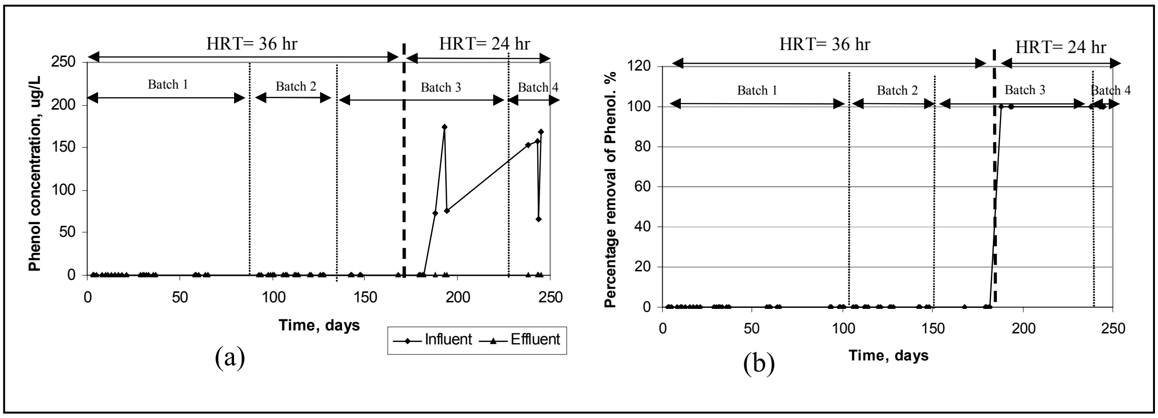

Figure 4. Phenol: (a) Influent and effluent concentrations and (b) percentage removal with both taken at HRTs of 36 hours and 24 hours

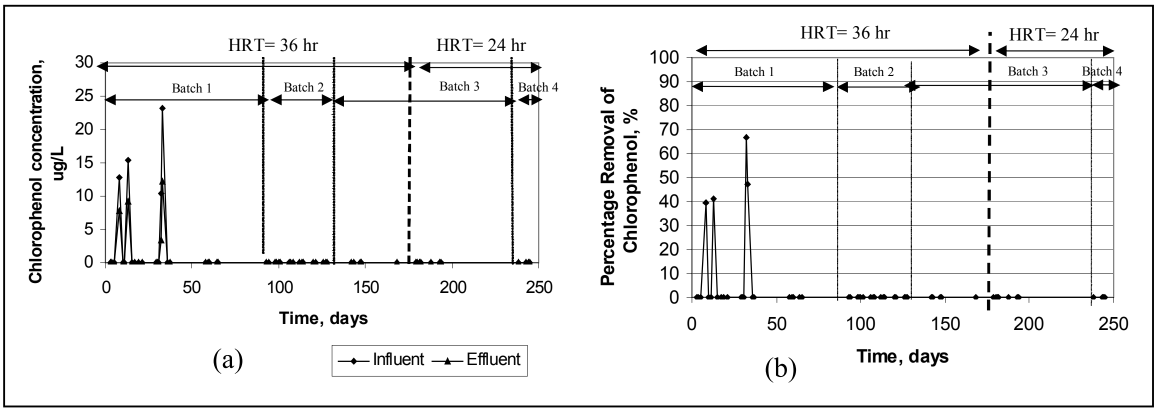

Figure 5. Chlorophenol: (a) Influent and effluent concentrations and (b) percentage removal with both taken at HRTs of 36 hours and 24 hours

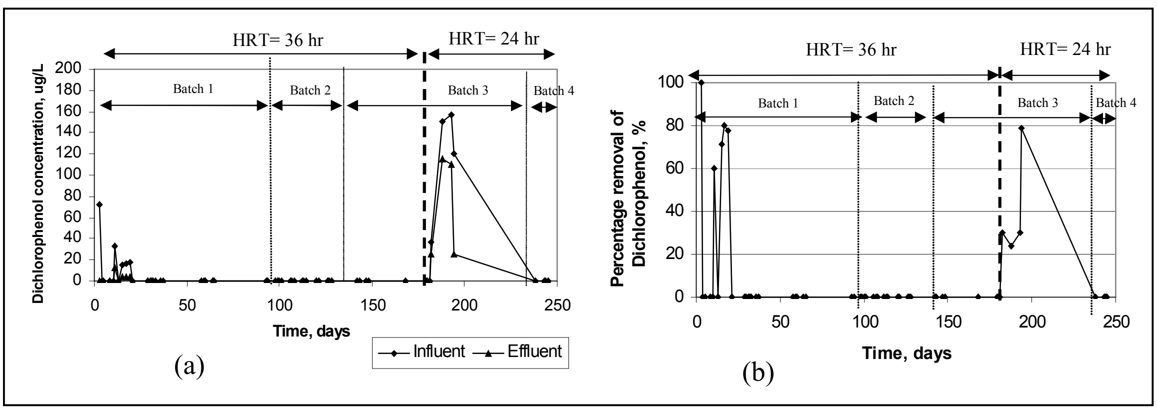

Figure 6. Dichlorophenol: (a) Influent and effluent concentrations and (b) percentage removal with both taken at HRTs of 36 hours and 24 hours

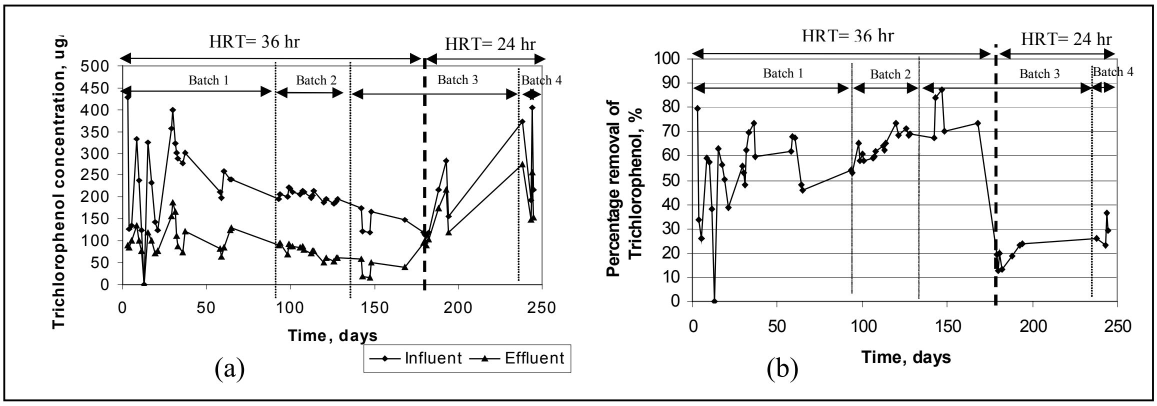

Figure 7. Trichlorophenol: (a) Influent and effluent concentrations and (b) percentage removal with both taken at HRTs of 36 hours and 24 hours

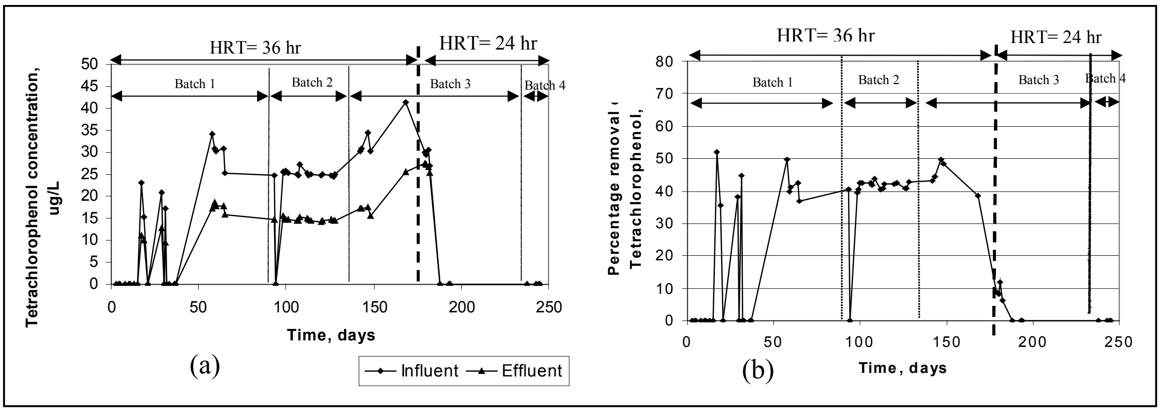

Figure 8. Tetrachlorophenol: (a) Influent and effluent concentrations and (b) percentage removal with both taken at HRTs of 36 hours and 24 hours

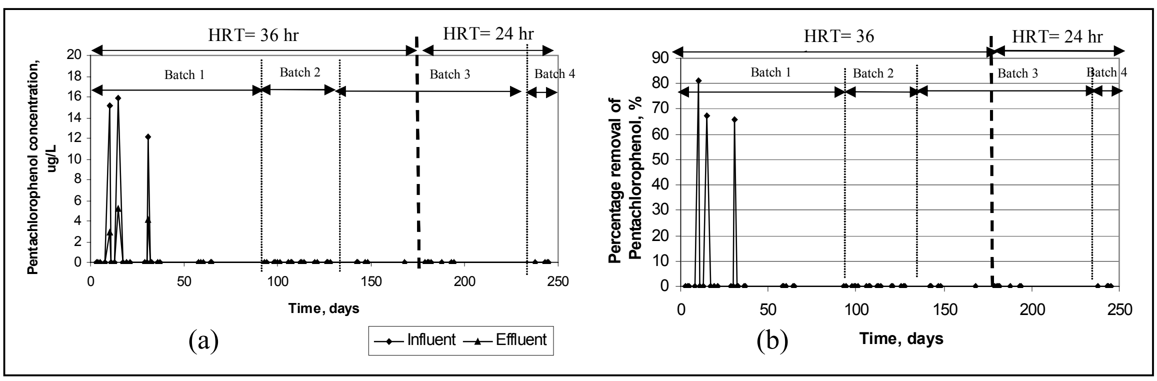

Figure 9. Pentachlorophenol: (a) Influent and effluent concentrations and (b) percentage removal with both taken at HRTs of 36 hours and 24 hours

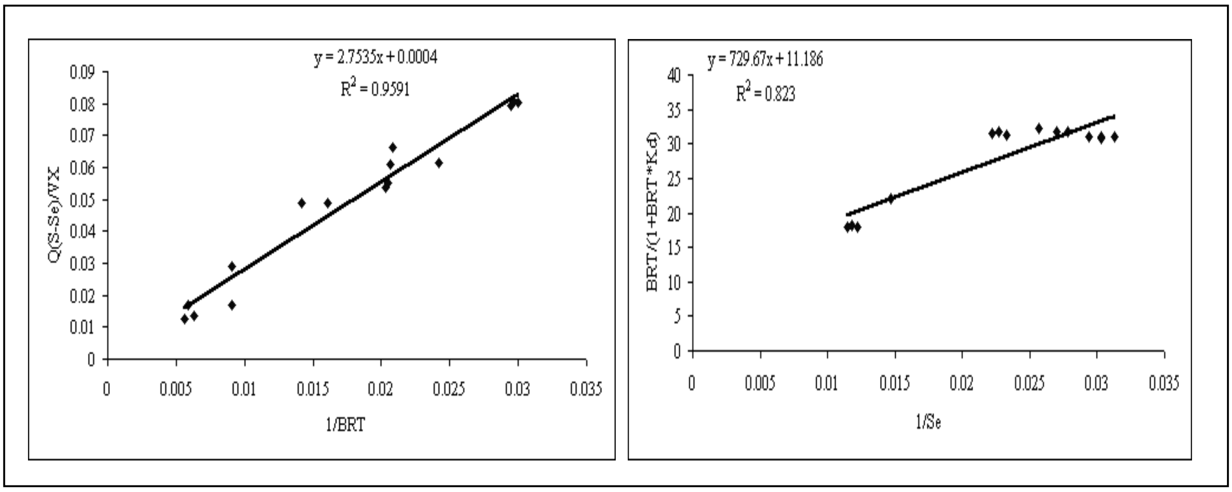

Figure 10. Growth kinetic parameters plot for recycled pulp and paper mill effluent samples