# Journal of Applied Sciences

ISSN 1812-5654

Journal of Applied Sciences 11 (13): 2388-2393, 2011
ISSN 1812-5654 / DOI: 10.3923/jas.2011.2388.2393


# Treatment of Adsorbable Organic Halides from Recycled Paper Industry Wastewater using a GAC-SBBR Pilot Plant System

M.H. Muhamad, S.R.S. Abdullah, A.B. Mohamad, R.A. Rahman and A.A.H. Khadum
Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment,
Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Malaysia

**Abstract:** Wastewater originating from recycled paper industry is known to be potentially toxic/inhibitory. Adsorbable Organic Halides (AOX) are among the toxic constituents generated from the recycled paper industry. The problems associated with AOX in the environment are their accumulation in the food chain and their persistence in nature. Hence, it is imperative to improve the effluent quality emanating from the recycled paper industry in order to meet the future discharge limits. One the plausible treatment technique is the use of the Sequencing Batch Biofilm Reactor (SBBR) with an option for Granular Activated Carbon (GAC) dosing. Pilot scale reactor based on combined physical-biological treatment of this GAC-SBBR system has been fabricated and evaluated for performance in the treatment of effluent from a recycled paper mill. The pilot GAC-SBBR was constructed in Muda Recycled Paper Mill located in Kajang, Selangor. It comprises of a High-density Polyethylene (HDPE) biofilm reactor with a diameter of 1.2 m, maximum water depth of 1.8 m and packed with 200 g $L^{-1}$ of 2-3 mm granular activated carbon (coconut shells). The entire plant set-up was successfully commissioned. As a first step in the design procedure, a pilot test was run for a period of 2 months which include biomass acclimatization process for 1 month. Preliminary results showed that the GAC-SBBR could be an appropriate technology for the treatment of the wastewater. Based on reactor operation, the removal efficiencies of Pentachlorophenol (PCP) from the treated effluent was in the range between 82-100%, while the COD removal efficiency was between 39-81%. The initial results of pilot scale showed that the biofilm attached onto granular activated carbon can substantially remove the PCP recalcitrant in the wastewater. This research uses PCP as a model for AOX compound to study the adsorption and biodegradation of PCP in pilot plant biofilm reactor system.

**Key words:** Pilot plant GAC-SBBR, adsorbable organic halides (AOX), recycled paper industry, pentachlorophenol

## INTRODUCTION

With the development of industrial economy and the increase in world population, enormous amounts of paper have been consumed causing large quantities of wastewater to be discharged by paper mills in natural water receptors thus affecting the ecological balance and causing aesthetic concerns. This kind of paper mill wastewater, containing many toxic and intensely colored, mainly organic substances, is characterized by high level of Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), chlorinated compounds (measured as Adsorbable Organic Halides AOX), suspended solids (mainly fibres), fatty acids, tannins, resin acids, lignin and its derivatives, sulphur and sulphur compounds, etc. (Ali and Sreekrishnan, 2001). AOX are among the most dangerous existing compounds as they are hardly biodegradable and accumulate in the fat tissue of animals (Savant *et al*., 2006). Thus, it is necessary to develop a novel approach to face more stringent environmental regulations on the quality of effluent discharged into the water bodies. Till now, the main efforts within the pulp and paper industry to eliminate and control environmental emissions were directed at control of AOX emission and reduction of organic loading discharged into rivers. Due to the severity of these toxic effects, most European countries, such as, Germany, Finland and other Scandinavian countries have set limit values of AOX in their respective environmental legislations (Muhamad *et al*., 2008; Savant *et al*., 2006). According to

**Corresponding Author:** M.H. Muhamad, Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Malaysia

PARCOM (Paris Convention for Prevention of Marine Pollution for Land Based Sources and Rivers), twelveEuropean countries have signed for a general AOX emission limit of 1 kg $ton^{-1}$ for bleached chemical pulp in 1995. The discharge limits were then lowered gradually up to 0.3-0.5 kg $ton^{-1}$.

The conventional adsorption technique using Activated Carbon (AC) source, as final treatment is indispensable for removal these recalcitrant organics from pulp and paper mill wastewater. Essentially, the conventional adsorption technique has the disadvantages of inadequate exploitation of the adsorptive capacity, high cost of conventional thermal or chemical regeneration process for spented AC and decreasing adsorptive capacity of the AC, the ultimate disposal problem and toxic products such as chlorodibezodioxins might be generated in the thermal oxidation. As a consequence of continuous flow operation, the driving force of the adsorption process is low and only a limited fraction of the AC capacity can be exploited for sorptive removal of wastewater components (Kolb and Wilderer, 1997; Jaar and Wilderer, 1992). In comparison, the periodic operation mode of AC filters provides a significant potential for higher exploitation of the adsorptive capacity of the AC and may decrease substantially the total operating costs. A further increase of cost effectiveness can be achieved, when the fill and draw operation of AC filters is combined with continuous biological regeneration which prolongs the operating life of the bed. Involvement of microorganisms capable of taking up and metabolizing pollutants may increase the time period during which the adsorber unit can be kept in service. Thus, per unit of time less AC has to be thermally regenerated and/or disposed. This concept is also one way to avoid mass transfer limitations for oxygen and substrates; and clogging of the packing caused by excessive growth of biomass in the inflow section of the reactor (Kaballo, 1997).

In order to effectively remove these recalcitrant organics from pulp and paper wastewater, combination between biofilm and Granular Activated Carbon (GAC) adsorption were proposed in our study as was introduced by Irvine and Ketchum (1989) and currently studied by Mohamad *et al.* (2008). This promising wastewater treatment technology was referred to as Granular Activated Carbon Sequencing Batch Biofilm Reactor (GAC-SBBR) where the process is characterized by a combination of physical and biological removal mechanism; adsorption onto GAC and biological degradation by microorganisms grown on GAC in the form of biofilm. GAC as adsorptive medium/carrier materials acts as buffer to reduce the concentration of toxic chemicals during process operation, thereby providing advantage for the treatment of low biodegradable industrial wastewater containing recalcitrant compounds such as AOX (Ong *et al.*, 2008; Rao *et al.*, 2005; Leenen *et al.*, 1996). The biological activity on the activated carbon plays the major role in removing pollutants from water and wastewater. This effect arises from the fact that pollutants present in wastewater are adsorbed on the biofilm coated activated carbon where they are biodegraded by the microbial community present in the biofilm. Several studies on the biological activity on activated carbon in water and wastewater treatment have been carried out (Mohamad *et al.*, 2008; Rahman *et al.*, 2007, 2004; Shim *et al.*, 2004; Wilderer *et al.*, 2000). These studies indicated that biological growth onto activated carbon has advantages in organic and nutrients removal.

The aim of this research is to investigate the effectiveness of the pilot GAC-SBBR with 2.0 $m^3$ effective capacity for the removal of chlorinated AOX and COD from recycled paper mill effluent. Besides, several characteristics PCP in paper mill treated effluent were also determined in this system set-up.

## MATERIALS AND METHODS

**Recycled paper mill wastewater:** Recycled paper mill wastewater effluent was used as the feed to the reactor. The wastewater was channeled to the reactor from clarifier tank (final discharge) of the existing effluent treatment plant specifically designed and operated for the treatment of recycled paper wastewater. The process flow wastewater treatment system of this plant is as shown in Fig. 1. The typical detailed characteristics (in average values) of the wastewater were presented in Table 1.

**Reactor configuration:** GAC-biofilm configuration operated in a sequencing batch mode in an aerobic condition was studied for the treatment of recycled paper wastewater. The reactor was setup at Muda recycled paper mill and fabricated using HDPE with a total working volume of 2.0 $m^3$ capacity. The reactor ratio of height/internal diameter (H/i.d) is~1.7 (H: 2.0 m and i.d.: 1.2 m). Schematic detail of the reactor along with the experimental setup is depicted in Fig. 2.

The GAC-SBBR system was divided into three compartments, namely GAC compartment and two of

Table 1: Typical characteristics of recycled paper wastewater used as feed for the pilot plant

| Parameters | Concentration |
|---|---|
| Dissolved oxygen (mg $L^{-1}$) | 4.8 |
| pH | 7.2 |
| SS (mg $L^{-1}$) | 8.0 |
| COD (mg $L^{-1}$) | 40.0 |
| AOX (μg $L^{-1}$) | 2.0 |

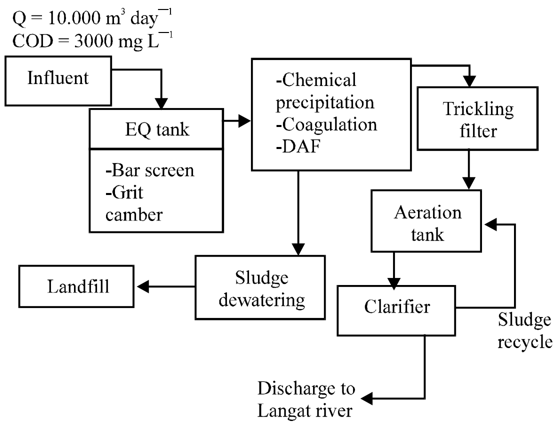


Fig. 1: Muda paper mill wastewater treatment system process flow

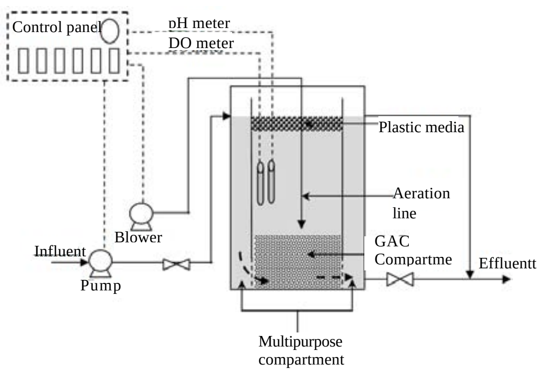


Fig. 2: Schematic diagram of pilot-scale GAC-SBBR at muda paper mill industry, kajang

Multipurpose (MP) compartments. The configuration of the pilot plant GAC-SBBR follows down flow mode, where the influent flows countercurrent to air. The reactor is fabricated with a proper inlet and outlet arrangement. The outlet arrangement was fabricated properly to prevent the loss of biomass in the reactor after the settling phase is over. Filling (down flow mode) and air sparging (up flow mode) operations were done with the assistance of single phase centrifugal pump (Hwang Hae, Korea) and three phase ring blower, (LOWARA ITT Industries, Italy), respectively, employing preprogrammed timers. The treated water draw operation was done with the help of gravity. A pH meter and a DO meter in respective GAC compartments provide efficient mixing by air sparging were installed to monitor the pH and DO values in the biological system.

**Start up:** The reactor was inoculated with aerobic biomass acquired from the activated sludge unit treating recycled paper effluents. The mixed liquor from aeration tank of Activated Sludge Process (ASP) was acquired (MLSS of 4600 mg $L^{-1}$ and SVI of 191.30 mL $g^{-1}$) and inoculated at a ratio of 1: 10 (v/v) with reactor working volume. Then, the aerobic biomass was acclimated by treated effluent from clarifier tank of the existing effluent treatment plant in the reactor for 1 month. Subsequently, GAC was loaded to the mixed liquor of the reactor (160g $L^{-1}$ of the wastewater treated) and fed with the treated effluent to support biomass formation on GAC. After the formation of biomass on GAC (0.0024 g TS g GAC), the reactor was operated at initial HRT of 24 h for the performance of biofilter.

Table 2: HPLC analysis conditions

| Column | Zorbax SB-C18 column (250 mm×4.6 mm, 5 μm) |
|---|---|
| Mobile phase | 20% ACN/80% 0.01M $H_3PO_4$ to 45% ACN in 7.5 min |
| Gradient | 80% ACN in 2.0 min |
| Flow rate | 1 mL $min^{-1}$ |
| Temperature | 35°C |
| Detection | 254 nm |

**Operation procedure:** Initially, the study was conducted employing a GAC-SBBR, containing 1.0 $m^3$ working volume, operated in aerobic condition and packed with 200 g $L^{-1}$ of 2-3 mm granular activated carbon (coconut shells) as a medium for biofilm growth. Additionally, plastic ball media are also added as bacteria attachment for biofilm growth in the system. The GAC-SBBR system was filled with 0.5 $m^3$ of recycled paper wastewater daily and was operated in FILL, REACT, SETTLE and DRAW periods in the time ratio of 0.5:21:2:0.5 for a cycle time of 24 h. During FILL and REACT periods, the influent which flows underneath from first MP compartment to second MP compartment through the middle of GAC compartment will be aerated. After the REACT and SETTLE periods, sample was collected during DRAW periods and analyzed for AOX, COD, SS and total biomass concentrations.

**Analytical methods:** All water samples collected were immediately analyzed. The samples were stored in 1L plastic bottle and kept at 4°C. Whatman type nylon membrane filters (0.45 μm) were used for vacuum filtration process to separate the suspended particulate matter. The PCP concentration was determined from the standard curve calibration using a HPLC analytical method with UV detector (Agilent Series 1100, USA) at operating conditions as listed in Table 2. In order to improve the sensitivity of the analysis, the samples were concentrated via Solid Phase Extraction (SPE) method prior to injecting in HPLC. The Chemical Oxygen Demand (COD) and Suspended Solid (SS) were determined according to HACH Reactor Digestion Method (EPA approved) and

Standard Method, respectively. Total biomass concentration in the reactor was measured via NaOH digestion (Koch *et al*., 1991).

## RESULTS AND DISCUSSION

**Treatment performance of pilot GAC-SBBR system:** This study was carried out by using recycled paper wastewater from Muda paper mill treated effluent. For the first month, the biomass required adaptation to the environment. This was performed by feeding the treated effluent from clarifier tank of the existing effluent into the pilot plant. All the COD (organic) was contributed by existing organic in the treated effluent. During the biomass acclimatization process, the COD removal efficiencies (within the first month of the experiment) were very low since no external carbon source was added into the feed as shown in Fig. 3.

After GAC was loaded (after 33 days), the effluent COD decreased sharply below 7 mg $L^{-1}$. However, the removal efficiency of the COD showed inconsistent removal from day to day as the system has not been fully acclimatized. Initially, the reactor was operated with HRT of 24 h to test for the performance of biofilter after the formation of biomass on GAC (0.0024 g TS/g GAC). As shown in Fig. 3, the average COD removal by GAC-SBBR system (after the acclimatization process) about 62% with initial HRT of 24 h, which indicated the effectiveness of the pilot GAC-SBBR system in the mineralization of AOX containing wastewater. The maximum influent concentrations of COD for all samples were below 50 mg $L^{-1}$ while the effluent concentrations were below 27 mg $L^{-1}$. In the second month of operation, poor performance observed was attributed in part to the startup and the time taken to develop an active biofilm on the GAC. Earlier study by Barr *et al.* (1996), showed that COD removal decreased with the decrease in the HRT. It was also observed that at the initial stage of the study (within the first 20 days), the COD removal was higher even though the biomass concentration was below 2000 mg $L^{-1}$. This was due to the adsorption of the COD onto the fresh GAC. Hence the optimization of HRT will need to be conducted to evaluate the performance of biofilter at a shorter HRT for this system. Later, this reactor will be adjusted to longer HRT of 48 h to study the performance of biofilter.

CP compound has been taken as the reference compound for the recalcitrant organic in the wastewater. This compound appears to be very resistant to microbial degradation due to its highly chlorinated organic nature. However, the ability to degrade this biocide has been demonstrated in the pilot GAC-SBBR. Figure 4 shows the influent and effluent of PCP concentrations for HRT of 24 in the pilot GAC-SBBR system during operation at the Organic Loading Rate (OLR) of 0.0171 kg $m^{-3}$.d for 42 days.

The concentration of PCP (Fig. 4) was found to be very low in influent with percentage removal in the range of between of 82-100% after treatment with the pilot GAC-SBBR. The maximum influent concentrations of PCP for all samples were below 3.40 μg $L^{-1}$ while the effluent PCP were below 0.23 μg $L^{-1}$. Barr *et al.* (1996) has confirmed the earlier presumption that an increased HRT could improve AOX removal and decreasing HRTs resulted in a decrease in the toxicity removal. It is likely that, as HRT decreases, a greater proportion of the more recalcitrant compound will resist to biodegradation. Lower PCP concentration in the effluent than influent indicated that microorganism in the GAC-SBBR might have degraded the PCP compound. At the initial stage of this

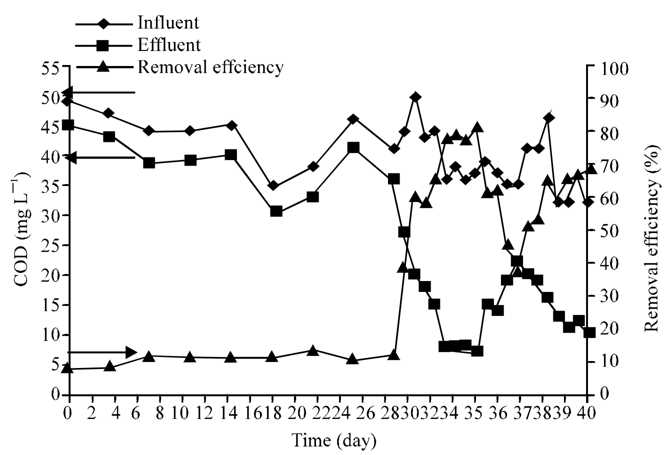


Fig. 3: Influent and effluent concentrations of COD and percentage of COD removal

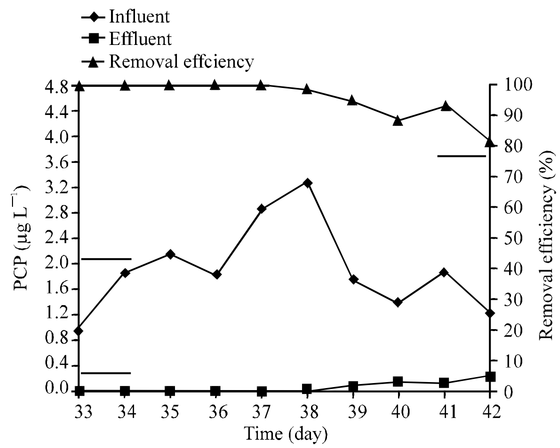


Fig. 4: Pentachlorophenol influent and effluent concentrations and percentage removal

study (on day 4), 100% of PCP removal was achieved which was probably due to adsorption process by GAC and the efficiency starts to reduce and stabilize in the days ahead. For the later period, the reductive dechlorination process pathway might be carried out by the microorganisms in the reactor through the conversion of the PCP to lesser chlorinated compounds (chlorophenol, dichlorophenol and phenol) as well as $CO_2$ gas based on previous results on AOX removal (Mohamad *et al*., 2008; Rahman *et al*., 2004). 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 usually less toxic and are more readily degraded either anaerobically or aerobically (Tsuno *et al*., 1996; Mikesell and Boyd, 1986). Hence, it is an added advantage for this GAC-SBBR pilot plant system to be able to obtain the complete dechlorination and mineralization of the PCP should it undergo this reductive dechlorination process.

## CONCLUSION

Based on this preliminary pilot study the GAC-SBBR process has shown to be potentially applicable for the treatment of wastewater from recycled paper industry for the removal of COD and AOX. The initial results of this study has reaffirmed the fact that the GAC-SBBR treatment of recycled paper mill effluents pilot plant process can be considered as an alternative option for downstream biodegradation of AOX recalcitrant, particularly PCP, before being discharged into the drinking waterways of the country. Further studies on acclimatization are being conducted with variable HRTs, in addition to efficiencies of AOX and PCP removals at workable OLR.

## ACKNOWLEDGMENTS

The authors gratefully acknowledge the Swedish International Development Agency (SIDA-ARRPET II programme) and UKM Fundamental Research Grant Scheme (UKM-KK-02-FRGS 0003-2006) for providing the financial support of this research project.

## REFERENCES

Ali, M. and T.R. Sreekrishnan, 2001. Aquatic toxicity from pulp and paper mill effluents: A review. Adv. Environ. Res., 5: 175-196.

Barr, T.A., J.M. Taylor and S.J.B. Duff, 1996. Effect of HRT, BRT and temperature on the performance of activated sludge reactors treating bleached Kraft mill effluent. Water Res., 30: 799-810.

Irvine, R.L. and L.H.J. Ketchum, 1989. Sequencing batch reactors for biological wastewater treatment. CRC Crit. Rev. Environ. Control, 18: 255-294.

Jaar, M.A.A. and P.A. Wilderer, 1992. Granular activated carbon sequencing batch biofilm reactor to treat problematic wastewaters. Water Sci. Technol., 26: 1195-1203.

Kaballo, H.P., 1997. Shock loading management with the sequencing batch biofilm reactor technology. Water Sci. Technol., 35: 35-40.

Koch, B., M. Ostermann, H. Hoke and D.C. Hempel, 1991. Sand and activated carbon as biofilm carriers for microbial degradation of phenols and nitrogen-containing aromatic compounds. Water Res., 25: 1-8.

Kolb, F.R. and P.A. Wilderer, 1997. Activated carbon sequencing batch biofilm reactor to treat industrial wastewater. Water Sci. Technol., 35: 169-176.

Leenen, E.J.T.M., V.A. P.D. Santos, K.C. F. Grolle, J. Tramper and R. Wijffels, 1996. Characteristics of and selection criteria for support materials for cell immobilization in wastewater treatment. Water Res., 30: 2985-2996.

Mikesell, M.D. and S.A. Boyd, 1986. Complete reductive dechlorination and mineralization of pentachlorophenol by anaerobic microorganisms. Applied Environ. Microbiol., 52: 861-865.

Mohamad, A.B., R.A. Rahman, A.A.H. Kadhum, S.R.S. Abdullah, Z.W. Sudin and S. Shaari, 2008. Removal of adsorbable organic halides (AOX) from recycled pulp and paper (P and P) mill effluent using Granular Activated Carbon-Sequencing Batch Biofilm Reactor (GAC-SBBR). Mod. Applied Sci., 2: 37-45.

Muhamad, M.H., S.R.S. Abdullah, A.B. Mohamad, R.A. Rahman, A.A.H. Kadhum and T.T. Hui, 2008. Determination of chlorinated adsorbable organic halides in Sg. Langat, Selangor. Proceedings of International Conference and Expo on Environmental Management and Technologies, PWTC, Kuala Lumpur, Malaysia.

Ong, S.A., E. Toorisaka, M. Hirata and T. Hano, 2008. Granular activated carbon-biofilm configured sequencing batch reactor treatment of C.I. acid orange 7. Dyes Pigments, 76: 142-146.

Rahman, R.A., A.Y. Zahrim and A. Abu Bakar, 2007. Chloro-organics in papermill effluent: Identification and removal by sequencing batch biofilm reactor. J. Applied Sci., 7: 2160-2163.

Rahman, R.A., H. Tsuno and K.M. Chea, 2004. Recalcitrant organics in river water treatment. Proceedings of the 2nd Seminar on Water and Wastewater Management and Technologies, Dec. 6-7, JSPS-VCC Core University Program, Kyoto University, Kyoto, Japan, pp: 31-38.

Rao, N.C., S.V. Mohan, P. Muralikrishna and P.N. Sarma, 2005. Treatment of composite chemical wastewater by aerobic GAC-biofilm sequencing batch reactor (SBGR). J. Hazard. Mater., 124: 59-67.

Savant, D.V., R. Abdul-Rahman and D.R. Ranade, 2006. Anaerobic degradation of adsorbable organic halides (AOX) from pulp and paper industry wastewater. Bioresour. Technol., 97: 1092-1104.

Shim, W.G., D.S. Chaudhary, S. Vigneswaran, H.H. Ngo, J.W. Lee and H. Moon, 2004. Mathematical modeling of Granular Activated Carbon (GAC) biofiltration system. Korean J. Chem. Eng., 21: 212-220.

Tsuno, H., M. Kawamura and I. Somiya, 1996. Anaerobic degradation of pentachlorophenol (PCP) in biological expanded-bed reactor. Water Sci. Technol., 34: 335-344.

Wilderer, P.A., P. Arnz and E. Arnold, 2000. Application of biofilms and biofilm support materials as a temporary sink and source. Water Air Soil Pollut., 123: 147-158.