[ENV01] Recalcitrant organics removal using adsorption and biofilm process

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Introduction

Recalcitrant organics compounds is one of the harden problem faced by the wastewater treatment engineer because of these compounds are hard to treat and can passed through the conventional WWTP. Some of the recalcitrant organics, such as pentachlorophenol had found toxicgenic and carcinogenic to human and animals. The carbon adsorption was one of the common conventional methods for removing of these compounds. However, the treatment does not destroy these recalcitrant organics but just merely transferring it to another medium. When the activated carbon is exhausted, the regenerating process (thermal or chemical regeneration) was applied for recycling the carbon. The regenerating process was costly and the toxic byproduct may also produce in the regeneration processes. In recent years, the idea of regenerating of these GAC via biodegradation of adsorbed organics appear attractive to reduce the cost of activated carbon as well as to destroy toxic organics. "Granular Activated Carbon Sequencing Batch Biofilm Reactor" (GAC-SBBR) is one of the combine technologies of adsorption and biofilm process. This technology was introduced by Irvine and developed by Wilderer, (Jaar, M.A.A. and Wilderer, P.A. 1992). It is a discontinuous process where the sequencing batch reactor (SBR) packed with GAC and the microorganisms grow in the reactor in the form of biofilm. Even the GAC-SBBR has been long time introduced, but the researches on this system for the treatment of recalcitrant organic were rare. To understand the mechanism and effectiveness of the GAC-SBBR process, it is essential to identify the characteristic of carbon adsorption and activity of microorganisms. Knowledge of these characteristics is an important factor in determining the parameters for operational control of the system. In this study, the GAC-SBBR was conducted and the characteristics of the processes in removing the recalcitrant organic compound were investigated. Pentachlorophenol (PCP) had been chosen as a representative recalcitrant compound because it is commonly found in industrial effluents especially those from pulp and paper mill and wood preservation industries.

Methodology

GAC-SBBR.

The GAC-SBBR has been conducted to observe the treatability and kinetic for the combined adsorption and biofilm process. The reactor was a glass reactor with a working volume of 1.0 liter operated at room temperature (25 ± 2 ^{o}C) and packed with 200g/l of 2-3mm granular activated carbon (GAC) as a medium for biofilm growth. The acclimatized sludge originated from the pulp and paper mill wastewater treatment plant was seeded in the GAC-SBBR and 1 liter of simulated wastewater as tabulated in Table 1 were fed to the reactors at different HRT. PCP concentrations in the Influent and effluent were monitored and analysis with the UV-Vis Spectrophotometer or high performance liquid chromatography (HPLC).

TABLE 1 Composition of simulated wastewater

Component	Concentration (mg/L)
Pentachlorophenol (PCP)	100
Nutrient salt	
- KH_2PO_4	2000
- $NaNO_3$	1000
- $MgSO_4.7H_2O$	100
- $CaCl_2.2H_2O$	10
- $FeSO_4.H_2O$	5
- $MnCl_2.4H_2O$	3.5
- $NaEDTA.2H_2O$	2
*NaOH 5 Molar (adjust the pH to ~7.0)	*5-10mL

PCP Analysis

The PCP concentrations along the experiment period were monitored with the UV-Vis Spectrophotometer (Shitmatzu Co.) by measuring the UV-Vis absorbance at 320nm and using the PCP-ABS standard curve. In the experiment's final stage, the samples GAC-SBBR were analyzed with HPLC. The HPLC was equipped with Zorbax

SB-C18 column (150mm x 4.6mm, 5µm). The solvents used in the analysis were 20% Aceton Nitril (ACN) and 80% 0.01M H_3PO_4. The HPLC was operated with solvent gradient of 80% ACN in 2.0 min and UV detection at 254nm. For improving the selectivity, the GAC-SBBR analysis samples were concentrated by the solid phase extraction (SPE) before inject for analysis. 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 minutes, respectively.

Microorganisms and Microbe Analysis

The mixed culture microorganisms were obtained from the wastewater treatment plant of Sabah Forest pulp and paper mill Co. in Sabah, Malaysia. The microbe were gradually acclimating to PCP as a sole source of carbon and then seeded inside the GAC-SBBR to form a combined biofilm and adsorption system. After the treatbility and kinetic study, the microbe analysis was done to identify the present microorganisms' spesies inside the reactor. Some sludge from the acclimatized GAC-SBBR were taken and spread on the agar plates. Then, the colonies growing on the agar were subsequently sub cultured and resulting in isolated pure culture. Gram staining was carried out to identify the bacteria's gram. API-20E kit (BioMérieux) and biolog system was used to identify the gram-negative bacterial isolates and gram-positive bacterial isolates, respectively.

Kinetic for the overall process

Refer to the figure 1 and applying the overall mass balance on the system, the kinetic equation for the overall process can be express as below:

$$Q(S_o - S_e)\Delta t - \{QXq_b\}\Delta t - \{QCq_c\}\Delta t = \Delta E - V\{\Delta S_e + \Delta X q_b + X\Delta q_b + \Delta C_c q_c + C_c \Delta q_c\} \quad (1.1)$$

The adsorption studies were carried out to obtain the GAC adsorption and biosorption isotherm (or q_b and q_c). After that, the amount of PCP biodegradation by microbe, ΔE were calculated from the equation and the percentage of PCP removal taken by each individual processes (adsorption, biosorption and biodegradation) in GAC-SBBR at different HRT were found.

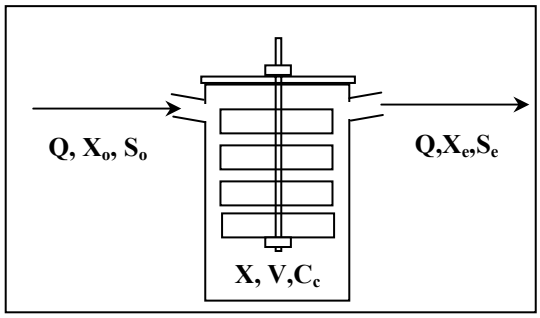

FIGURE 1 Material Flow Diagram for GAC-SBBR

Kinetic for the microbial growth

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

$$V\frac{dX}{dt} = (QX_o) + (\mu XV) - (b_H XV) - (QX_e) \quad (1.2)$$

$$\frac{dS}{dt} = \frac{Q(S_o - S_e)}{V} - \left(\frac{X}{Y_H}\right)\left(b_H + \frac{1}{\Theta}\right) \quad (1.3)$$

Solve these equations at the steady state and used the Graph method, the growth kinetic parameters for theY_H, b_H, μ_h and K_s were found.

Result and dicussion

Treatability studies

Figure 2 was the percent removal of PCP by the GAC-SBBR compared with the suspended growth SBR in the treatability study. The result has shown that the GAC-SBBR system has a high PCP removal efficiency than the suspended growth SBR. Beside, the study also revealed that the GAC-SBBR system can well withstands the PCP shock loadings.

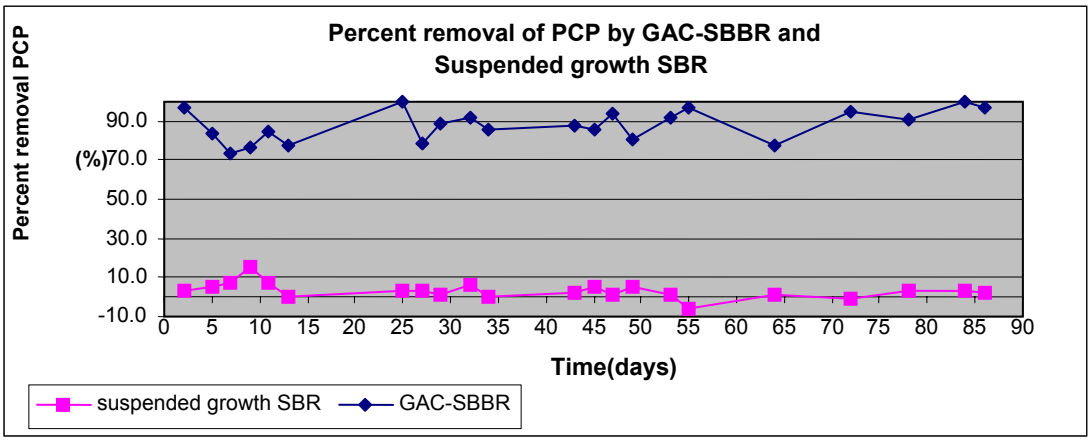

FIGURE 2 Percent removal of PCP by GAC-SBBR and Suspended growth SBR

After the three month of continuous operation, it had found that the system still can maintain approximately 90% of its PCP removal efficiency. The high removal efficiency and the good stability of GAC-SBBR was due to GAC has a large number of internal pores and rough surface texture that can be a good bacterial immobilization matrix to form the biofilm. The recalcitrant organics can be adsorbed on the GAC at first, and are then slowly degraded by microorganisms. This can partially regenerate the activated carbon while the system is in operation. Beside, the GAC adsorption process also can reduce the toxic effects of the pollutants and increase the stability of the GAC-SBBR system (Xiaojian et al., 1991; Caldeira et al., 1999; Jaar and Wilderer, 1992).

To testify the treatability of GAC-SBBR on real industrial wastewater, secondary effluent from the paper mill factory was taken, analysis and treated by the GAC-SBBR. Figure 3 showed the HPLC chromatograms for the GAC-SBBR's influent and effluent. The chlorophenol compounds (monochlorophenol, Dichlorophenol, Trichlorophenol and pentachlorophenol) have been taken as the reference compounds for the recalcitrant organic in the wastewater. From the PCP standard curve calculation, approximately 70% of PCP in the wastewater could be removed by GAC-SBBR system within one-day time. These have shown the potential of application of combination of biofilm and adsorption system in real industrial application for the treatment of high-strength wastewater polluted by recalcitrant organic compounds.

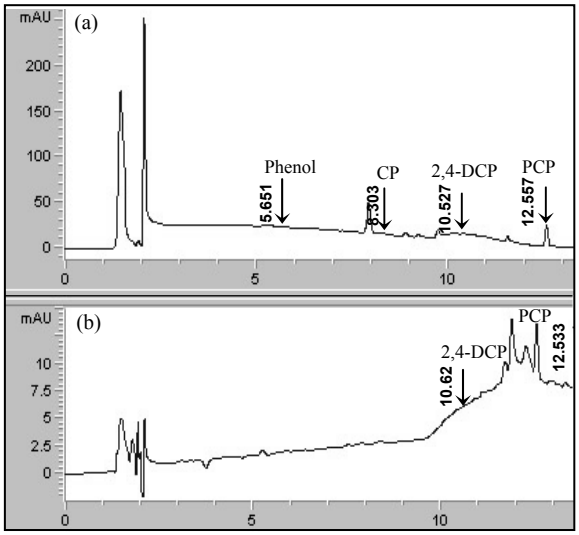

FIGURE 3 HPLC chromatograms for GAC-SBBR's (a) influent and (b) effluent.

Kinetic Process

The experiment data obtained for the equilibrium adsorption of PCP onto GAC and biomass was fitted to six possible models to determine the best isotherm model described the adsorption or biosorption system. Freudlich isotherm was found to be the most convenient model to describe the adsorption and biosorption systems. The Freudlich Isotherm for the GAC adsorption and biosorption systems was as shown in equation (2) and (3), respectively. : -

$$q_c = \frac{X}{M}(mg/g) = 52.79C_e^{0.3862} \qquad (1.4)$$

$$q_b = \frac{X}{M_B}(mgPCP/gBiomass) = 1.19C_e^{0.56} \qquad (1.5)$$

Substituted the q_c and q_b into the equation (1) and calculation using the data obtained in the experiment, the percentage of PCP removal taken by each individual processes (adsorption, biosorption and biodegradation) in GAC-SBBR system were found as shown in figure 4.

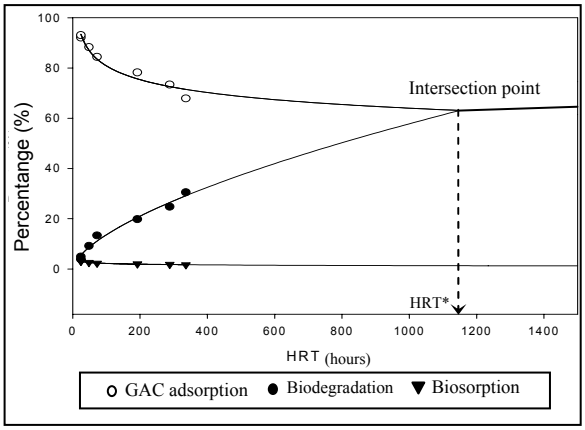

FIGURE 4 The percentage of PCP removal taken by adsorption, biosorption and biodegradation in GAC-SBBR system

Result of the calculation had showed that the percentage of PCP removal taken by each individual processes (adsorption, biosorption and biodegradation) in GAC-SBBR system is related to the system's HRT. Biodegradation and adsorption were the major mechanisms for removing the PCP inside the system compared with biosorption. Extrapolating the graph lines for biodegradation and GAC adsorption have found their intersection point at 47 days. This was the ideal HRT operation where adsorption and biodegradation stay in the equilibrium state. However, the long resident time seem not very realistic for the industrial operation, it can be reduce by replacing the GAC in the system.

Growth kinetic

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 GAC-SBBR were founded by plotting the graph $(S_o-S_e)/(f_A.X_T.\tau)$ Vs $1/\Theta_c$ and Hane plot (graph $S_S/(1/\Theta_c+b_H)$ Vs Ss) (data not shown). The results of the growth kinetic properties (Y_H, b_H, μ_h and K_S) were summarized in table 2 below.

TABLE 2 Growth kinetic properties for GAC-SBBR

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

According to Kleacka 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 Ks). Alternatively, organisms that grow efficiently at low substrate concentrations generally exhibit low growth rates at high substrate affinities (low K_s). Grady JR et al. (1999) also noted that a system which have a higher value of μ_H and a lower value of K_s allow 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 facts meant that the culture of GAC-SBBR that have the low μ_h and high K_s value, had to be operated at a longer SRT cause the by the low PCP affinities and growth rate. In contrast to the Monod parameters (K_s and μ_h), the primary effect of the decay coefficient, b_H and biomass yields, Y_H is on the biomass concentration and the oxygen requirement at longer SRTs. A high b_H means that the bioreactor require high oxygen for oxidizing the substrate to carbon dioxide, and a high yields will require less oxygen because more of the electrons in the substrate will be retained in the biomass synthesized (Grady JR et al., 1999). Analysis for these two parameters had deduced that the GAC-SBBR system is consumed less oxygen or suitable to be operating in the anaerobic condition (high Y_H and low b_H values).

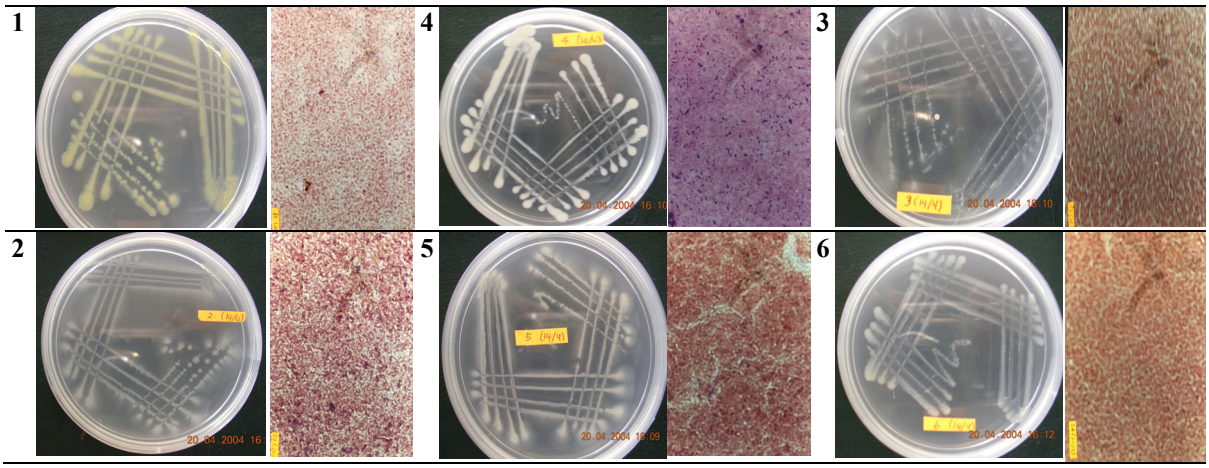

FIGURE 6 Bacteria for each dominant isolate found in the experiment 1) *Pseudomonas aeruginosa* 2) *Bordetella/ Alcaligenes/ Moraxella spp*.3) *Pseudomonas putida* 4) *Corynebacterium nitrilophilus* 5) *Ochrobactum anthropi* 6) *Non fermenter sp*

Microbe Analysis

Microbe analysis on the bacteria inside the GAC-SBBR has found five gram-negative isolates and one gram-positive isolate of rod type bacteria. Test with API-20E system have managed to identify isolate 3 as *Pseudomonas putida.* As for the others (Isolate 1,2,5 and 6), there were tentatively identified as Pseudomonas *aeruginosa* for isolate 1, *Bordetella/Alcaligenes/ Moraxella spp.*for isolate 2, *Ochrobactum anthropi* for isolate 5 and *Non fermenter spp*. for isolate 6. For the gram positive bacteria (isolate 4) tested with biolog system, the result shown that the isolate was *Corynebacterium nitrilophilus*. Figure 6 shown the bacteria for each dominant isolate found in the experiment. All these bacteria are classified as facultative bacteria which able to grow in the aerobic and anaerobic condition.

PCP Metabolic pathway

HPLC analysis has been carried out to determine the PCP metabolic pathway for GAC-SBBR. Figure 3 (a) and (b) below shown the HPLC chromatograph for the influent and effluent of GAC-SBBR for 2 days hydraulic resident time, HRT. From the GAC-SBBR influent chromatograph (figure 3 (a)), the major substrate, PCP was detected at the resident time of 12.5 minute. However, some traces of phenol and chlorophenol peak were also found in the influent, this may be due to the impurity of the chemicals when preparing the PCP synthetic wastewater (Crosby et al. 1981). HPLC analysis on GAC-SBBR effluent has found the trace of PCP, 2,4-DCP, CP and phenol (figure 3(b)). The lower PCP concentration in the effluent than the influent indicated the recalcitrant PCP has been degraded by microorganism in the GAC-SBBR to the other components.

The reductive dechlorination process pathway might be carried out by the microorganisms in the reactor, convert the PCP to lesser-chlorinated compounds (CP, DCP and Phenol) and gas CO_2 (figure 7). Reductive dechlorination, or removal of Cl atoms directly from the ring of aromatic compounds in a single step is a significant process because the dechlorinaetd products are usually less toxic and are more readily degraded either anaerobically or aerobically (Mikesell & Boyd, 1986)

As a conclusion, it is an advantage for GAC-SBBR system to obtain the complete dechlorination and mineralization of PCP under this reductive dechlorination process.

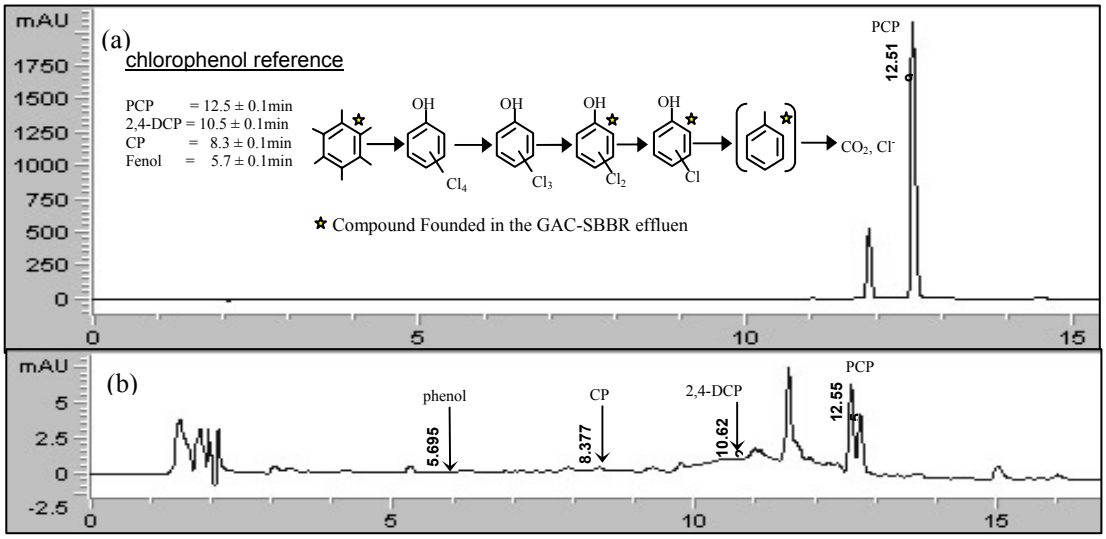

FIGURE 7 Suggested PCP metabolite pathway and HPLC chromatograph for GAC-SBBR (a) influent and (b) effluent

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