

Effect of hydraulic retention time (HRT) on pentachlorophenol (PCP) and COD removal in a pilot GAC-SBBR system for the post-treatment of recycled paper mill wastewater

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ABSTRACT

This study investigates the feasibility of using a pilot-scaled sequencing batch biofilm reactor (SBBR) with an option for granular activated carbon (GAC), at different hydraulic retention times (HRT) for the post-treatment of treated recycled paper industry wastewater containing potentially persistent and toxic pollutants, especially adsorbable organic halides (AOX). The environmental problems associated with AOX include their accumulation in the food chain and their persistence in nature. The pilot plant consists of a high-density polyethylene (HDPE) biofilm reactor with a diameter of 1.2 m, and a maximum water depth of 1.8 m, that is packed with 1111 g/L of 2–3 mm granular activated carbon (coconut shells). The effect of HRT on AOX (specifically PCP) and COD removal was investigated at varying hydraulic loading rates of 0.3–0.8 m³/(m² day). The HRT was investigated at three different levels varying from 1 to 3 days and the most suitable retention time, resulting in maximum overall removal of COD and PCP, was determined. The study demonstrated that at a workable HRT of 3 days and an average organic loading rate of 0.008 kg COD/m³ d, the PCP and COD removal efficiencies of the reactors were 100% and 86.9 ± 2.4%, respectively, at optimum pH of 7–8 and DO of 4–6 mg/L.

Keywords: Pilot GAC-SBBR; HRT; Adsorbable organic halides (AOX); Recycled paper industry; Pentachlorophenol (PCP); Post-treatment

1. Introduction

Wastepaper recycling for the production of pulp and paper is becoming increasingly important in order to reduce wood consumption and protect the environment. Paper recycling is growing in Malaysia, and many of the mills use as much as 100% waste paper in their raw material base [1]. The activities of pulp and paper

production in Malaysia generate significant quantities of wastewater in natural water receptors, affecting the ecological balance and causing aesthetic concerns. Historically, the pulp and paper industry throughout the world was known to be the sixth largest polluter (after the oil, cement, leather, textile and steel industries), discharging a variety of gaseous, liquid and solid wastes into the environment [2]. Until 1950s, it was common for pulp mills and many other industries to discharge untreated, toxic effluents directly into rivers and seas [3]. In recent

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years, the pulp and paper manufacturing industry has been obliged to significantly reduce wastewater discharge due to the stringent regulations. Meanwhile, increasing awareness of natural resource conservation and sustainable development has led to increased public concern about the serious pollution industries, particularly about pulp and paper manufacturing plants.

Untreated paper mill effluent discharges cause considerable damage to the receiving waters because they have high biochemical oxygen demand (BOD), chemical oxygen demand (COD), organochlorine compounds, suspended solids (mainly fibres), fatty acids, tannins, resin acids, lignin and its derivatives, sulphur and sulphur compounds [2]. Several organochlorine compounds that are collectively termed as adsorbable organic halides (AOX) are usually biologically persistent, recalcitrant and highly toxic to the environment [4,5]. Among compounds categorised under AOX are chlorophenols, chloroform, chlorate, resin acids, chlorinated hydrocarbons, catechols, guaiacols, furans, dioxins, syringols, vanillins, etc. [5,6]. AOX are among the most dangerous existing compounds because they are resistance to biodegradation and accumulate in the animal fat tissue [5]. Thus, it is necessary to develop a novel approach to meet more stringent environmental regulations for the quality of effluent discharged into water bodies. Until now, the main efforts within the pulp and paper industry to eliminate and control environmental emissions have been focused on controlling AOX emissions and reducing the organic loading discharged into rivers. Due to the severity and the increased awareness of the toxic effects of these pollutants, most European countries, such as Germany, Finland and other Scandinavian countries, have stringent regulations for AOX discharge into the environment that force industry to treat the effluents to the required compliance level not only for the conventional parameters like COD, BOD, and colour, but also for AOX, prior to its discharge into the environment [5,7]. According to PARCOM (Paris Convention for Prevention of Marine Pollution for Land Based Sources and Rivers), 12 European countries agreed to a general AOX emission limit of 1 kg/ton of bleached chemical pulp in 1995. The discharge limits were then gradually lowered to 0.3–0.5 kg/ton [5]. Currently, in Malaysia, there is no regulation on AOX limit because the Environmental Quality Regulation 2009 (Industry Effluents) under Malaysia Environmental Quality Act 1974 (Act 127) still does not address these issues [8].

Wastewater treatments that have effectively removed AOX include coagulation, adsorption, chemical oxidation, ozonation, membrane filtration, anaerobic biological processes, aerobic biological processes and combinations of these [5,9,10]. Recently, aerobic and anaerobic biological treatments of toxic organic compounds have received significant attention. However,

biological treatment systems have been hindered by fluctuations in the influent composition. Disruption of biological activity affects the removal efficiency, and recovery from such disturbances can be extremely slow. Addition of activated carbon (AC) to the biological system has been reported to increase the removal of toxic substances [11,12]. Increased cost effectiveness can be achieved by combining the fill and draw operation of AC filters with continuous biological regeneration that prolongs the operating life of the bed [11]. The use of microorganisms capable of taking up and metabolising pollutants may increase the time period during which the adsorber unit can be kept in service [11]. Thus, per unit of time, less AC has to be thermally regenerated and/or disposed. This concept also avoids the mass transfer limitations of oxygen and substrates and the clogging of the packing caused by excessive growth of the biomass in the inflow section of the reactor [13].

The biological treatment of pulp and paper mill wastewater has often been studied in aerobic reactors that utilise activated carbon to adsorb the toxic pollutants and to act as a carrier for bacterial growth [14–16]. In order to effectively remove these recalcitrant organics from pulp and paper mill wastewater, a combination of biofilm and granular activated carbon (GAC) adsorption is proposed in our study, as was introduced by Irvine and Ketchum [17] and is currently being studied by Muhamad et al. [18]. This promising wastewater treatment technology is referred to as granular activated carbon-sequencing batch biofilm reactor (GAC-SBBR). The process is characterised by a combination of physical and biological removal mechanisms: adsorption onto GAC and biological degradation by microorganisms grown on GAC in the form of a biofilm. Previous publications [15,16,19–24] demonstrate that the GAC-SBBR provides the following advantages:

1. The GAC is very adsorptive and has a very high surface to volume ratio due to its large number of internal pores and rough surface texture, providing a good bacterial immobilisation matrix for the biofilm formation.
2. The less biodegradable organics (mostly chlorinated organics) are adsorbed on the GAC at first, and then slowly degraded by microorganisms. This partially regenerates the activated carbon while the system is in operation, renewing the adsorptive potential.
3. The GAC adsorption process reduces the toxic effects of the pollutants and increases the stability of the system.

The aim of the present work is to evaluate the effect of HRT on AOX and COD removal from treated recycled paper mill effluent in a pilot GAC-SBBR system.

Pentachlorophenol (PCP) was chosen as a model for AOX compounds because it was known to be the most toxic among the chlorinated phenolic AOX in the pulp and paper industry wastewater and is widely used in industries including textile and leather manufacture, and in agriculture as an antiseptic agent [25–27]. Since the COD and PCP concentrations in the treated effluent were very low, the treatment study is a polishing step to further remove any additional COD and PCP. Due to its characteristics, PCP is a good surrogate indicator for other halogenated compounds and it is expected that if a process is able to degrade PCP, it will also be able to degrade other compounds measured as AOX. Some benefits will be gained from this study include a specific treatment can be prescribed by Malaysia guidelines for treatment of AOX in wastewater to achieve the more stringent environmental regulations for the effluent quality discharged into water bodies and discharge limit for AOX can be regulated in Malaysia.

2. Materials and method

2.1. Recycled paper industry wastewater

The wastewater used in the present investigation was recycled paper industry wastewater flowing out of a clarifier tank unit of an existing effluent treatment plant specifically designed and operated for the treatment of recycled paper wastewater. The final discharge from the wastewater treatment system was channelled to the pilot plant as the feed. The detailed characteristics of the treated effluent from the clarifier tank of the recycled paper plant used as feed in this experiment are presented in Table 1. The process flow diagram for the wastewater treatment system of the recycled paper plant is shown in Fig. 1. The plant relies on 100% recycled fibre for the raw material used in paper making and is situated in the western part of Malaysia.

2.2. Reactor configuration

The GAC-biofilm configuration operated in a sequencing batch mode and in an aerobic condition to treat the recycled paper wastewater. The reactor was setup at the recycled paper wastewater treatment plant and made of high density polyethylene (HDPE) with a total working volume of 2.0 m³. The reactor height/internal diameter ratio (H/D) is ~ 1.7 ($H = 2.0$ m and $D = 1.2$ m). A schematic diagram of pilot-scale GAC-SBBR and a complete pilot plant setup at a recycled paper plant are depicted in Fig. 2.

The GAC-SBBR system was divided into three compartments: the GAC compartment and two multi-purpose (MP) compartments. The configuration of the pilot GAC-SBBR followed the down flow mode, where

Table 1
Characterisation of the recycled paper mill wastewater flowing out of the clarifier system

Parameter	Units	Value
pH		7–8
COD	mg COD/L	30–50
SS	mg SS/L	3–10
NH ₃ -N	mg NH ₃ -N/L	0.3–1.0
PO ₄ ³⁻⁻ P	mg PO ₄ ³⁻⁻ P/L	0.003–0.037
PCP	µg PCP/L	42–145

the influent flows countercurrent to the air. The reactor had proper inlet and outlet arrangements. The outlet arrangement properly prevented the loss of biomass in the reactor after the settling phase was over. Air was supplied through air diffuser provided at the intermediate of the reactor (Fig. 2), which resulted an aeration rate of 3.4 m³/min and feed was introduced in down flow mode with the assistance of a three phase ring blower (Hwang Hae, Korea) and a single phase centrifugal pump (LOWARA ITT Industries, Italy), respectively, employing preprogrammed timers. Additionally, air diffusion by the blower was done to ensure efficient mixing. The treated water draw operation was done with the help of gravity. A pH meter (GLI International Model 33, USA) and a DO meter (GLI International Model 33, USA) in the respective GAC compartments were installed in control system (Fig. 2) to monitor the pH and DO values in the biological system.

2.3. Reactor start up and operation procedure

The reactor was inoculated with aerobic biomass acquired from the activated sludge unit treating recycled paper effluents. The mixed liquor from the aeration tank of the mill activated sludge process (ASP) was acquired (MLSS of 4600 mg/L and sludge volume index (SVI) of 191.30 mL/g) and inoculated at a ratio of 1:10 (v/v) to the reactor working volume. Then, the aerobic biomass was acclimated using treated effluent from the clarifier tank of the treatment plant in the reactor. Subsequently, GAC was loaded to the mixed liquor of the reactor (89 g/L of wastewater treated) and fed with the treated effluent to support biomass formation on GAC. After the formation of biomass on GAC (0.0024 g total solids, TS/g GAC) and 350 mg/L of MLSS concentration was achieved, the reactor was operated at an initial HRT of 1 day to assess the performance of system.

The GAC-SBBR was operated in an aerobic condition and packed with GAC from coconut charcoal of

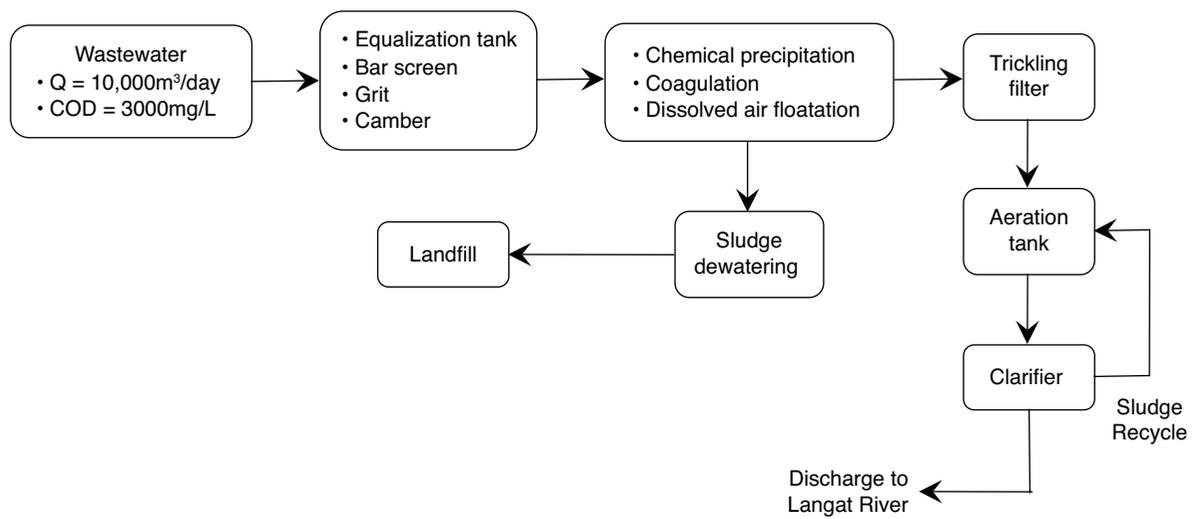


Fig. 1. Process flow diagram of the recycled paper industry wastewater treatment system.

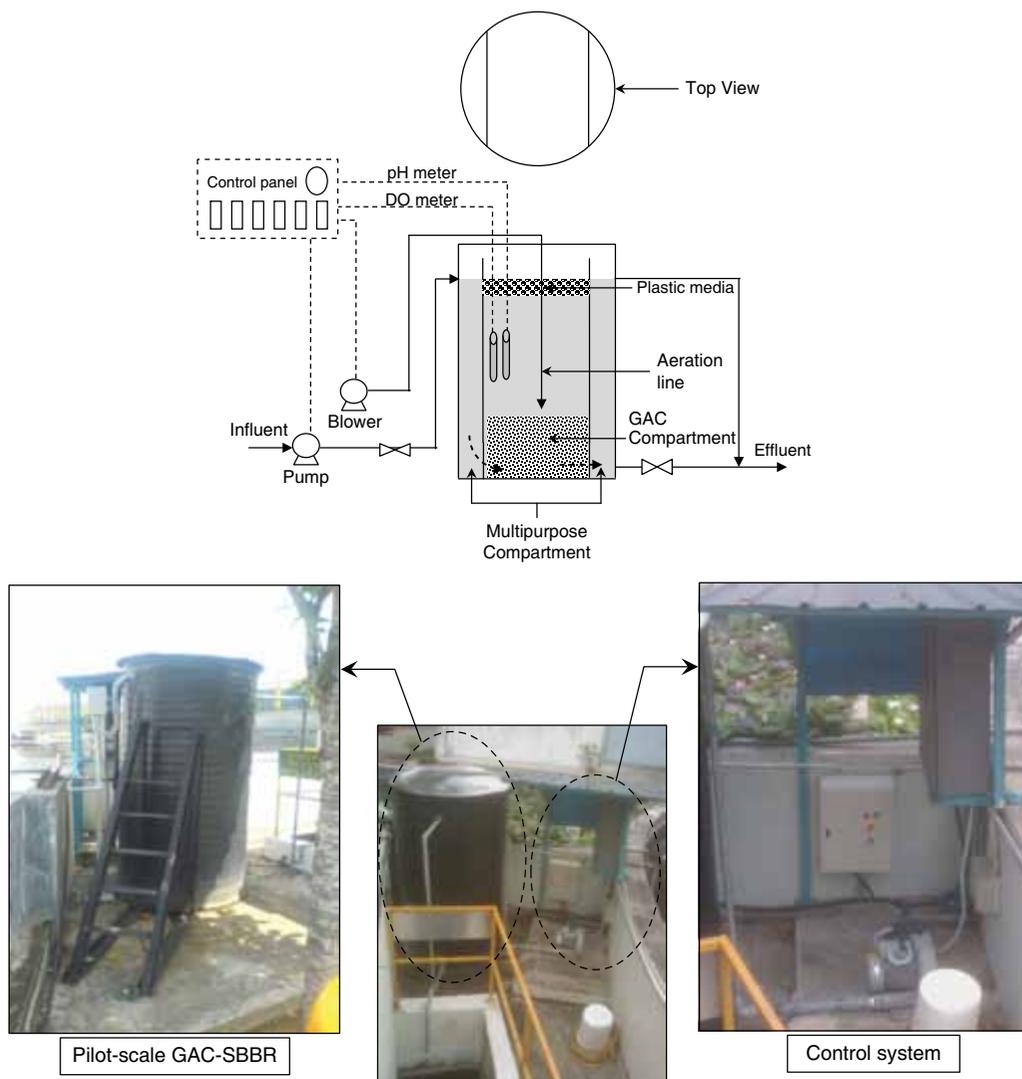


Fig. 2. Pilot-scale GAC-SBBR at a recycled paper plant.

2–3 mm size and 1111 kg/m³ density as fixed bed material for supporting the formation of biofilm. Plastic ball media of 30 mm size (in diameter) and 1087 kg/m³ density was also added to promote bacteria attachment for biofilm growth in the system. The GAC-SBBR system was filled with 0.9 m³ of recycled paper wastewater daily and was operated in a sequence of Fill, React, Settle and Draw. During the Fill and React periods, the influent that flowed underneath from first MP compartment to second MP compartment through the middle of GAC compartment was aerated. The DO concentration maintained in the ranges of 4–6 mg/L during both sequence periods. After the React and Settle periods, the samples

were collected during the Draw periods and analysed for PCP and COD.

The GAC-SBBR system for the study is operated in a batch-wise divided in five operational periods (Table 2). Initially, the system was operated with a HRT of 1 day consisting of 30 min of Fill phase, 21 h of React (aerobic) phase, 2 h of Settle phase and 30 min of Draw phase (Table 2). The HRT study was initiated after the acclimatisation of the biomass on the GAC with the treated effluent as a feed (average influent COD of 40 mg/L). After stable performance was achieved, the reactors were operated at HRTs of 1, 2 and 3 days with average organic loading rates (OLR)

Table 2
Treatment operating conditions of AOX and COD removal

Metabolic function	Operational period (days)	Configuration	HRT (days)	Average influent COD (mg/L)	OLR (kg COD/m ³ .d)	Sequence phase details			
						Phase	Period	Micro-environment	Air supply
Aerobic	0–8	Without GAC (acclimatisation)	1	43 ± 9	0.04	Fill	30 min	Aerobic	On
						React	21 h	Aerobic	On
						Settle	2 h	Anoxic	Off
						Draw	30 min	Anoxic	Off
	9–36	With GAC (acclimatisation)	1	38 ± 5	0.04	Fill	30 min	Aerobic	On
						React	21 h	Aerobic	On
						Settle	2 h	Anoxic	Off
						Draw	30 min	Anoxic	Off
	37–44	With GAC	1	34 ± 3	0.04	Fill	30 min	Aerobic	On
						React	21 h	Aerobic	On
						Settle	2 h	Anoxic	Off
						Draw	30 min	Anoxic	Off
	45–52	With GAC	2	33 ± 3	0.013	Fill	30 min	Aerobic	On
						React	45 h	Aerobic	On
						Settle	2 h	Anoxic	Off
						Draw	30 min	Anoxic	Off
	53–65	With GAC	3	28 ± 4	0.008	Fill	30 min	Aerobic	On
						React	69 h	Aerobic	On
						Settle	2 h	Anoxic	Off
						Draw	30 min	Anoxic	Off

as listed in Table 2, to test the performance of the system for PCP and COD removal. In this experiment, pH was not controlled; it varied between 7 and 8 during a cycle.

The performance of reactor was evaluated by estimating substrate (COD or PCP) removal efficiency of each parameters by comparing the initial substrate (COD or PCP) concentration in the feed with the substrate (COD or PCP) concentration in the reactor outlet.

2.4. Analytical methods

All water samples collected were immediately analysed for COD. For the analysis of PCP, the samples were stored in 1-L plastic bottles and kept at 4 °C before being analysed using HPLC. Whatman type nitrate cellulose membrane filters (0.45 µm) were used for vacuum filtration to separate the suspended particulate matter. Sample COD determinations were made by HACH's COD method using a COD reactor and HACH DR/2000 spectrophotometer. The PCP concentration was determined from a standard curve calibration using HPLC (Agilent 1200 Series, USA) with a Jones Genesis C18 column (250 mm × 4.6 mm, 5 µm) and a UV detector (Agilent 1200 Series, USA) setting at 254 nm. The mobile phases used for HPLC were 0.01 M phosphoric acid (H₃PO₄) and acetonitrile (ACN). The eluent flow rate was 1 mL/min and the column temperature was 35 °C. The chromatography was performed with a gradient from ACN:H₃PO₄ 20:80 to 45:55 in 7.5 min and then to 80% ACN after 2 min. In order to improve the sensitivity of the analysis, the samples were concentrated via solid phase extraction (Jones Chromatography, USA) prior to performing HPLC.

2.5. Statistical analyses

The results were analysed using a one-way analysis of variance (ANOVA) in order to assess whether the applied changes caused distinct effects on the performance of the reactor. Statistical calculations were executed with SPSS software for Windows, version 16.0 (SPSS Inc. USA). Statistical significance was reported at $p < 0.05$ level.

3. Results and discussion

3.1. Start-up of the pilot GAC-SBBR

During reactor start-up (days 0–8), the treated effluent from the clarifier tank was fed into the pilot plant to allow adaptation of the biomass to the environment. All the COD originated from existing organic content in the treated effluent. During the biomass acclimatisation

process, the average COD removal efficiency was about $10.9 \pm 1.6\%$ for a HRT of 1 day. As observed by Oeller et al. [28], the biologically treated effluent contains residual COD loads, which originates from persistent substances in paper mill wastewaters, cannot be further reduced by means of biological process alone. Franta and Wilderer [29] considered that the residual COD, which is defined by concentration of slowly biodegradable and nonbiodegradable organics is mainly made up by remaining lignin. The application of advanced treatment processes are required to meet narrower discharge limit values in the future and to achieve purification levels that enable the effluent to be reused into production [28,30,31].

As can be observed from Fig. 3, after GAC was loaded (after 8 days), the effluent COD decreased sharply to 27 mg/L from an influent of 44 mg/L, resulting in 40% removal. This was due to the adsorption of the COD onto the fresh GAC. However, the removal efficiency of the COD was inconsistent from day to day as the system was not fully acclimatised. To achieve stable treatment, the biomass was acclimated for 1 month before the HRT was varied. Initially, the reactor operated with a HRT of 1 day to test the performance of the biofilter after the formation of the biomass on GAC (0.0024 g TS/g GAC). Further explanation on the biomass acclimatisation process has been reported by Muhamad et al. [18].

3.2. Effect of HRTs on COD and PCP removals

HRT was increased from 1 to 3 days corresponding to a decrease of average OLR from 0.04 to 0.008 kg COD/m³ d. The performance of the reactors for each HRT period is shown in Figs. 3 and 4. The HRT periods (in days) are shown in the figures as boxed sections. As shown in Fig. 3, the HRT of the reactors remained at 1 day between days 37 and 44 and the average OLR was 0.04 kg COD/m³ d. The average COD removal was about $44.0 \pm 4.6\%$ with an initial HRT of 1 day as shown in Table 3. The maximum influent concentrations of COD for all samples were below 50 mg/L and the effluent concentrations were below 27 mg/L.

During days 45–52, the average OLR was decreased to 0.013 kg COD/m³ d by increasing the HRT to 2 days. The average COD concentration in the effluent and the COD removal efficiency stabilised in the range of 18–20 mg/L and 64–67%, respectively (Fig. 3). On day 53, the average OLR was decreased to 0.008 kg COD/m³ d by increasing the HRT to 3 days. A significant improvement in COD removal was observed with the increased contact time. The experimental data indicate that the reactor performance with respect to COD removal was influenced by the HRT. An earlier study by Barr et al. [32] showed that COD removal decreased with decreasing HRT. The statistical analysis using a one-way analysis of

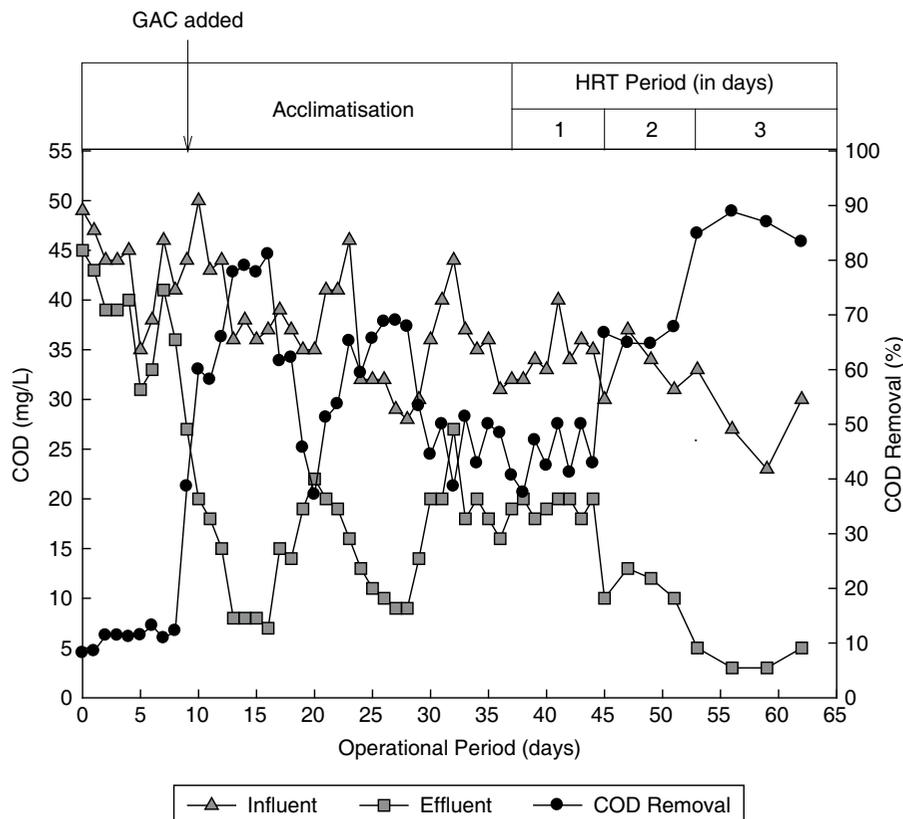


Fig. 3. Variation of influent and effluent COD and COD removal efficiency during acclimatisation and for HRTs 1–3 days.

Table 3
Summary of COD and PCP removal percentages for different HRTs.

Operational period (days)	Configuration	HRT (days)	Removal average (%)	
			COD	PCP
0–8	Without GAC (inconsistent removal efficiency)	1	10.9 ± 1.6	–
9–36	With GAC (inconsistent removal efficiency)	1	58.0 ± 12.8	52.6 ± 13.1
37–44	With GAC	1	44.0 ± 4.6	50.9 ± 3.9
45–52	With GAC	2	66.0 ± 1.5	71.4 ± 4.3
53–65	With GAC	3	86.0 ± 2.4	100

variance (ANOVA) resulted that there was a significant effect of the three levels HRTs on the COD removal with the *F*-ratio of 186.73 ($p < 0.05$).

PCP was chosen as the reference compound for the recalcitrant organics in the wastewater. This compound appears to be very resistant to microbial degradation due to its highly chlorinated organic nature [16]. However, this biocide was removed in the pilot GAC-SBBR. PCP levels were measured after GAC was added to the

system (on day 9). Fig. 4 shows the influent and effluent PCP concentrations during the operational period. The concentration of PCP (Fig. 4) was found to be very low in the influent with a removal percentage in the range of 16–100% after being treated with the pilot GAC-SBBR. The maximum influent PCP concentrations for all samples were below 145 $\mu\text{g/L}$ and the effluent PCP concentrations were below 92 $\mu\text{g/L}$. The lower PCP concentration in the effluent than in the influent indicated that

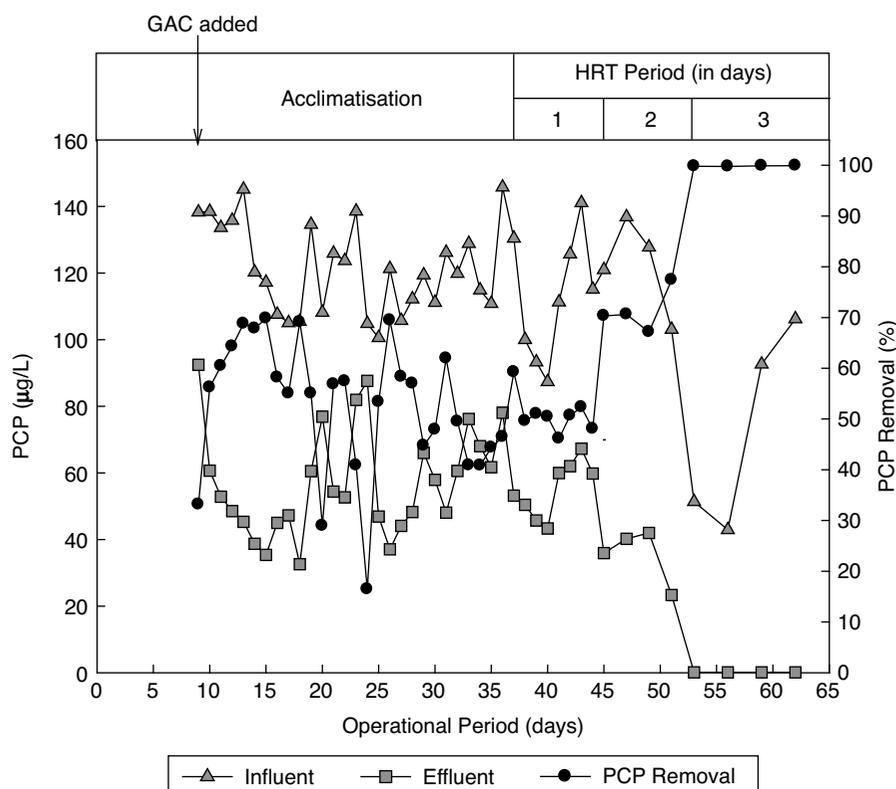


Fig. 4 Variation of influent and effluent PCP and PCP removal efficiency during acclimatisation and for HRTs 1–3 days. PCP levels were measured after GAC was added to the system (on day 9).

a combination of biofilm and GAC in the GAC-SBBR effectively removed the PCP compounds.

After GAC addition (days 9–36), the PCP removal efficiency started to increase due to the adsorption of the PCP onto the fresh GAC and stabilised in the days ahead. As the HRT was increased from 1 to 3 days, the PCP concentration in the treated effluent decreased from 55 to 0 µg/L. From day 53 to 65, it was almost impossible to detect any organics compounds in the effluent. Therefore, the non-readily biodegradable substances (PCP) were essentially adsorbed on the GAC and on the biomass and PCP was possibly biodegraded [33]. It was expected that the more easily degradable substances would allow the biomass to grow and to gain the energy needed to take up and metabolise the non-readily degradable components. The results indicated that the percentage of PCP removal for this process was dependent on the HRT. When the HRT increased, biodegradation improved and the GAC adsorption decreased. Previous work has demonstrated that the adsorptive capacity of GAC will likely decrease with increased usage time in biological activated carbon (BAC) systems due to adsorption of nondegradable compounds in the influent or microbial products produced within the reac-

tor [34,35]. For longer HRTs, the time for the microbes to react with PCP in the reactor increased and there was more biomass to aid in biodegradation. Based on the pilot scale study, the process gave a good removal of PCP, varying in the range of 50–100% and it is expected that the system will also be able to remove other compounds measured as AOX. From our experience, changing HRT from one value to another one will not cause immediate response on COD and PCP removals. Normally, it takes 1–3 days to stabilise. Studies by Barr et al. [32] have confirmed that increased HRT improved the AOX removal and that decreased HRT decreased the toxicity removal. For lower HRTs, a greater proportion of the more recalcitrant compounds likely resist biodegradation. Hall and Randle [36] also have confirmed that an increased HRT improved AOX removal in the optimised activated sludge treatment process. ANOVA tests with data of HRT study showed that there was significant differences for PCP (F -ratio = 260.84) removal in the reactor at three HRTs. A comparison of COD and AOX removal with other biological treatment systems is reported in Table 4. As shown in Table 4, the maximum PCP removal of 100% in this study were achieved at HRT of 72 h indicating that it was almost impossible to detect any PCP

Table 4
Comparative summary of COD and AOX removal according to HRT

Treatment system	Wastewater type	HRT (h)	Removal (%)		References
			COD	AOX	
GAC-SBBR	Recycled paper mill	24–72	44–86	50–100 (specifically PCP)	This study (2011)
Activated sludge	Bleach kraft mill	24–48	60–70	36–40	[37]
Hybrid-loop bioreactor	Sythetic	5–30	78–90	68–99 (specifically TCP)	[38]
Activated sludge	Bleach kraft mill	4.5–48	30–58	–	[40]
Moving bed biofilm reactor (MBBR)	Newsprint mill	4.5	85–95	–	[41]

compounds in the effluent after being treated with the pilot GAC-SBBR. Schnell et al. [37] reported that, at varying HRT of 24–48 h, the COD and AOX removals from bleached kraft mill effluents using activated sludge were in the range of 60–70% and 36–40%, respectively. In another study using Hybrid-loop bioreactor, Eker and Kargi [38] observed that percent 2,4,6-trichlorophenol (TCP) and COD removals increased with increasing HRT resulting in more than 90% COD and TCP removals at HRT values above 25 h. As according to Rao et al. [23], microorganisms assembled in biofilms may be able to metabolise critical substances more effectively than suspended cells. Mohan et al. [39] reported that biofilm configured sequencing batch reactor (SBBR) showed comparatively higher efficiency to the corresponding suspended growth and granular activated carbon (GAC) configured systems studied with similar wastewater. They had found that biofilm configured system coupled with periodic discontinuous batch mode resulted in a more even distribution of the biomass throughout the reactor and imposed regular variations in the substrate concentration on biofilm organisms.

4. Conclusions

The results of this study showed that recycled paper industry wastewater could be treated effectively by a pilot GAC-SBBR system at HRTs between 1 and 3 days. PCP removal efficiencies increased from $50.9 \pm 3.9\%$ to 100% and COD removal efficiencies increased from $44.0 \pm 4.6\%$ to $86.0 \pm 2.4\%$ as HRT was increased from 1 to 3 days at optimum pH of 7–8 and DO of 4–6 mg/L. Based on this pilot study, the GAC-SBBR process is applicable for the post-treatment of treated recycled paper industry effluents to remove COD and PCP and it is expected that the system will also be able to degrade

other compounds measured as AOX. The GAC-SBBR treatment of recycled paper mill wastewater is an alternative for the downstream biodegradation of recalcitrant AOX, particularly PCP, prior to its discharge into the drinking waterways of the country.

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