

## CHAPTER 4

### RESULTS AND DISCUSSION



#### 4.1 Preliminary study

##### 4.1.1 Pyrene adsorption on pumice

The adsorption of pyrene with different concentration ranging 1000-10000 ppm on pumice with three sizes was carried out. Figure 4.1 shows the adsorption isotherm for pyrene at pumice/toluene interface at 30°C. As noticed, the adsorption isotherm can be categorized to type II according to the classification of BDDT (Gregg and Sing, 1982), though type II isotherms describe physical adsorption of gases by non-porous solids. This implies that monolayer coverage is succeeded by multilayer adsorption at higher concentration value. The adsorption isotherms are affected by the specific area of adsorbents since the amount of adsorption increased with decreasing size of pumice.

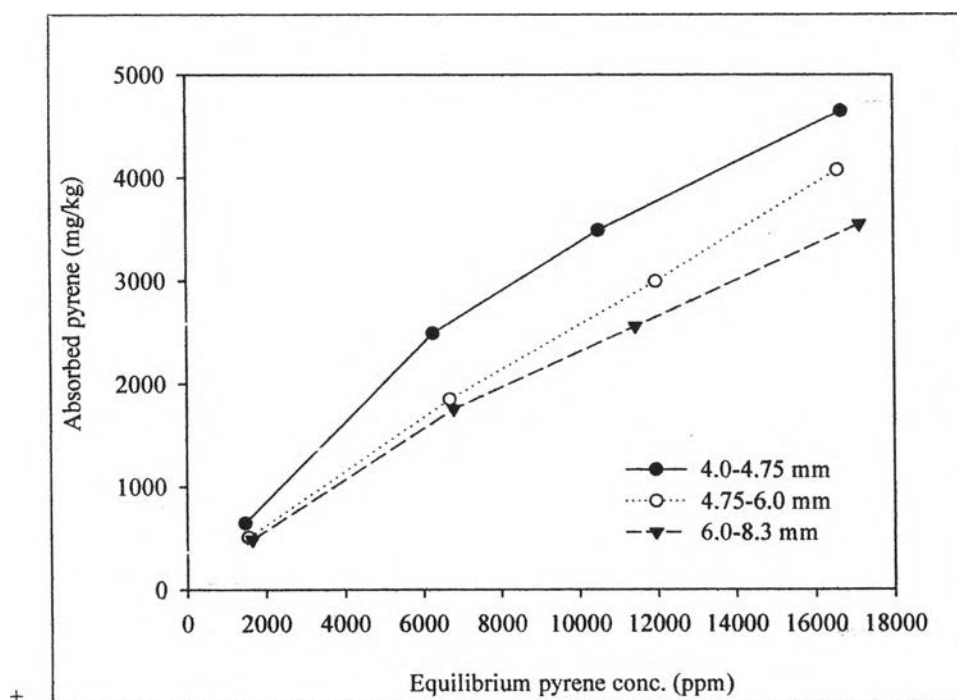


Figure 4.1 The adsorption isotherm for pyrene at pumice/toluene interface at 30°C.

Table 4.1 Adsorption of pyrene on three sizes pumice.

Concentrations of pyrene in toluene solutions (ppm)	Pumice 4.0-4.75 mm		Pumice 4.75-6.3 mm		Pumice 6.3-8.0 mm	
	Absorbed pyrene (mg/kg)	Absorbed pyrene (%)	Absorbed pyrene (mg/kg)	Absorbed pyrene (%)	Absorbed pyrene (mg/kg)	Absorbed pyrene (%)
1000	646.85	64.68	506.38	50.64	485.03	48.50
4000	2490.42	62.26	1849.05	46.23	1753.56	43.84
7000	3488.54	49.84	2993.55	42.77	2556.40	36.52
10000	4647.49	46.47	4073.57	40.74	3545.86	35.46

#### 4.1.2 Pyrene removal by toluene extraction

Pyrene was removed from pumice by toluene extraction. Figure 4.2 showed percentage of pyrene removal after toluene extraction in orbital shakers at rotation speed of 100 rpm for 3 hours. Three different sizes of pumice were used as a soil model. Four levels of pyrene contamination were obtained by soaked with 4 initial concentrations of 1000, 4000, 7000 and 10000 ppm pyrene in toluene solutions. After extraction by toluene, pumice loaded with initial concentration of pyrene at 1000 ppm had less pyrene removal efficiency than that contaminated with the more concentrated pyrene solutions. It can be seen that the more pyrene is adsorbed on pumice, the more of that amount can be removed.

Pumice grain size also influenced pyrene removal efficiency but the difference was not as significant as that influence on pyrene adsorption, as presented in Figure 4.2. The smaller size pumice had better pyrene removal efficiency due to the greater surface area per unit weight. Pyrene at initial concentration of 1,000 ppm could be removed only 15%, 9% and 6% on pumice size 4.0-4.75 mm, 4.75-6.3 mm, and 6.3-8.0 mm, respectively. Pyrene at initial concentration of 10,000 ppm could be removed as much as 77%, 71% and 66% on pumice size 4.0-4.75 mm, 4.75-6.3 mm, and 6.3-8.0 mm, respectively.

When effect of initial pyrene concentrations was considered, it can be seen that pyrene removals did not vary linearly with the initial concentration of pyrene used. Like

other NAPL, pyrene in the subsurface form a visible, separate oily phase in the subsurface whose migration is governed by gravity, buoyancy, and capillary forces (Bedient, et al., 1994). When release at the surface, free-phase or mobile NAPL is forced into the pores of the soil matrix by the hydrostatic pressure on the NAPL. When the supply of new NAPL is exhausted, however, the pressure on the free-phase NAPL is removed and small blobs of NAPL “snap-off” or “bypass” the once continuous NAPL body and become trapped in individual pores or small groups of pores by capillary forces. The residual saturation, defined as the fraction of total pore volume occupied by residual NAPL that is trapped in the subsurface. So total pyrene contaminated onto pumice can be classified as free-phase pyrene and residual pyrene. Adding surfactant to the aqueous solution makes more pyrene becomes mobile and removable by solubilization and mobilization mechanisms.

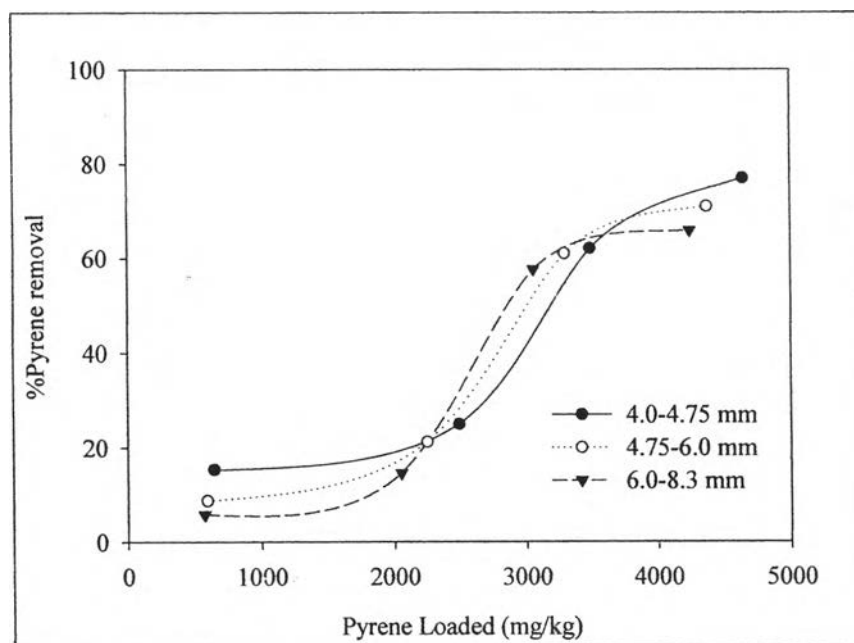


Figure 4.2 Influence of pumice size and initial pyrene concentration on the pyrene removal efficiency.

### 4.1.3 Pyrene removal from real soil

A test of pyrene removal from natural soil was performed in the batch experiment and the results were compared with those of small size pumice. The natural soil was obtained from the field and contained about 3% organic matter. Pyrene was loaded to both real soil and pumice using an initial pyrene concentration of 1000 ppm. Natural soil adsorbed about 400 mg pyrene/kg soil while pumice adsorbed about 750 mg pyrene/kg pumice. Pyrene removal from pumice and natural soil using 5 vol% BioNonex solutions was shown in Figure 4.3. The rate of pyrene removal from the real soil was slower than that from pumice during the initial washing stage. However, at the end of the experiment, pyrene removal from natural soil is higher than that from pumice. It would be ascribed to the initial amount of pyrene loaded on the adsorbents and the difference in structures of the adsorbents. After 20 hours of surfactant washing, pyrene removals attained 58% for natural soil and 55% for pumice. Based on the results, organic matter seemed to have no influence on the pyrene removal.

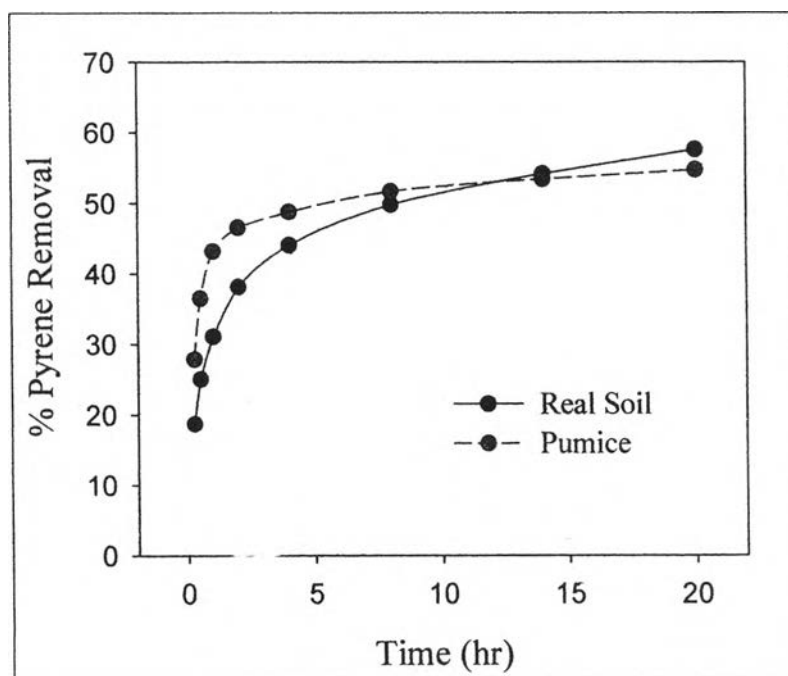


Figure 4.3 Pyrene removal in pumice and natural soil using 5 vol% BioNonex solution in batch experiment.

#### 4.1.4 Solubility of pyrene

Table 4.2 shows pyrene solubility in water and 1-10vol% surfactant solutions. Figure 4.4 shows the variation in pyrene solubility in BioNonex and BioSolve solutions in concentration range of 1-10 vol%. All experiments were conducted at 25°C (room temperature).

Table 4.2 Pyrene Solubility in water and surfactant solutions

Solution	Equilibrium Pyrene solubility (mg/L)
Water	0.165
BioNonex 1 vol%	559.11
BioNonex 3 vol%	1214.81
BioNonex 5 vol%	1860.28
BioNonex 7 vol%	2454.71
BioNonex 10 vol%	3247.94
BioSolve 1 vol%	92.75
BioSolve 3 vol%	427.59
BioSolve 5 vol%	824.08
BioSolve 7 vol%	1262.26
BioSolve 10vol%	1912.39

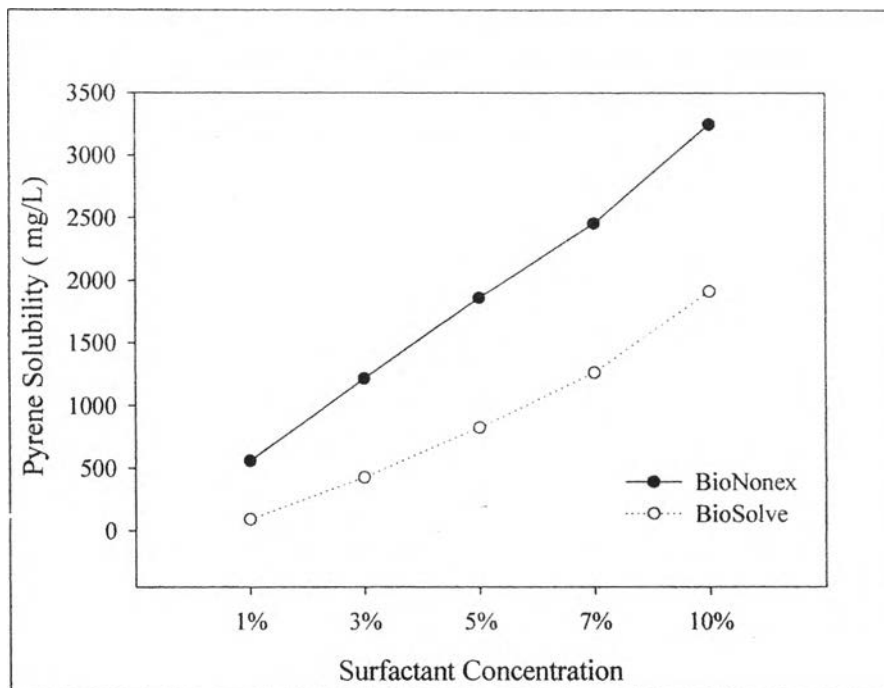


Figure 4.4 Pyrene solubility in BioNonex and BioSolve solutions at 25°C.

Solubility of pyrene in 10 vol%-BioNonex solution increased several thousand times than that in water. There appeared to be a linear relationship between solubility and surfactant concentration for both BioNonex and BioSolve. It was found that with an increase in concentration of surfactant, the amount of pyrene solubilized in the solution also increased. Above the CMC an increase in concentration of the surfactant solution results in a larger number of micelles formed. Hence the solubilization of pyrene in the micelle phase also increases. Solubilization of nonpolar compounds tends to increase with an increase in the concentration of the compound. This is due to the fact that as more solubilize is incorporated in the core of the micelle, the core becomes more like the solubilize, resulting in an increase in the solubilizing capacity of the core (Roy et. al., 1995). The slopes of the lines obtained in this study show the superior of pyrene solubility in BioNonex than that in BioSolve solution.

#### 4.1.5 Removal of pyrene from pumice by surfactant solutions

Five concentrations 1, 3, 5, 7 and 10 vol% of BioSolve and BioNonex were subject to test for the removal capacity of pyrene from pumice. Pumice was loaded with pyrene in toluene solution of the initial concentration of 1000 to 10000 ppm.

##### BioNonex

Figure 4.5 shows the influence of the concentration of BioNonex on the removal of pyrene loaded on pumice. It is evident that pyrene removal was affected by surfactant concentration and varied with pyrene loading. For 1300 mg/kg pyrene loading, there was no significant difference among the 5 concentrations of BioNonex. The amount of pyrene removal was ranged from 184-513 mg-pyrene/kg-pumice, and average pyrene removal was 325 mg/kg. In the case of high-contaminated pyrene loading, 12000 mg/kg, pyrene removal was significantly varied with BioNonex concentration. BioNonex 1, 3, 5, 7 and 10 vol% solutions resulted in removing 443, 1322, 2251, 3079 and 3477 mg pyrene/kg pumice, respectively. Pyrene removal increased with increasing BioNonex concentration.

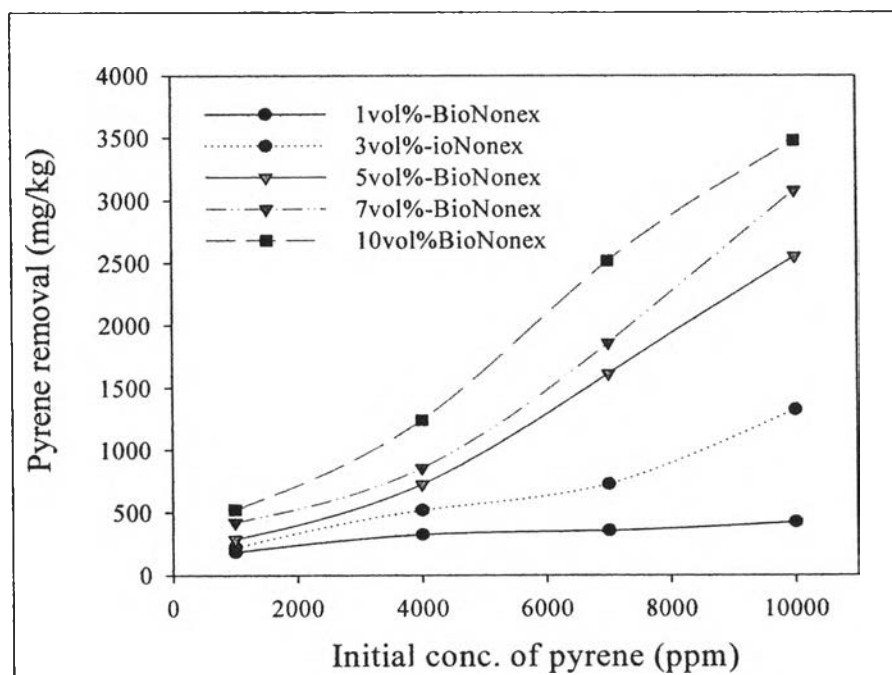


Figure 4.5 Influence of concentration of BioNonex solutions on pyrene removal.

### BioSolve

Figure 4.6 shows the influence of initial pyrene concentration and concentration of BioSolve solutions on pyrene removal. It can be seen that the percentage of pyrene removal was affected by concentration of BioSolve and varied with pyrene loading. For low-contaminated loading, there was no significant difference among the 5 concentrations of BioSolve. Amount of pyrene removed ranged from 47-194 mg pyrene/kg pumice, and average pyrene removed was 100 mg/kg. In the case of higher pyrene loading, pyrene removal was significantly varied with BioSolve concentration. BioSolve 1, 3, 5, 7 and 10% solutions removed 284, 1232, 1840, 2344 and 2479 mg pyrene/kg pumice, respectively. Increased BioSolve concentration resulted in increased pyrene removal. However, increasing BioSolve concentration from 7% to 10% did not affect pyrene removal significantly

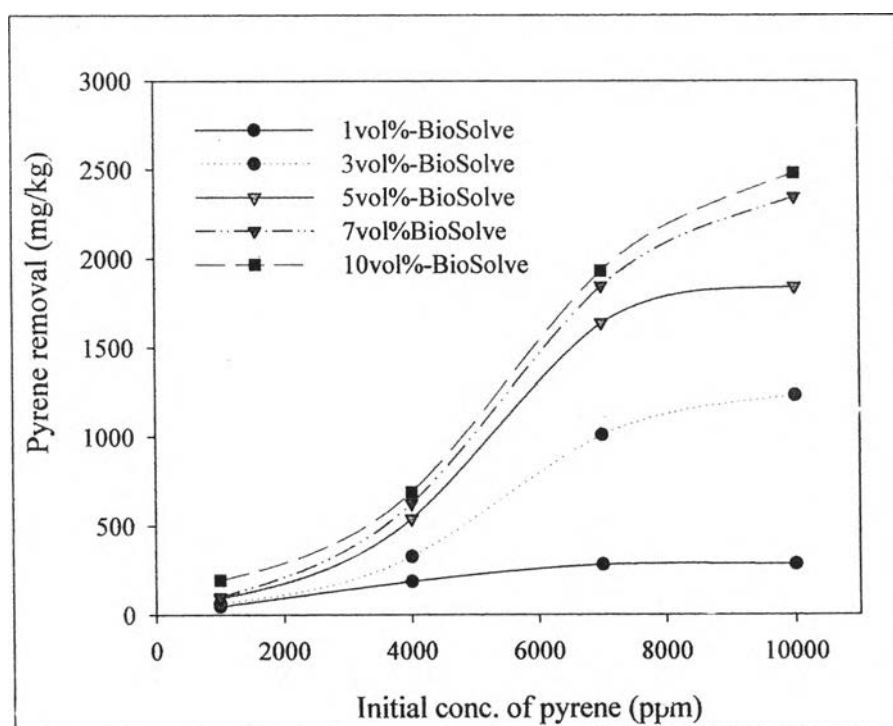


Figure 4.6 Influence of concentration of BioSolve solutions on pyrene removal.



Figure 4.7 shows the effect of surfactant concentration used to prepare conventional surfactant solutions using concentrations of surfactant ranging from 1 to 10 vol%. Pumice was loaded with pyrene at initial concentration of 1300 mg pyrene/kg pumice. After 3 hours of extraction by BioSolve solutions, pyrene removal was 11, 15, 24, 45 and 53% for solution concentrations at 1, 3, 5, 7 and 10 vol%, respectively. BioNonex solution removed about 27, 37, 52, 70 and 76% of pyrene at 1, 3, 5, 7, and 10 vol%, respectively. With an increase in surfactant concentration the number of micelles formed increased and also the number of surfactant molecules per micelle will increase and thus can solubilize more PAH. It can be seen that pyrene removal increased with increasing surfactant concentration ranging from 1 to 7 vol%, for both BioNonex and BioSolve. However, increasing surfactant concentrations beyond 7 to 10 vol% did not affect pyrene removal significantly. This apparent anomaly can be explained by observations reported by Roy D. (1995). They found that increasing SDS surfactant concentration from 8 to 30 mM did not enhance the pollutant removal efficiency because changing surfactant concentration affected the hydraulic conductivity and pore geometry of the soil matrix. Excessive surfactant concentration may cause pore blocking. Pore blocking prevents the wash media from reaching all pore spaces and thus decreases the removal of contaminant.

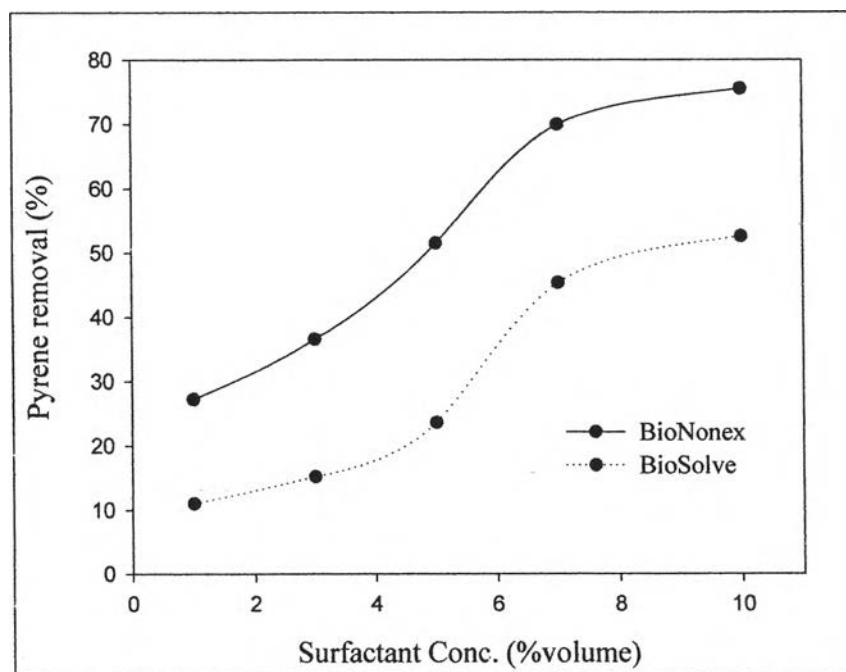


Figure 4.7 Pyrene removals by BioSolve and BioNonex solutions.

From these experiments, it can be clearly seen that based upon the same vol% concentration, the amount of pyrene removed by the BioNonex solutions is superior to that removed by BioSolve solutions. The percent removal of pyrene observed from the preliminary soil washing studies indicate that BioNonex is more effective than BioSolve at the same concentration in pyrene removal. So BioNonex was selected to use in the pumice flushing experiment in column afterwards. It should be noted that both BioNonex and BioSolve have been proven in the laboratory and in the field as a cost effective, environmentally sound answer to soil and groundwater remediation efforts involving a wide range of contaminants. This experiment showed the superiority of BioNonex over BioSolve only in pyrene removal, not other contaminants. Performance of surfactant in soil washing depends on the compatibility of the surfactant used with the specific type of pollutant.

#### 4.1.6 Contact time

Figure 4.8 shows a comparison between the conventional surfactant solution of 5 vol% BioNonex, 5 vol% BioSolve, and water flood in removing pyrene from pumice in the batch experiments using Erlenmeyer flask and orbital shaker. Initial pyrene loading was about 1300 mg/kg pumice. Concentration of pyrene in solution was measured with time from 0.25-24 hours. It is obvious that both BioNonex and BioSolve surfactant solutions are more effective than water in removing pyrene from pumice. After 24 hours extraction, percentage of pyrene removal was 77, 25 and 8% by 5 vol% BioNonex, 5 % vol BioSolve and water, respectively.

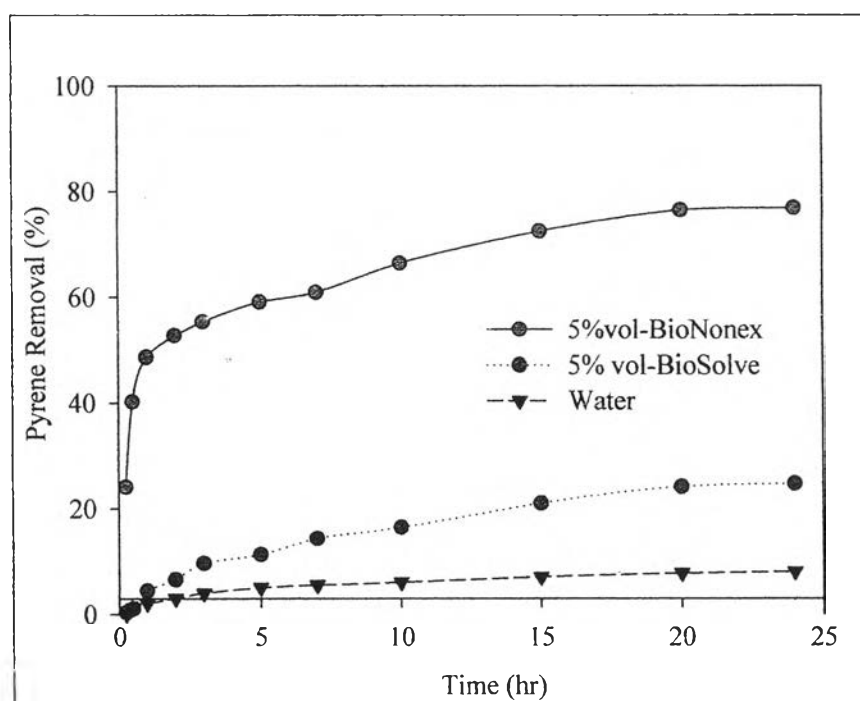


Figure 4.8 Time course of pyrene removal with 5 vol% BioNonex, BioSolve and water.

The removal rate of pyrene was high in the early stage and reached maximum rapidly in about 30 min, in particular with 5 vol% BioNonex. Then the adsorption rate decreased to steady state and remained fairly constant after 15 hours of operation. The high removal rate at the early stage was attributed to desorption of free-phase pyrene attached loosely at the external surfaces of pumice.

In addition for the case of water flood, the only mechanism that is responsible for the removal of pyrene is likely to be displacement. Due to water wetting properties of the soil matrix, at a large enough pressure head, the trapped contaminant is displaced from pumice. The inadequacy of water flooding is primarily due to immobilization of NAPL in the porous media as a result of snap-off and bypassing (Roy et al., 1995; Newell et al., 1994) Snap-off is prevalent in a soil matrix with high aspect ratio pores. Bypassing phenomena is noted when a section of larger pores containing the NAPL are in an earlier study by Roy et al. (1995), which used a down flow mode with a fine silty loam soil in a 5.75 x 10 cm long column. They reported that water remove only 20% of auto transmission fluid (ATF) in 7 pore volumes. The pyrene removal rate obtained in this study is about 8% in down flow mode with water, 12 % less than ATF removal rate. The reason for decreased removal of pyrene compared to ATF is explained to be higher molecular weight and stronger adsorption of pyrene on pumice because pumice is porous in structure and it has more surface area per unit weight than the silty loam soil.

#### 4.1.7 Specific surface area and pore size of pumice

Pumice was ground and then analyzed by Brunauer, Emmett and Teller (BET) pore size analyzer apparatus. The specific surface area, total pore volume, average pore diameter of pumice samples as received, 1300 mg pyrene/kg pumice loading , and after washed by BioNonex are shown in Table 4.3.

After pyrene adsorption, the specific surface area and pore volume of pumice significantly decreased. This could be attributed to the adsorption of pyrene molecules into pumice pores, thus cause pore blocking. When washed with BioNonex solution, pyrene and other materials in pumice pores were solubilized and mobilized. Sequentially, specific surface area, total pore volume and also average pore diameter was resumed.

Table 4.3 Specific surface area and pore size of pumice

Pumice sample	Specific surface area (m <sup>2</sup> /g)	Total pore volume (cc/g)	Average pore diameter (Å <sup>o</sup> )
As received	4.373403	0.00192	21.976
Adsorbed pyrene 1300mg/kg	3.843203	0.00152	21.960
Wash with BioNonex 7 vol%	5.802872	0.00196	22.001

#### 4.1.8 Stability of colloidal gas aphon (CGA)

The stability of colloidal gas aphon (CGA) was measured in term of half-life, which was defined as the time required for half the amount of original liquid to drain. Half-life of CGA can be determined by plotting time versus volume of aqueous solution that arise after the CGA bubbles coalesce and become aqueous phase, as shown in Figure 4.9. Total volume of surfactant solutions after 1 L of CGA bubbles generated from 3 and 7 vol% of BioNonex coalesced and became liquid phase were 700 and 680 ml, respectively. The half life for 3 vol% BioNonex and 7% BioNonex CGA or the volume of the aqueous phase reached 350 and 340 ml were 8 and 11 min respectively.

Surfactant concentration had influence on CGA stability i.e., the more concentrated the solution, the more stable the CGA bubbles or the longer half-life. In addition to this, 7 vol% BioNonex solution required less fluid volume, 680 ml compared to 700 ml of 3 vol% solution, to generate 1 L of CGA suspensions. Overall CGA bubbles vanished after approximately 30 minutes for both 3 and 7 vol% BioNonex solutions.

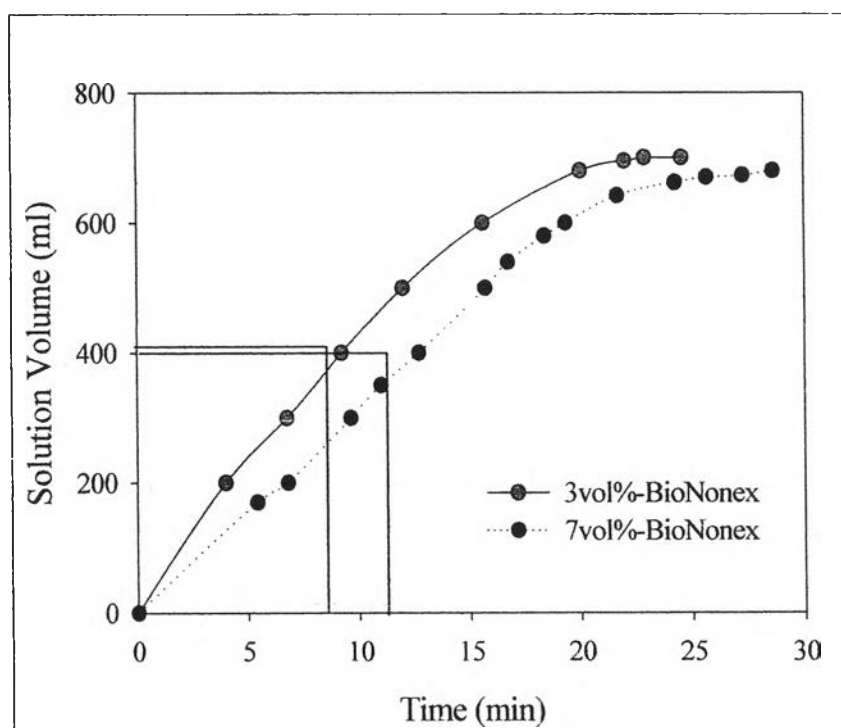


Figure 4.9 Half life of CGA generated from 3 and 7 vol% BioNonex solutions.

## 4.2 Column flushing experiments

All flushing experiments were conducted in duplicate up-flow mode. A typical result of selected run showing percentage of pyrene removal 5 vol% BioNonex is presented in Figure 4.10. The reproducibility was considered to be satisfactory and the average of the two experimental runs was used for comparisons and discussion.

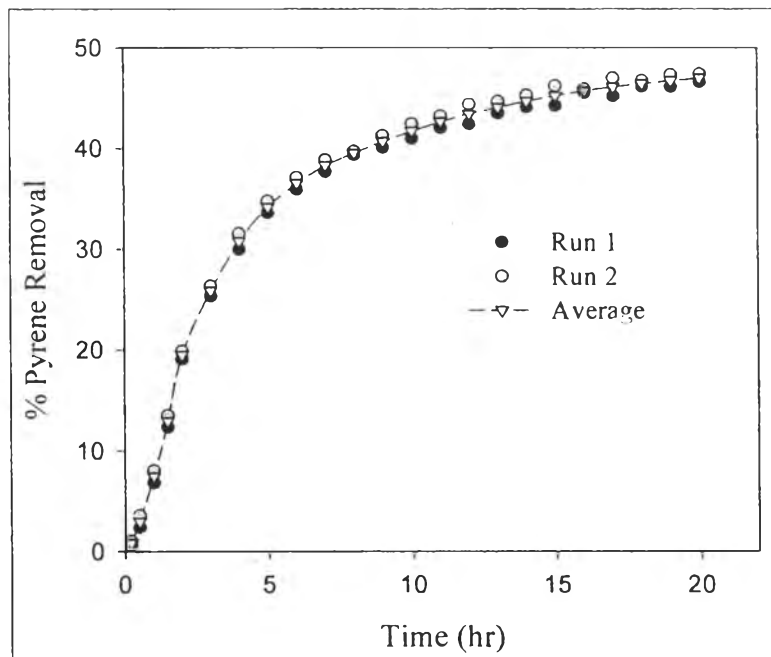


Figure 4.10 Duplicated percentage of pyrene removal with 3 % BioNonex solution in the column experiment.

In column flushing experiments, performances of CGA and conventional surfactant solution in removing pyrene from pumice in up flow operation with 3 and 7 vol% BioNonex were compared. Total pyrene loadings of 1300 and 12000 mg-pyrene/kg-pumice were obtained from 2 initial pyrene concentrations of 1000 ppm and 10000 ppm respectively. As mentioned before from the preliminary study, 1 vol% BioNonex solution could not remove pyrene effectively compared to the higher concentrated solution. However, increasing surfactant concentration from 7 to 10 vol% did not increase pyrene removal significantly. Therefore 3 and 7 vol% BioNonex were selected as the concentrations of flushing media in soil washing experiments in column and their performance in the forms of CGA and aqueous solution were compared.

#### **4.2.1 Influence of surfactant concentration on pyrene removal**

The effect of surfactant concentration used to prepare CGA and conventional solutions was studied using two concentrations of BioNonex, 3 vol% and 7 vol%. As in the batch operations, the rate of pyrene removal reached maximum at the early stage and inclined rapidly towards the end of the experiments. The pyrene removal rates in all the cases were high in the initial stage of the flushing followed by a slower rate as the experiment continued. This was attributed to desorption of any free-phase pyrene that attached loosely to the external surface of pumice. For pyrene loaded at 1300 mg/kg pumice as shown in Figure 4.11 (a), pyrene removal from the pumice column was 47 and 55% after flushing with BioNonex-3 vol% solution and CGA, respectively for 20 hours. Changing the flushing media to BioNonex-7 vol% solution and BioNonex-7 vol% pyrene removal was increased to 68 and 78%, respectively. On the other hand, flushing water removed only 11% of pyrene.

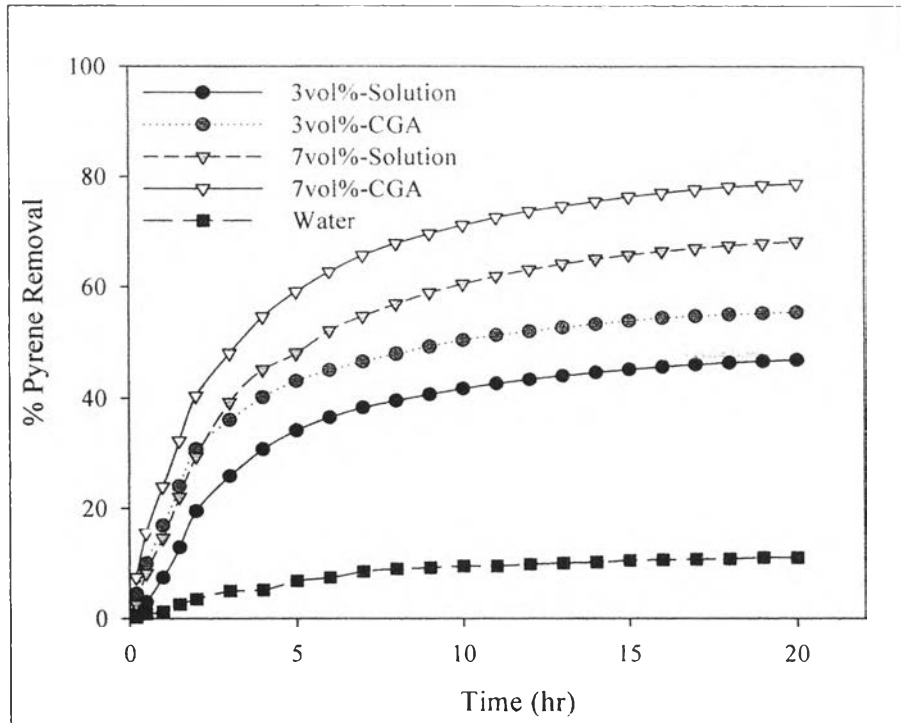
For higher levels of pyrene contamination at 12000 mg/kg pumice in Figure 4.11 (b), pyrene removal from the pumice column was 29 and 36% after washing with BioNonex-3 vol % solution and CGA, respectively for 20 hours. Changing the flushing media to BioNonex-7 vol% solution and BioNonex-7% CGA removed 43 and 53% of pyrene, respectively. Using water alone as the washing media removed only 7.5% of pyrene. (change in the same manner as above)

Surfactant solution decreases oil/water interfacial tension and increases the displacement and dispersion of pyrene resulting in enhancing higher removal of pyrene from pumice. The enhancement of pyrene removal in the case of CGA suspension and the surfactant solution was explained by the four mechanisms suggested in the literature, i.e., displacement, solubilization, dispersion, and electric repulsion at the surface of the soil particles. In the case of water flood, Abdul and Gibson (1992) assumed that displacement of waste was the main removal mechanism. They found that as the water front advanced into the porous media, the trapped oily waste droplets became mobile, were displaced, carried by the water through the soil pores, and removed. They also noticed that as the oily waste droplets accumulated and coalesced to form longer streams of oil, they were more difficult to remove from the soil matrix.



It is clear that pyrene removal from the pumice column increased with increasing surfactant concentration. This can be explained by the solubility of pyrene in the surfactant micelles. We consider that the number of micelles formed relates with the solubilization of pyrene. Since solubilized pyrene is easily mobilized and washed from the pumice column. Similar trends were observed for all levels of contamination. When BioNonex concentration was increased from 3% to 7%, the pyrene removal increased significantly. Changing surfactant flushing media to CGA can also enhance the removal of pyrene

(a)



(b)

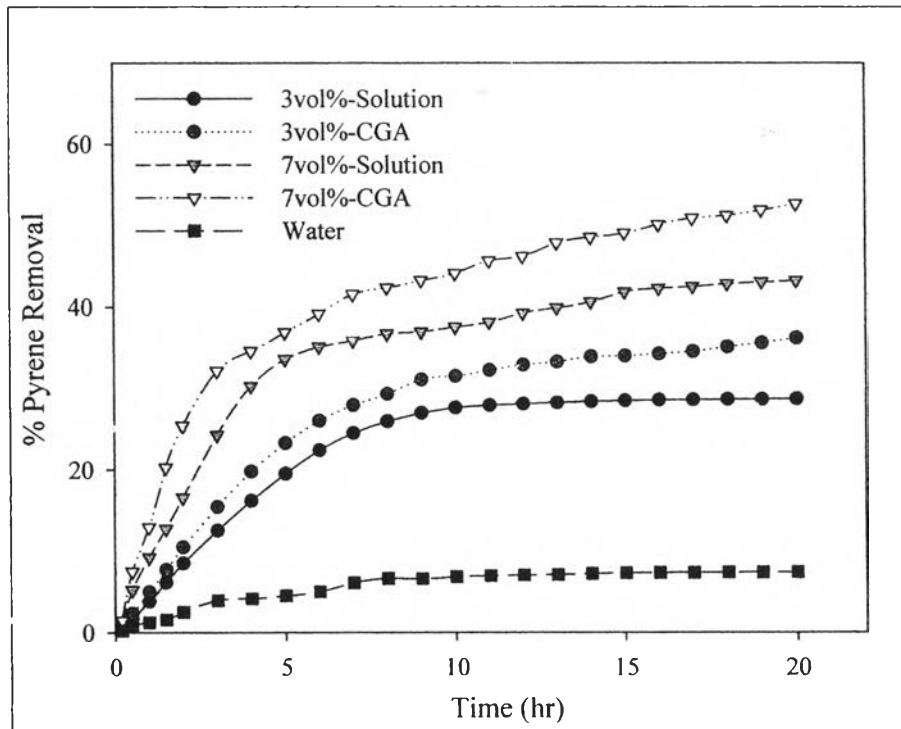


Figure 4.11 Pyrene removals in column operation with different flushing media (a) 1300mg/kg and (b) 12000 mg pyrene/ kg pumice.

#### 4.2.2 Comparison of CGA and surfactant solutions

It is evident from the Figure 4.11 (a) and (b) that CGA was more effective in removing pyrene than the conventional surfactant solution on the same concentration basis. In case (a) the contamination level of 1300 mg pyrene/kg pumice, changing flushing media from aqueous solution to CGA suspension resulted in an 8 % increase of pyrene removal in the case of 3 vol%-BioNonex and 10 vol% for the case of 7 vol%-BioNonex. For pyrene contamination of 12000 mg/ kg pumice in case (b), changing flushing media from aqueous solution to CGA suspension resulted in a 7 vol% increase of pyrene removal for 3 vol %-BioNonex and 9 vol % in the case of 7 vol%-BioNonex

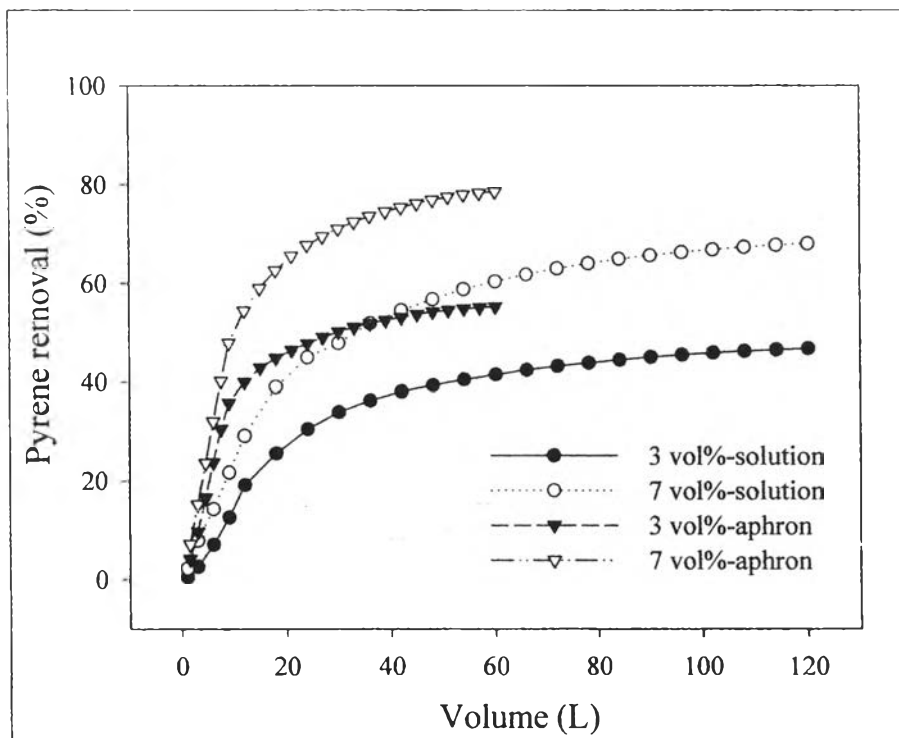
Experimental results of pyrene removal from column flushing with different flushing media are shown in Figure 4.12 (a) and (b). Percentage of pyrene removal is plotted as a function of the aqueous volume of flushing media for each data set. In the case of CGA flushing, the aqueous volume of surfactant solutions was measured after most of CGA bubbles coalesced and turned to liquid. It is obvious that at the same aqueous volume, pyrene removal by CGA flushing was significantly greater than that by conventional surfactant solution washing. The increase in pyrene removal when flushing media was changed from conventional surfactant solution to CGA was greater when comparison was based on volume of flushing media instead of time. Similar trends were observed both in the case of 3 vol% and 7 vol%-BioNonex and also in the two contamination levels, 1300 mg pyrene/kg pumice and 12,000 mg pyrene/kg pumice. CGA required less fluid volume to use in column flushing compared to that required in conventional solution washing. Total liquid volume in the case of CGA was about 60 L compared to 120 L in the case of conventional surfactant solution. Based on the results, it can be concluded that changing flushing media from surfactant solution to CGA not only enhanced pyrene removal but also decreased volume of surfactant fluid used in the experiments.

Even though the CGA generated from surfactant solution is homogeneous fluid at the time of pumping, within the porous medium separation of the gas and liquid phase occur, resulting in a two-phase flow system. The collapse of CGA bubbles in the column

depends on several factors such as the flow rate, pore structure and the type of medium. The gas and liquid phases propagate through the porous medium at different rates with the liquid advancing faster than the gas phase (Roy et al., 1995). In this case, the effluent from the pumice column appeared as a series of gas bubbles and liquid drops. The gas portion that existed in the column may carry some volatiles present in the column, however, the gas phase was not monitored for volatiles in this study. Because pyrene has high boiling point and also melting point, it is hard to be vaporized. The removal mechanisms in the case of CGA were thought to be the same as those of aqueous surfactant solution, which are displacement, solubilization, dispersion, and electric repulsion at the surface of the soil particles.

CGA bubbles should have the same charges on the surfaces as the surfactant from which it is generated (Hashim, 1998). The surface area provided by the CGA bubbles may also play a significant role in the removal of pyrene from pumice pore spaces. The small CGA bubbles can move through the pores of pumice effectively thus enhanced pyrene removal. The difference in density of CGA and conventional solutions may influence pyrene removal. The specific gravity of CGA suspensions is in the range of 0.3-0.4 (Sebba, 1987). The conventional aqueous solution has estimated specific gravity of 1.0, equal to water. Because the CGAs are lighter than the conventional solution, they can move in the up flow direction throughout the pumice column and their performance of pyrene removal is superior to the conventional surfactant solution.

(a)



(b)

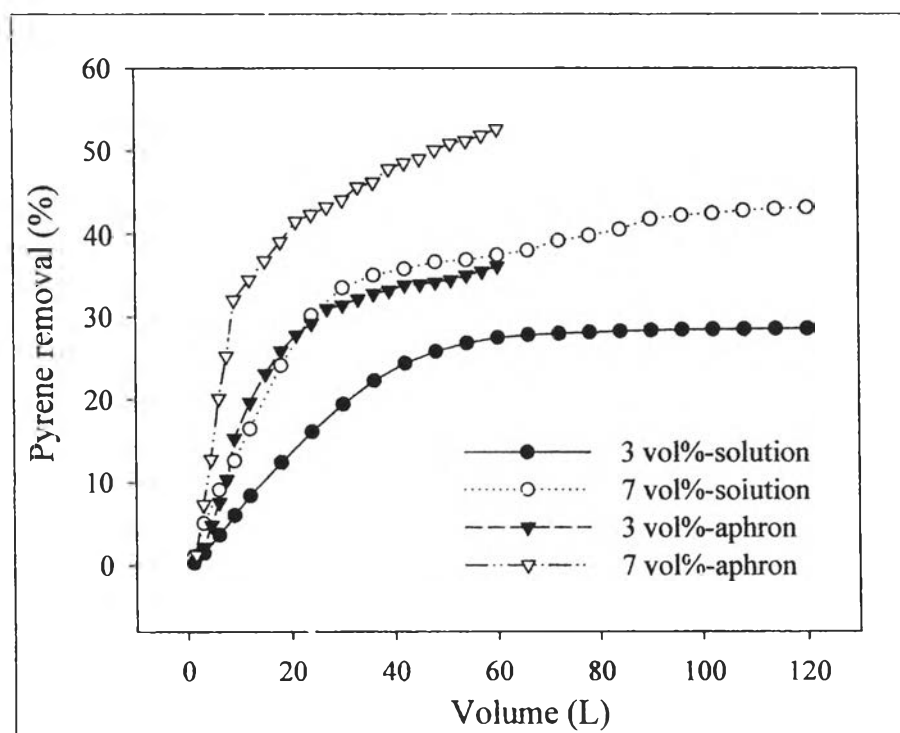


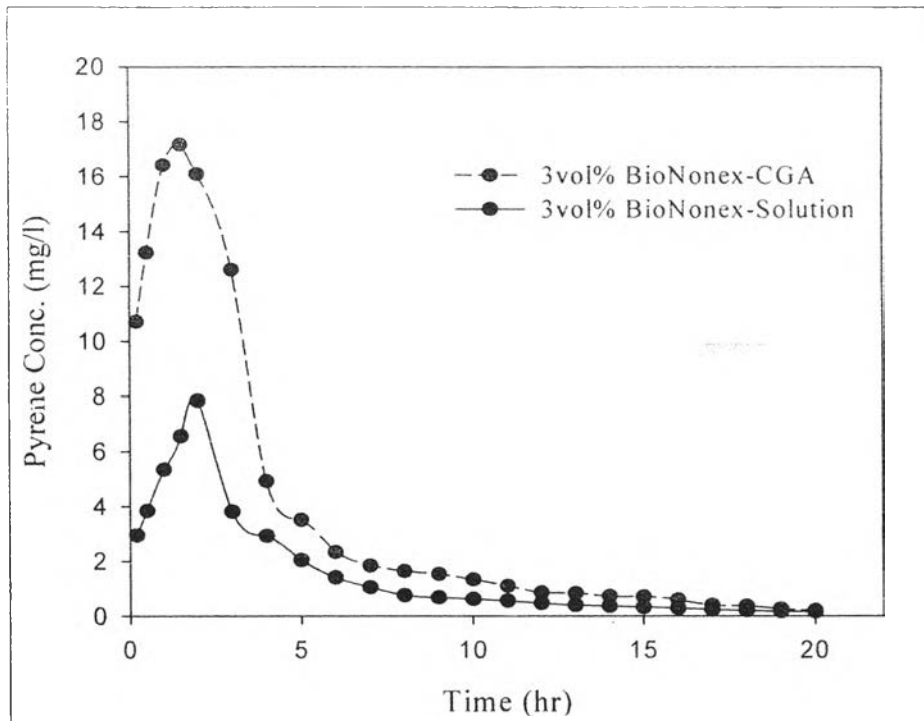
Figure 4.12 Pyrene removals in column operation based on aqueous volume of flushing media (a) 1300 mg/kg and (b) 12000 mg pyrene/kg pumice

### **4.2.3 Concentration of pyrene in the effluents**

Figure 4.13 shows the concentration of pyrene in the effluents of soil flushing in column of contamination level at 1300 mg pyrene/kg pumice using (a) BioNonex-3 vol% and (b) BioNonex-7 vol%, both in the forms of conventional aqueous solution and CGA suspension.

The figure shows that pyrene concentrations in the effluent using CGA as the flushing media are much higher than in those using conventional surfactant solution, both for 3 vol% and 7 vol% concentrations. For 3 vol%-BioNonex, concentration of pyrene in the effluent increased steadily at the initial washing stage and approached the maximum value in 2 hours of operation. The maximum concentration of pyrene was 17.2 mg/l when CGA was used as the flushing media compared to 7.8 mg/l in the case of conventional solution. For 7 vol%-BioNonex, concentration of pyrene in the effluent reached maximum in about 1.5 hours of operation. The maximum concentration of pyrene was 20.2 mg/l when CGA was used as the flushing media compared to 11.3 mg/l in the case of conventional solution. It can be seen that the higher surfactant concentration required less time to achieve the maximum pyrene concentration in the effluents. Pyrene concentrations in the case of CGA flushing were about two times greater in magnitude than those in the case of conventional aqueous flushing. In addition to this, CGAs typically consist of 65% gas by volume and therefore require less volume of surfactant fluid used in column flushing.

(a)



(b)

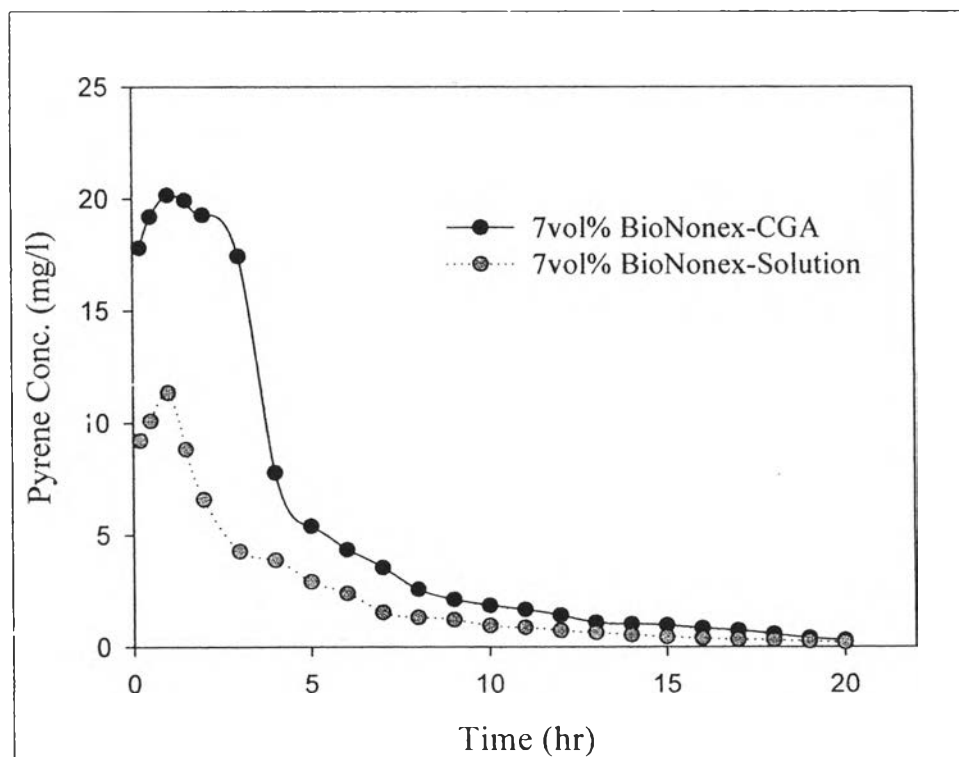


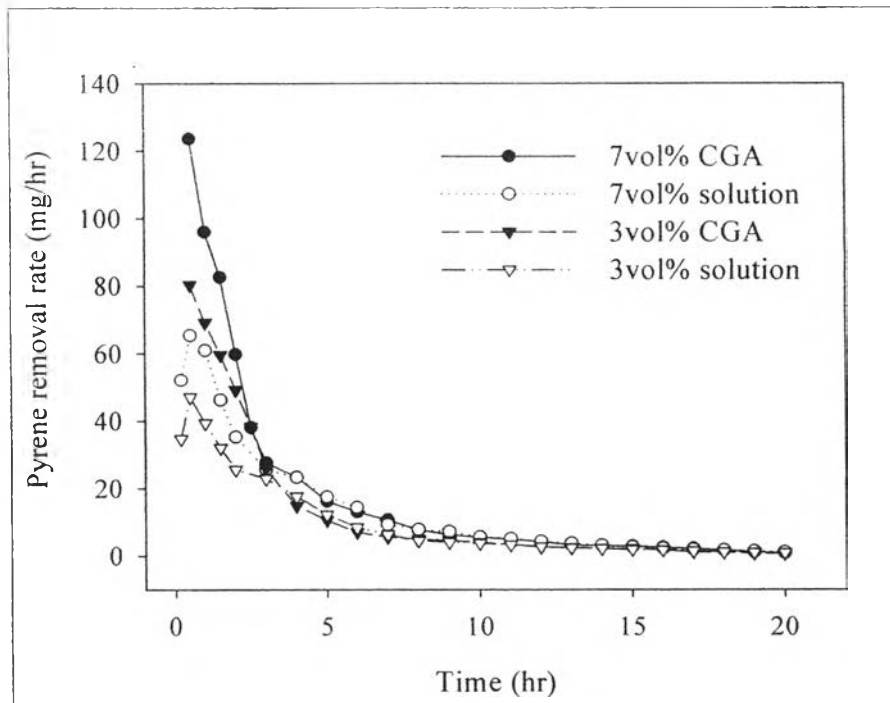
Figure 4.13 Concentration of pyrene in the effluents of soil flushing in column using (a) BioNonex-3% and (b) BioNonex-7%

#### **4.2.4 Rate of pyrene removal**

Figure 4.14 (a) and (b) show pyrene removal rates from column flushing experiment 2 levels of pyrene contamination, 1300 mg/kg and higher contamination level of 12000 mg pyrene/kg pumice, respectively. Pyrene removal rate in all the cases was high in the initial stage of the flushing followed by a slower rate as the experiment continued. Rate of pyrene removal reached maximum at the earlier stage and declined rapidly towards the end of experiments in the case of CGA flush. The higher removal rate in the initial stage was attributed to the removal of pyrene that adsorbed loosely on the external surface of pumice. As the experiments continued, surfactant molecules moved deeper to solubilize and mobilize pyrene in pumice pores. Some molecules of pyrene that deeply adsorbed in pumice pores were hard to be mobilized thus slower the rate of pyrene removal. Pyrene removal rate in using CGA flush was significantly higher compared to that in the case of conventional surfactant solution for both 3 vol% and 7 vol%-BioNonex. Trends of the results were similar for pyrene removal rate in contamination levels of 1300 and 12000 mg pyrene/kg pumice.



(a)



(b)

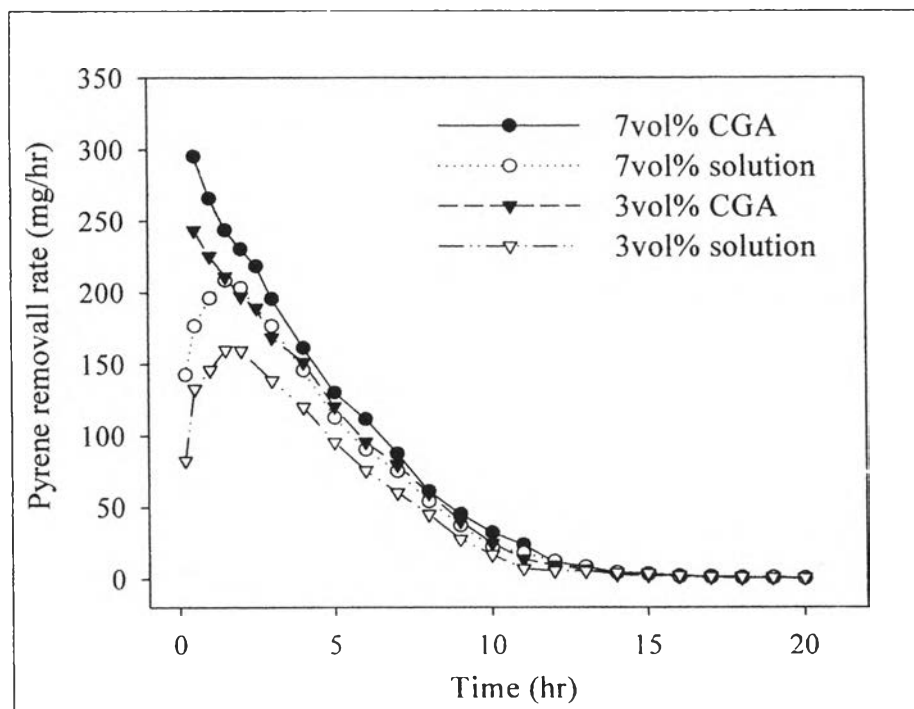
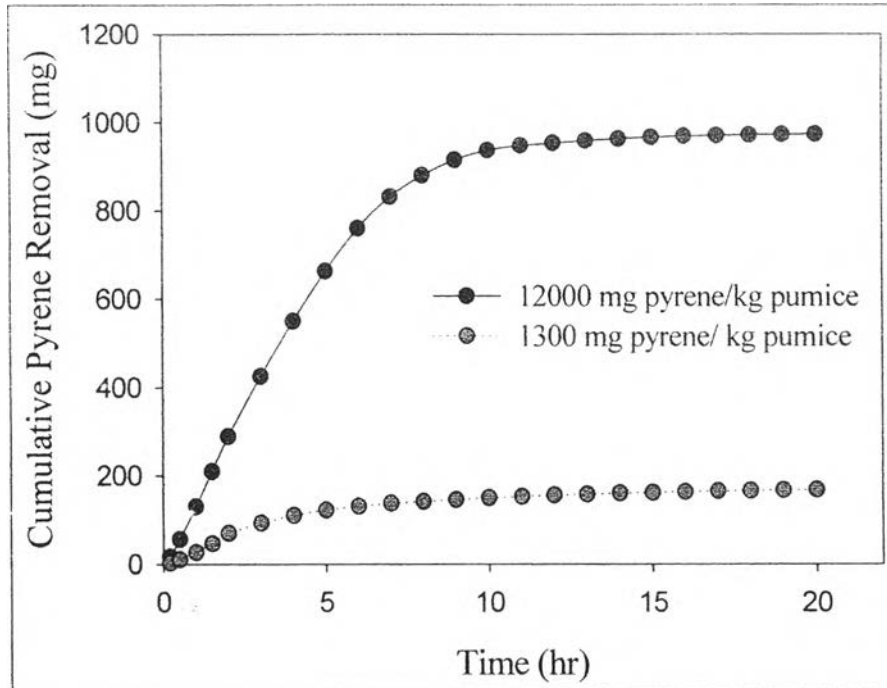


Figure 4.14 Pyrene removal rate in column operation with different flushing media (a) 1300mg/kg and (b) 12000 mg pyrene/ kg pumice.

#### **4.2.5 Influence of initial pyrene concentration loaded on pumice**

Figure 4.15 shows the accumulative pyrene removal in column showing 2 levels of pyrene contamination, 1300 mg/kg and higher contamination level of 12000 mg pyrene/kg pumice, using (a) 3 vol% BioNonex solution and (b) 3 vol% BioNonex CGA as flushing media. It is evident from the figure that accumulation of pyrene removal increased as the surfactant was pumped through the column. Using 260 g pumice for all experiments, total pyrene loaded was about 340 and 3120 mg in contamination level of 1300 mg/kg and 12000 mg/kg, respectively. After 20 hours of flushing operation, pyrene concentration in the effluents became steady state. Using 3 vol% BioNonex solution as a flushing media totally removed 168.5 mg of pyrene in the case of 1300 mg/kg contamination compared to 973.5 mg in the case of 12000 mg/kg contamination. Similar trends were observed in the case of CGA flushing. Total pyrene removed using 3%-BioNonex CGA was about 198.1 mg in the level of 1300 mg/kg contamination and 1044 mg in the case of 12000 mg/kg contamination. It can be seen that as the contamination level increased, pyrene removal increased, but the removals were limited by the pyrene solubility in the flushing media at higher contamination level.

(a)



(b)

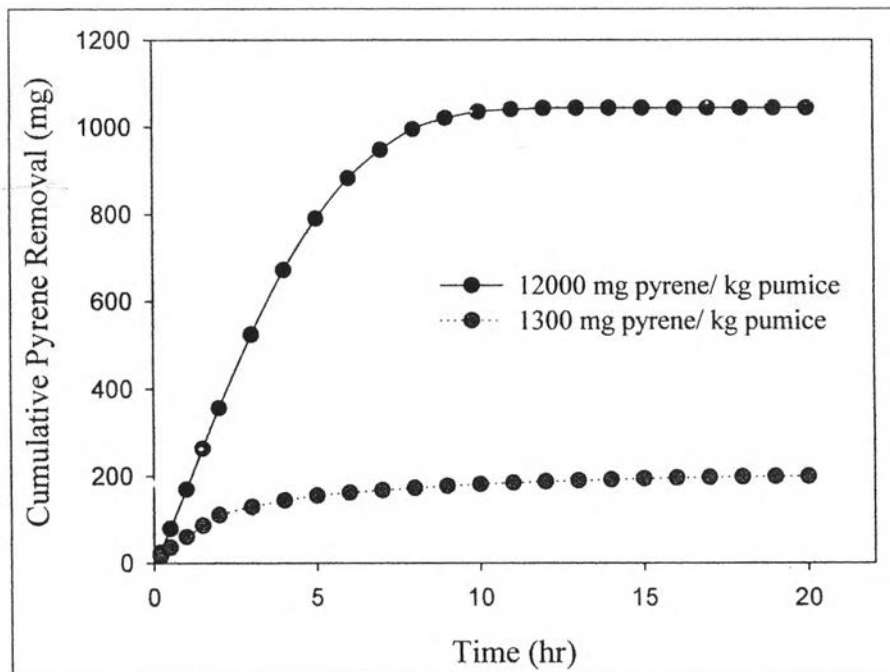


Figure 4.15 Accumulative pyrene removals in column showing 2 levels of pyrene contamination using (a) BioNonex-3% solution and (b) BioNonex-3% CGA as flushing media.

#### 4.2.6 Mass balance of pyrene

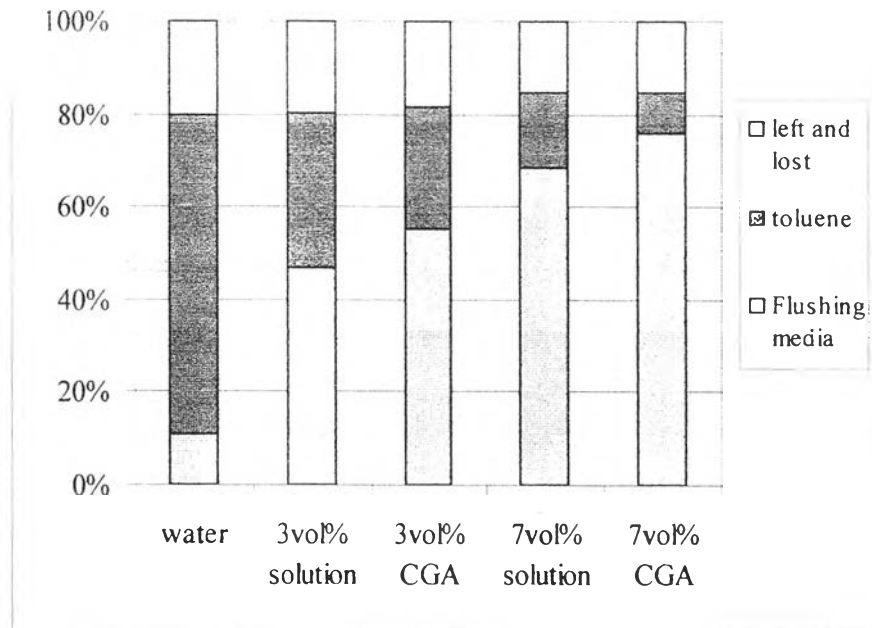
Figure 4.16 shows mass balance of pyrene in the experiments based on total pyrene adsorbed in pumice at the contamination levels of (a) 1300 mg/kg and (b) 12000 mg/kg pumice. After washing column with different flushing media, pumice in the column was then extracted by toluene to determine the residual concentration of pyrene that may be left in the pumice. Total pyrene loaded in pumice was characterized as four phases:

- (1) pyrene that was removed from pumice by the flushing media
- (2) pyrene that was removed from pumice by toluene extraction
- (3) pyrene that was left in pumice and was considered as the residual unremovable pyrene
- (4) pyrene lost due to sediment flushing out of the column and also other reasons.

Amount of pyrene removed by the flushing media and by toluene extraction were considered together as the mobile phase pyrene. As discussed before, adding surfactant to the solutions made pyrene more mobile. Increase in surfactant concentration and change in flushing media from conventional surfactant solution to CGA suspension enhanced the removal of pyrene in all contamination levels. Similar trends were observed for 1300 mg/kg and 12000 mg/kg contamination levels.

However, the results of mass balance calculating indicate that even toluene extractions could not remove most of pyrene loaded on pumice. There was some pyrene that was deeply trapped in pumice pores and that amount was considered the residual pyrene. The residual pyrene in all experiments was around 20% of initial pyrene loaded on pumice. In addition, some pyrene that might be lost during the experiments was considered together with the residual pyrene. Pyrene lost was considered to be pyrene that was adsorbed on pumice sediment and washed out of the column with the flushing media.

(a)



(b)

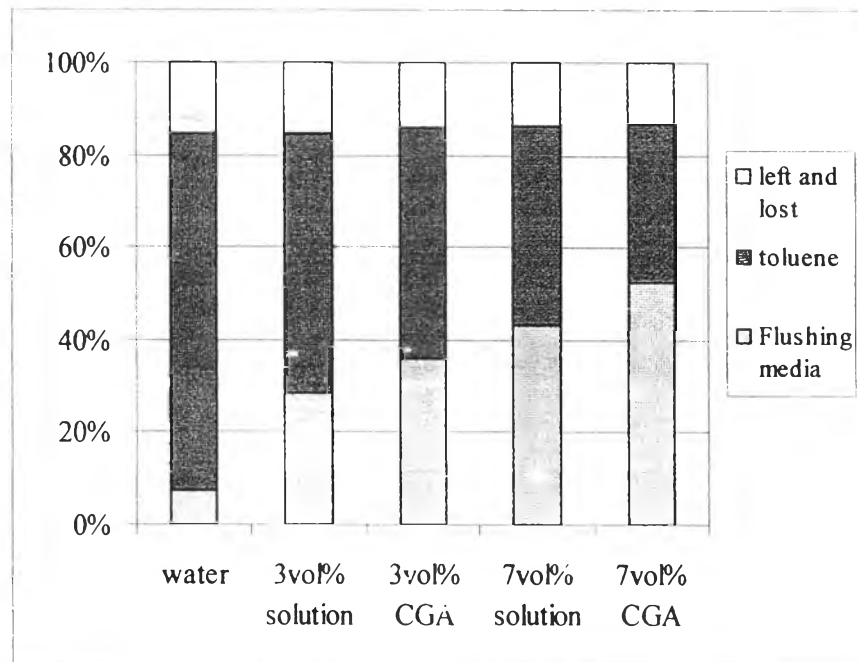


Figure 4.16 Mass balance of pyrene in the experiments based on total pyrene adsorbed in pumice at the contamination levels of (a) 1300 mg/kg and (b) 12000 mg/kg pumice.