EFFECT OF CHEMICAL ADDITION ON THE PACT PROCESS UNDER DIFFERENT ADSORPTION/DESORPTION AND BIODEGRADATION CONDITIONS

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Abstract

Many kinds of hazardous waste water contain a variety of different biologically inhibitory compounds that affect the efficiency of biological treatment. The majority of the components in complex waste water may be easily biodegraded if the inhibitory compounds are removed by physical adsorption. Powdered activated carbon (PAC) has been used to decrease the concentration of inhibitory compounds in the powdered activated carbon treatment (PACT) process. The combined biological and physical adsorption mechanisms decrease the concentration of inhibitory compounds using the large adsorptive capacity of PAC in the PACT reactor making the reactor resilient to changes in operation and wastewater composition. The main aims of the study were to evaluate the performance of PACT process for shock loading of substances with different adsorbility/desorbility to PAC and biodegradability.

This experiment used synthetic wastewater with polypepton as the main component. A continuous bioreactor was used, with a flow rate of 7 l h^{-1}. The pH value was adjusted from 6.5 to 7.5 by the addition of 0.01 N-sodium hydroxide or 0.01 N sulphuric acid. Dissolved oxygen concentration was maintained at around 2 mg/L by aeration. Coal-based PAC (Mitsubishi chemical: Diahope 008 N) at a concentration of 1,500 mg/L was added to the aeration tank of PACT reactor. Mixed liquor suspended solids (MLSS) in the aeration tank were maintained at 4,500 mg/L (biomass = 3,000 mg/L, PAC = 1,500 mg/L) and at 3,000 mg/L for the control reactor. Solid retention time (SRT) was about 15 days. The 3,5-dichlorophenol (3,5-DCP), bromo phenol (BP) and bromo acetic acid (BAA) were chosen as toxic compounds.

The PACT reactor showed high performance for 3,5-DCP, 3-BP and BAA removals. In the PACT process, 3,5-DCP was removed only by adsorption, but the 3-BP was removed by biodegradation and adsorption. This is due to the difference in biodegradabilities between 3,5-DCP and 3-BP irrespective of similar absorbilities. Although adsorption was the main mechanism to remove 3,5-DCP with low desorbility, both adsorption and biodegradation contributed to remove of 3-BP and BAA with high desorbilites. In the PACT reactor, the 3-BP and BAA were biodegraded both directly and indirectly. For indirect biodegradation, both substances were adsorbed on PAC and then desorbed from PAC after the shock loading, and finally they are biodegraded. Although the biodegradability and desorbility of BAA was higher than that of 3-BP, the biodegraded BAA was 54% smaller than that of 3-BP. This is because the biodegradability of BAA in the PACT process was due to the chemical desorbility. The performance of the PACT processes was affected by adsorbility and desorbility of the chemicals, in which the desorbility of the chemicals had significant impacts on the biodegradability.

Keywords: biodegradation, adsorption, desorption, PACT, PAC, inhibitory

1. INTRODUCTION

Many hazardous wastewaters contain a variety of different biologically inhibitory compounds that prevent the application of biological treatment. The majority of the components in a complex wastewater may be easily biodegraded if the inhibitory compounds are

removed by physical adsorption (Fox and Suidan, 1994). It is well known that the combination of adsorption and biodegradation processes can maintain a stable performance and increase biodegradability of the activated sludge (Specchia *et al.*, 1988; Orshansky and Narkis, 1997; Meild, 1997).

Powdered activated carbon (PAC) has been used to decrease the concentration of inhibitory compounds to a concentration lower than the toxicity limit for microorganisms to biodegrade the inhibitory compounds in the powdered activated carbon treatment (PACT) process (Specchia and Gianetto, 1984; Maria *et al*., 2002; Park *et al*., 2003). On the other hand, the combined biological and physical adsorption mechanisms decrease the concentration of inhibitory compounds using the large adsorptive capacity of PAC in the PACT reactor making the reactor resilient to changes in operation and wastewater composition (Sublette *et al.*, 1982; de Jonge *et al*., 1991; Xiaojin *et al*., 1991). Therefore, the goal of physical adsorption is to suppress the concentration of absorbable compounds and also simultaneously to facilitate the biodegradation of the inhibitory compounds (Fox and Suidan, 1994; Kargi and Pamukoglu, 2003).

However, the mechanism of PAC enhancement of the activated sludge process is not entirely clear. At present, the mechanisms involved the relation between the presence of microbial film as mixture of bacterial cell and PAC on the liquid phase of the substances in activated sludge and toxic substances. In the presence of microbial film, the removal of substances is mechanistically complex and involves: (i) transport of substances from bulk liquid to the surface of microbial film, (ii) simultaneous mass transfer, adsorption and biochemical reaction within microbial film, and (iii) simultaneous mass transfer and adsorption within adsorbent (Olmstead and Waber, 1991; Zhao *et al*., 1999; Syamsiah and Hadi, 2004). As biochemical reaction may occur in both adsorbed substances and that in suspension, the presence of biomass in adsorption process may also result, to some extent, to generate the adsorbent and thus long life operation may be expected. On the other hand, de Jonge et al.,1996 and Ha *et al*., 2000 reported that desorption of sorbed compounds is an important process in the powdered activated carbon-activated sludge (PAC-AS) wastewater treatment system, where sorption and biodegradation interact. Therefore, the study of adsorption cycle and effect of microorganisms on phenol removal in fixed bed was also done by Syamsiah and Hadi, 2004. It was reported that the mechanisms of reaction occurred: starting with fast adsorption followed by biodegradation process, and finally with a much slower desorption process.

As commonly known, if toxic substances are present in activated sludge process, the ability of microorganisms to degrade organic substances may be deteriorated. The biodegradation could be increased, if the microorganisms are exposed to lower concentration than the toxicity limit. In the shock loading on PACT process with various toxic substances, different response may occur and can be correlated with absorbability, biodegradability and desorbability of PACT on toxic substances. The main aims of the study were to evaluate performance of PACT process for shock loading of substances with different adsorbability/desorbability to PAC and biodegradability.

2. MATERIALS AND METHODS

Operation of PACT system

The activated sludge aeration tank was made of polyacrylate material and consists of aeration and a sedimentation tanks. The two tanks are separated by a partition wall that has an opening at the bottom to ensure effluent from the aeration tank into the sedimentation and return of activated sludge from the sedimentation tank. The aeration and sedimentation tanks had working volumes of 2.5 L and 0.2 L respectively. A schematic

diagram of the PACT process used in this study is shown in Figure 1.

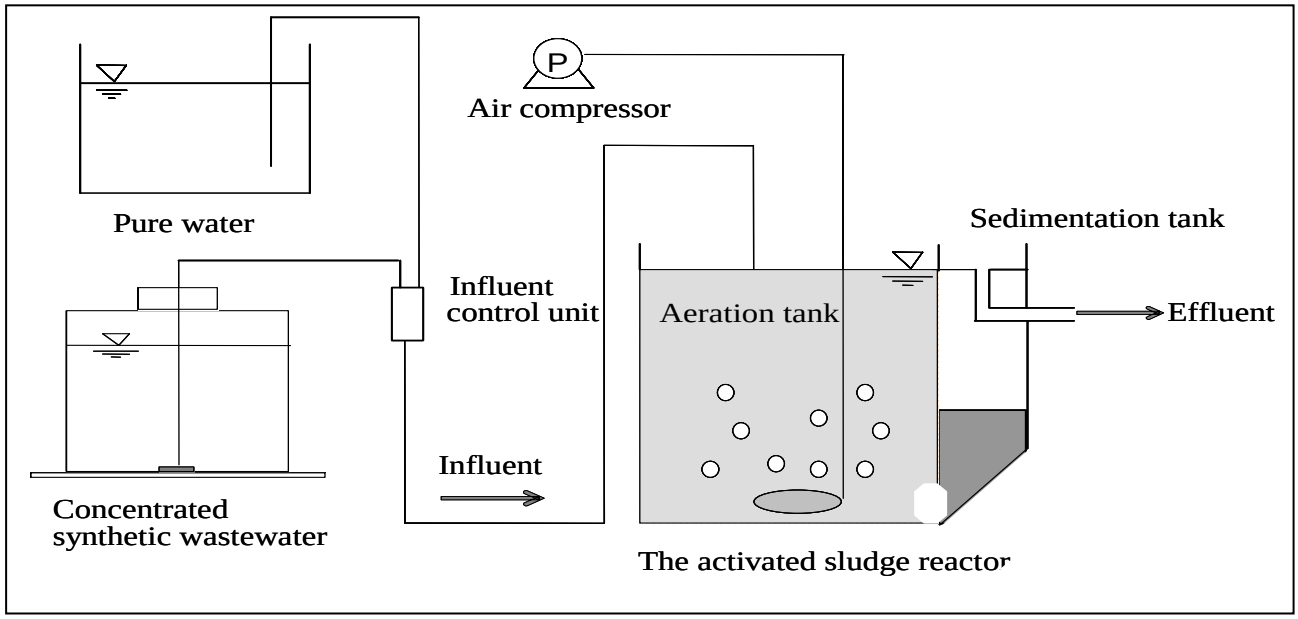

Figure 1. Schematic of Experiment Apparatus

The activated sludge was acclimated by a synthetic wastewater for more than 20 days to have stable operation of the PACT process before the start of shock loading. The composition of the synthetic wastewater is listed in Table 1. Concentrated synthetic wastewater was diluted with tap water at a ratio of 1:20 and fed continuously into the reactor at a flow rate of 7 L/day. pH was adjusted from 6.5 to 7.5 by 0.01 N-NaOH or 0.01 N-H_2SO_4. Dissolved oxygen concentration was maintained at around 2 mg/L by aeration. The activated sludge was acclimated by a synthetic wastewater for more than 20 d to have stable operation of the PACT process before the start of shock loading.

Table 1. Composition of Synthetic Wastewater (Nishijima *et al.*, 1993)

Component	Concentration (mg/L)
Polypepton	446
KH_2PO_4	17.40
$NaHCO_3$	111
$MgSO_4.7H_2O$	5.20
$CaSO_4.5H_2O$	2.11
$FeSO_4.7H_2O$	0.06
TOC	200

Mixed liquor suspended solid (MLSS) in the aeration tank was maintained at about 3,000 mg/L for the control reactor without added of PAC. Coal-based PAC (Mitsubishi chemical: Diahope 008 N) at a concentration of 1,500 mg/L was added to the aeration tank of PACT reactor. MLSS in the aeration tank were maintained at 4,500 mg/L (Biomass=3,000 mg/L, PAC=1,500 mg/L) and at 3,000 mg/L for the control reactor. Solid retention time (SRT) was about 15 days. The amount of PAC removed from the aeration tank by sampling and excess sludge removal was supplied using new PAC to keep PAC concentration at 1,500 mg/L. PAC was sieved in order to obtain particles with diameter ranging from 53 to 75 m. Adsorption capacity of PAC for 3,5-DCP, 3-BP and BAA was determined by batch adsorption experiment. The characteristics of the PAC used are shown in Table 2.

Shock-loading experiments

Shock-loading experiments were carried out after the acclimation of activated sludge for more than 20 days with the synthetic wastewater. The synthetic wastewater with 50 mg/L of toxic compounds was fed at a flow rate of 7 L/day for 24 hour as a shock loading. Effluent was sampled periodically for about 7 days.

Table 2. Surface Characteristics of PAC (Morinaga *et al.*, 2003)

Raw Material	Coal
Activation	steam
BET specific surface area ($m^2 g^{-1}$)	885.60
Total surface acidity (mmol g^{-1})	0.60
Total surface basicity (mmol g^{-1})	0.28
pH_{PZC}	7.50
Zeta potential (mV)	- 16.40
Iodine Number (mg g^{-1})	1160

The amount of toxic compounds adsorbed by PAC was estimated from the balance of toxic compounds in the influent, effluent and amount biodegraded. The amount biodegraded was estimated from the increase of the Chloride ion (Cl^-) or Bromide ion (Br^-) concentration in the effluent. Biodegradation of 3,5-DCP, 3-BP and BAA were determined from Cl^- and Br^- concentration in effluent.

Analytical methods

The concentrations of 3,5-DCP and BP were determined by High Performance Liquid Chromatography (JASCO LC2000 plus HPLC) with a Zorbax SB-C18 column and the UV detector at wavelength of 280 nm, mobile phase with 0.1 % phosphoric acid-water/acetonitrile in a 40/60 ratio, and flow rate of 0.8 ml/min (Barbeni *et al*., 1987). On the other hand, the concentration of BAA was determined according to the headspace method (Japan Industrial Standard K0125, 1985) using a gas chromatograph with electron capture detector (Shimadzu, GC-14B). MLSS was determined following to the Standard Methods for Examination of Waster and Wastewater (APHA, 1989). The Cl^- and Br^- concentrations were determined by ion-chromatography (Dionex DX-500). Dissolved organic carbon (DOC) concentration was determined by TOC analyzer (Shimadzu TOC-500).

3. RESULTS AND DISCUSSION

The adsorption capacities of PAC for 3,5-DCP and 3-BP were similar (*K* value; 270.6 and 203.6 mg g^{-1}), whereas the adsorption capacity of PAC for BAA was low 12.5 mg g^{-1}. From an initial adsorbed amount of 100 mg g^{-1} of each analyze, 2, 15 and 65% of 3,5-DCP, 3-BP and BAA, respectively, were desorbed from PAC. Based on the batch experiments, BAA and 3-BP have specific biodegradation rates of 0.73 and 0.40 mgBr^- g^{-1}MLSS d^{-1}, respectively, while 3,5-DCP was not biodegraded at all. Thus 3,5-DCP, 3-BP and BAA may be classified as low, medium and high biodegradability, respectively. The chemical, physical, and biodegradation characteristics of target substances, collected from batch experiments, are listed in Table 3.

Table 3. Characteristics of Target Substances Used in The Experiments

Target Substances	Adsorption Capacity by Freundlich (mg/g)	Biodegradability	Desorption rate (%)
3,5-DCP	270.6	Low	2
3-BP	203.6	Medium	15
BAA	12.5	High	65

Figure 2 shows that most 3,5-DCP supplied was removed in the PACT reactor. This is confirmed by the peak of 3,5-DCP concentration in PACT reactor that was only 6 mg/L. On the other hand, only little amount of 3,5-DCP was removed in control reactor. Since the peak of 3,5-DCP concentration was as high as 45 mg/L (The concentrations of 3,5-DCP, 3-BP and BAA added for shock loading are 50 mg/L each).

Figure 3 shows that after 24 h, the peak concentration of 3-BP in effluent of PACT reactor was 9 mg/L. This indicate that most of 3-BP was removed in PACT reactor. However, only little amount of 3-BP was removed in control reactor. The peak of 3-BP concentration was as high as 35 mg/L.

Figure 4 shows that the peak concentration of BAA in effluent of PACT reactor was 11 mg/L. This indicates that most of 3-BP was removed in PACT reactor. However, the amount of BAA removed in control reactor is high compared with 3,-DCP and 3-BP. The peak of BAA concentration was only 23 mg/L.

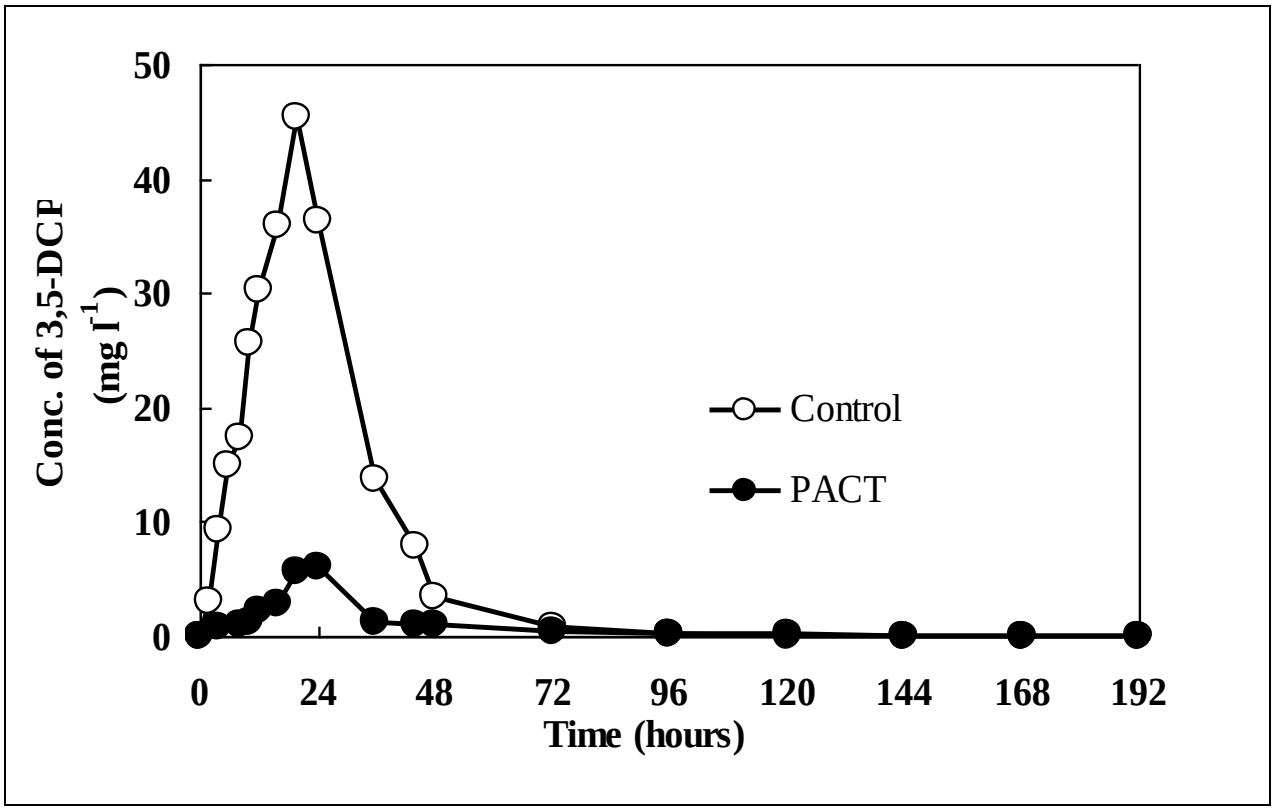

Figure 2. Comparison of the Biodegradability and Adsorbability of Substances (3,5-DCP) in Control and PACT Reactors

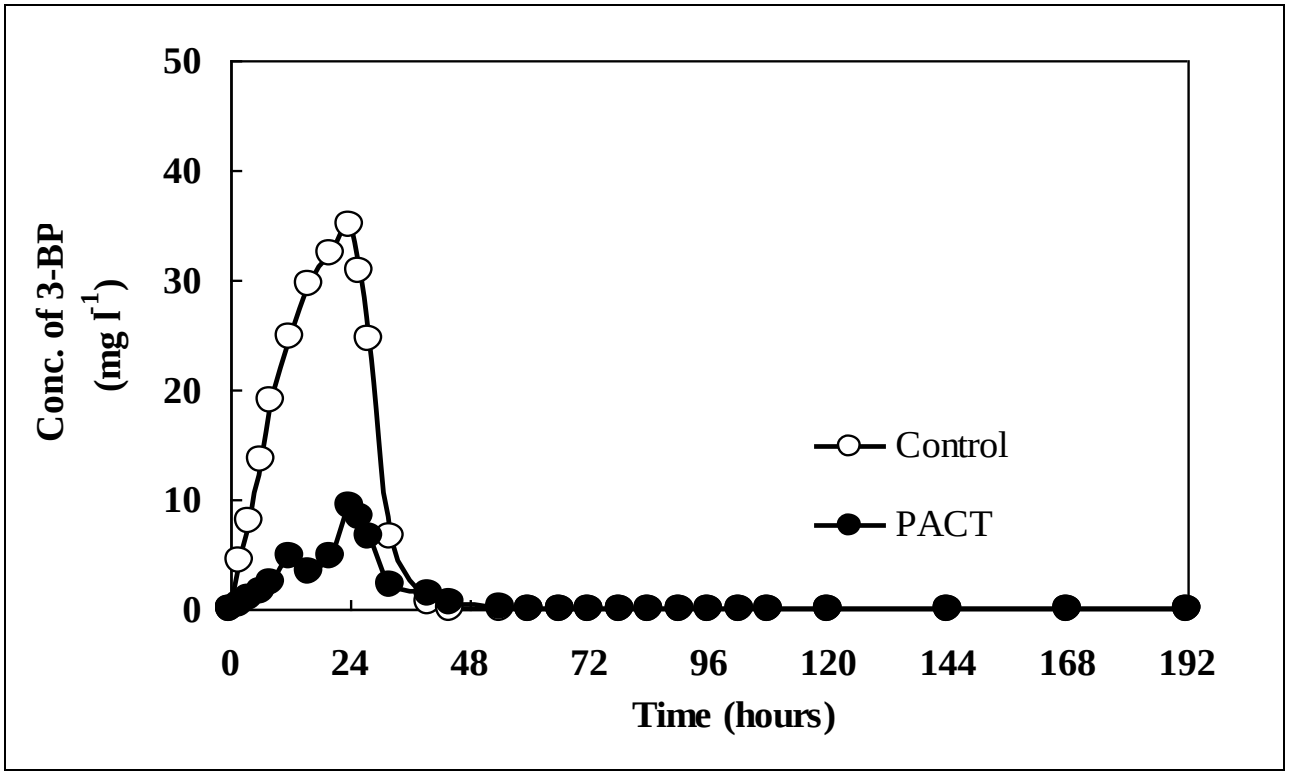

Figure 3. Comparison of The Biodegradability and Adsorbability of Substances (3-BP) in Control and PACT Reactors

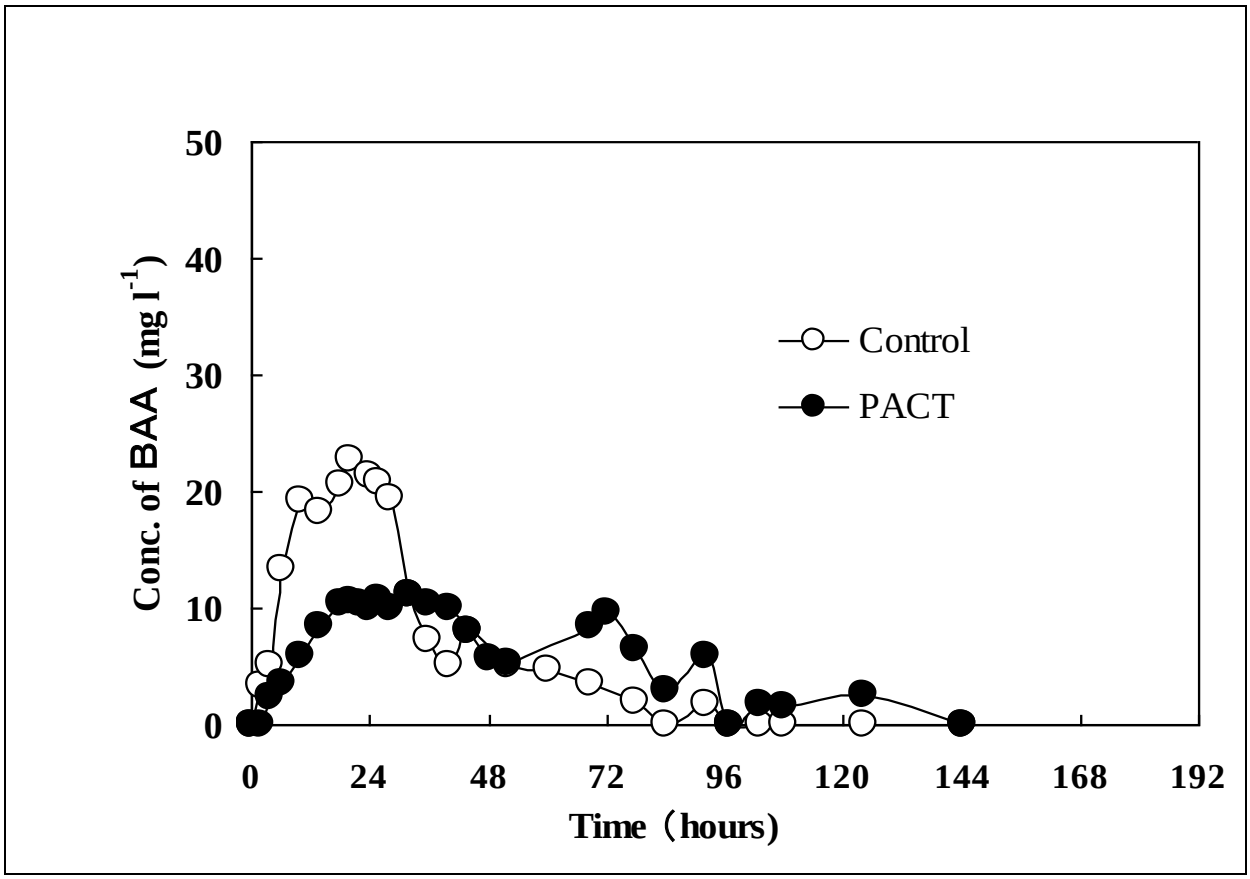

Figure 4. Comparison of The Biodegradability and Adsorbability of Substances (BAA) in Control and PACT Reactors

Based on mass balance, the amount of adsorbed, biodegraded and discharged of 3,5-DCP, 3-BP and BAA in each reactor could be compared (Figure 5). When 3,5-DCP was fed into aeration tank, most of 3,5-DCP supplied (88%) was removed in the PACT reactor. Only 9% 3,5-DCP was removed in the control reactor. When 3-BP was fed into the aeration tank, 87% and 38% of the supplied amount was removed in the PACT and control reactors, respectively. In PACT reactor, biodegraded and adsorbed of 3-BP were 37% and 50%, respectively. In control reactor, biodegraded and adsorbed of 3-BP were 25% and 13%, respectively.

On the other hand, when BAA was fed into aeration tank, 48% and 33% of BAA supplied was removed in the PACT and control reactors, respectively. In PACT reactor, biodegraded and adsorbed of BAA were 17% and 31%, respectively. In control reactor, biodegraded and adsorbed of BAA were 17% and 16%, respectively.

Adsorption capacity of PAC in 3-BP solution is lower compared with 3,5-DCP. Mazet and Baudu (1994) reported that the adsorption capacity for phenol decreased when surface charge of PAC is more negative. Therefore, the negative charge of PAC may be responsible for the decrease in adsorption capacity. This is due to decrease in the electrostatic interactions between the negatively charged carbon surface of PAC and the partial negative charge of the aromatic ring of phenolic molecules (Franz *et al.*, 2000).

On the other hand, the amount of 3-BP biodegraded in the PACT reactor was 1.5 times higher than that in the control reactor, whereas amounts of BAA biodegraded in PACT and control reactor were the same. This shows that the combination of activated sludge and

activated carbon processes has made the biodegrability of activated sludge in inhibitory compounds increased (Orshansky and Narkis, 1997; Morinaga *et al*., 2003).

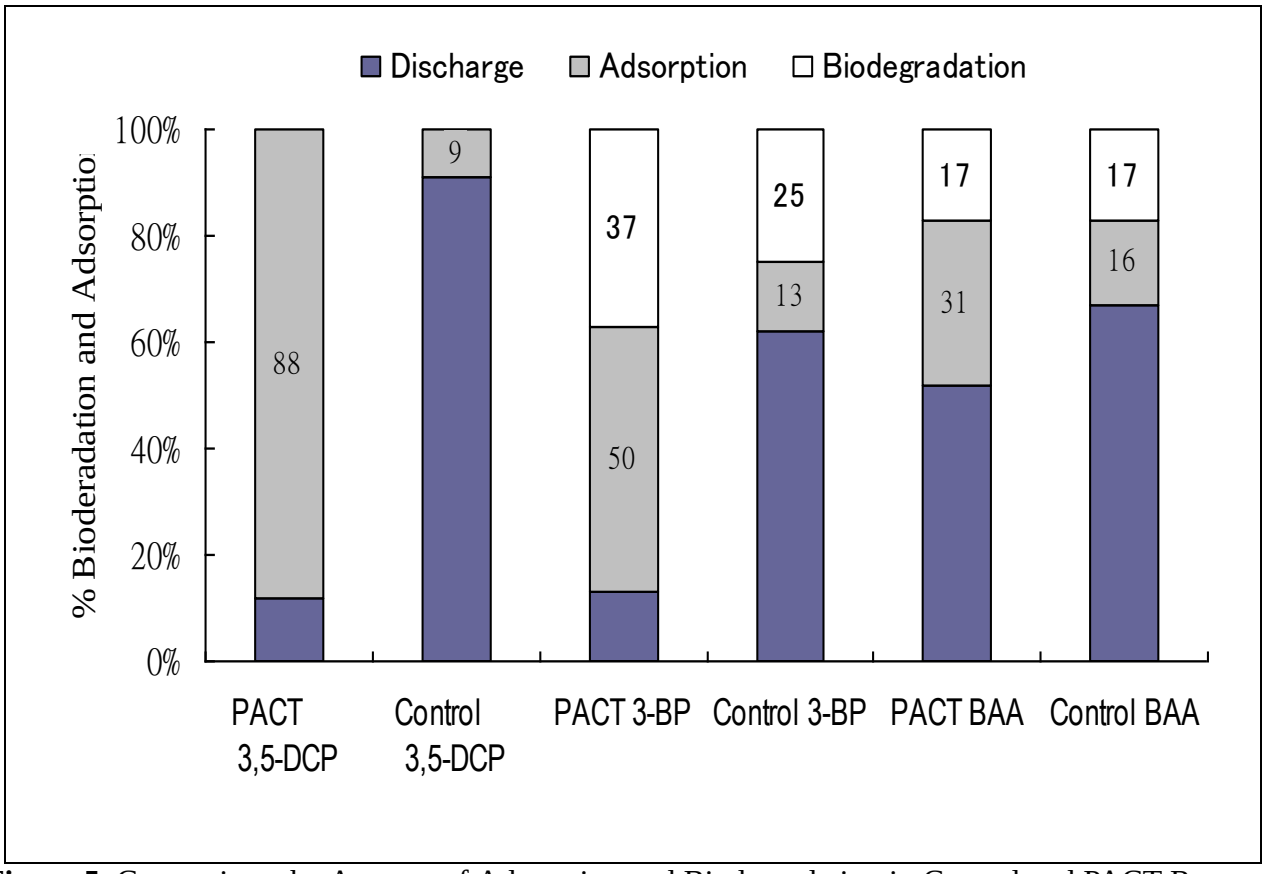

Figure 5. Comparison the Amount of Adsorption and Biodegradation in Control and PACT Reactors for 3,5-DCP, 3-BP and BAA Chemical Substances

Figure 6 shows that the biodegradation of 3-BP and BAA were noted in the control reactor for 78 hour and 48 hour, respectively, whereas biodegradation continued until 168 hour and 96 hour in the PACT reactor, respectively. This indicates that 3-BP and BAA were biodegraded both directly and indirectly. At indirect biodegradation, both substances were adsorbed on PAC and then desorbed from PAC after the shock loading and finally, biodegraded.

However, Cl^- concentration in effluent monitored to detect biodegradation of 3,5-DCP shows around 1 mg/L before, during and after the shock loading in PACT and control reactors, indicating that biodegradation did not occur significanly. Theoretical calculations suggest that 21.78 mg/L of Cl^- is produced when 50 mg/L of 3,5-DCP added for shock loading biodegrade. Thus, 3,5-DCP was removed by adsorption only.

When about 88% of 3,5-DCP supplied was removed only by adsorption in the PACT reactor, about 37% of 3-BP inflow was removed by biodegradation and 50% was by adsorption. This is due to the difference in biodegradabilities between 3,5-DCP and 3-BP irrespective of similar adsorbabilities.

In control reactor, biodegraded and adsorbed BAA were 17% and 16%, respectively. When BAA with high desorbability was fed into PACT reactor, biodegraded and adsorbed BAA were 17% and 31%, respectively. It indicates that the biodegradability of PACT process was due to the desorbability of chemical.

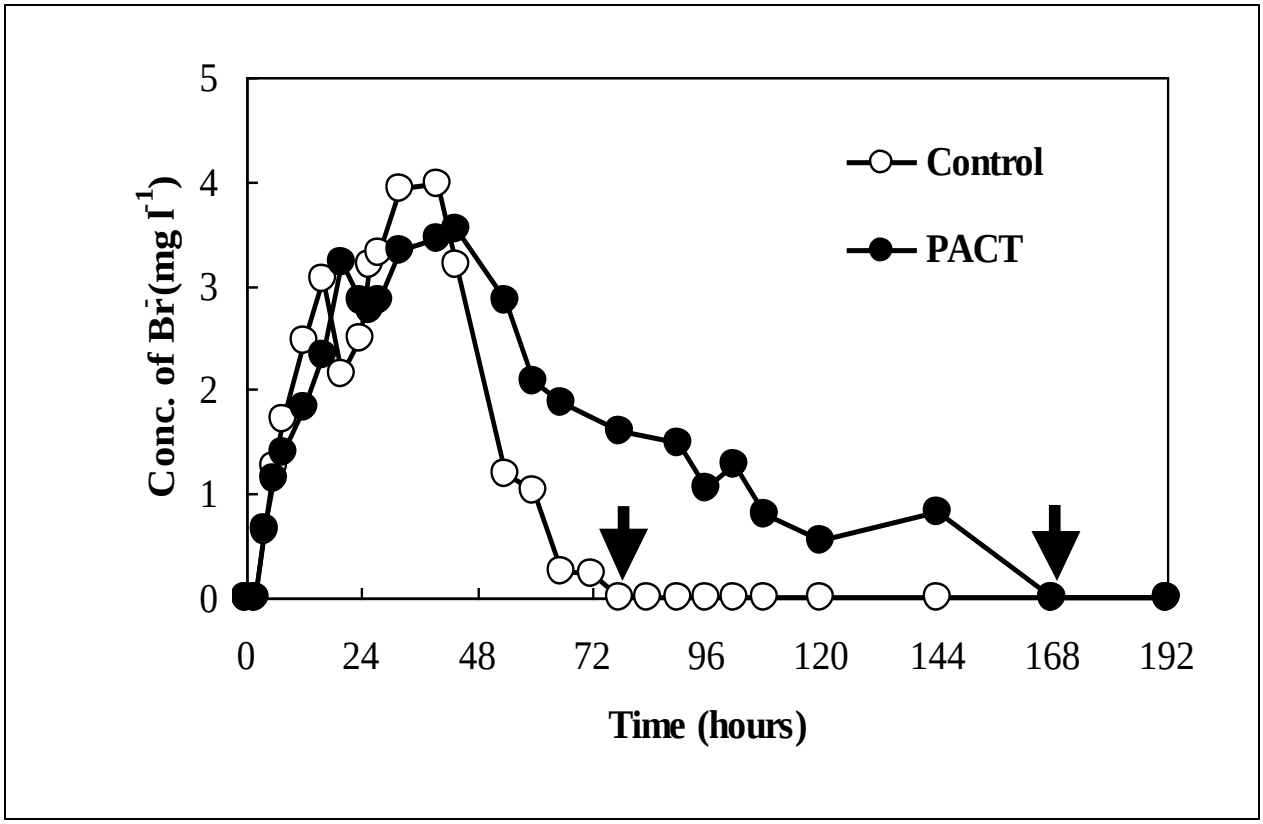

Figure 6. Comparison of Biodegradibility and Desorpability of 3-BP as Target Compounds in Control and PACT Reactors

Although biodegradability and desorbability of BAA was higher than that in 3-BP, the biodegraded BAA was 54% smaller than that in 3-BP. Therefore, performance of PACT processes was affected by adsorbability and desorbability of chemicals, and especially desorbability of chemicals had significant impacts on the biodegradability of chemical in PACT processes.

4. SUMMARY AND CONCLUSIONS

The objective of this study was to evaluate the performance of PACT process for shock loading of substances with different adsorbability/desorbability to PAC and biodegradability. Specific conclusions derived from this study are as follows: (1) The PACT reactor showed high performance for 3,5-DCP, 3-BP and BAA, (2) In PACT process, 3,5-DCP supplied was removed only by adsorption, but the 3-BP inflow was removed by biodegradation and adsorption. This is due to the difference in biodegradabilities between 3,5-DCP and 3-BP irrespective of similar absorbabilites.; (3) Although adsorption was the main mechanism to remove 3,5-DCP with low desorbability, both adsorption and biodegradation contributed to remove of 3-BP and BAA with high desorbabilites, (4) In the PACT reactor, the 3-BP and BAA were biodegraded both directly and indirectly. At indirect biodegradation, both substances were adsorbed on PAC and then desorbed from PAC after the shock loading and finally, biodegraded. (5) Although biodegradability and desorbability of BAA was higher than that of 3-BP, the biodegraded BAA was 54% smaller than that of 3-BP. This is because the biodegradability of BAA in the PACT process was due to the desorbability of the chemical. (7) Performance of the PACT processes was affected by adsorbability and desorbability of chemicals, especially desorbability of chemicals had significant impacts on the biodegradability of chemical.

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