

# CHAPTER 3

## METHODOLOGY



### 3.1 Materials

#### 3.1.1 Pumice

Pumice was purchased from a local market and used as a model for soil in order to avoid the interference of organic matters etc. existing in natural soil. Pumice as received is porous, brown in color and has a diameter of 3.0-6.0 cm as shown in Figure 3.1 and its properties are shown in Table 3.1. After drying in an oven at 110°C for 6 hours, pumice was ground and sieved through a US standard sieve to sort into three sizes; 4.0-4.75 mm, 4.75-6.3 mm and 6.3-8.0 mm. The fraction 4.75-6.30 mm was used for the soil washing experiments.

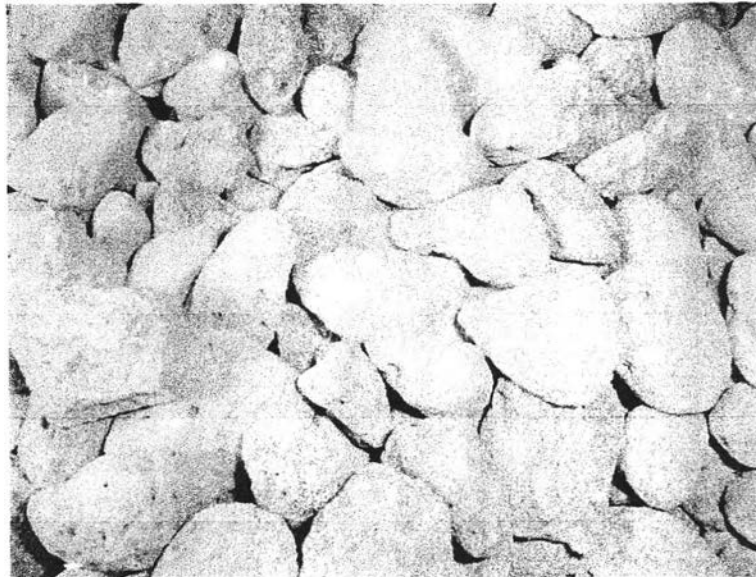


Figure 3.1 Pumice as received from a local market.

Table 3.1 Properties of pumice use in this experimental study.

Properties	Value
Particle size, cm	2.5-6.0
Specific surface area, m <sup>2</sup> /g	4.373403
Pore volume, cm <sup>3</sup> /g	0.00192
Moisture loss @110°C, %	5
pH	7



Figure 3.2 Grind pumice from coarse grinder.



Figure 3.3 4.0-4.75 mm pumice with the US standard sieve.

### 3.1.2 Pyrene

Pyrene, a 4 benzene-rings polycyclic aromatic hydrocarbon (PAH), was purchased from MERCK-Schuchardt Chemical Company, Germany, was 99% pure, as an analytical grade, and was used as target contaminant. As purchased, pyrene is a pale yellow-green solid and has a melting point of 145-148°C. The empirical formula of pyrene is determined to be C<sub>16</sub>H<sub>10</sub> and the molecular weight is 202.26 g/mol. Pyrene has low solubility in water, 0.013-0.171 mg/l at 25°C. The chemical structure of pyrene is shown in figure 3.2.

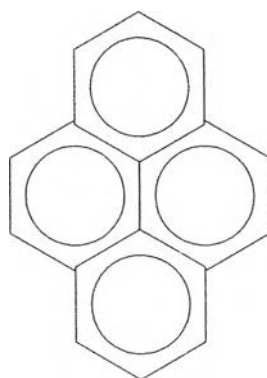


Figure 3.4 Structural molecule of pyrene.

### 3.1.3 Surfactants

Two commercial types of non-toxic and readily biodegradable surfactants were used: BioSolve and BioNonex. BioNonex, obtained from Apels Cheminvest AB, Mossv, Sweden, is a Swedish oil clean up product that has been used for over eight years in Sweden where it is now well accepted. In Sweden BioNonex is used as a first line of defense against petrol and diesel ignition and in the clean up operation of petrol, diesel and oil spills. It was recognized that BioNonex can be utilized in a number of other technologies associated with land remediation and pollution clean up as well as in its essential role as a safety and cleaning tool.

BioSolve, obtained from The Westford Chemical Corporation, Massachusetts, USA, is a patented, water based BioSurfactant/Bioremediation accelerant that offers

superior desorption and/or solubilization of a wide range of contaminants in the soil matrix. BioSolve has 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. BioSolve offers distinct advantages in the treatment of aquifers and soils contaminated by non-aqueous phase liquids (NAPLs) and dense non-aqueous phase liquids (DNAPLs). Many times contaminate removal at existing pump and treat and other systems has failed to yield desired results; BioSolve can play a major role achieving positive results in a cost effective and time effective manner. Physical properties of the surfactants from the suppliers are listed in Table 3.2.

Table 3.2 Properties of BioSolve and BioNonex.

Properties	BioSolve	BioNonex
Boiling Point, °C	100	100
Melting point, °C	<0	0
Solubility with water, %	100	100
Density, kg/m <sup>3</sup>	Approx. 1000	Approx. 1000
pH	9.1*/-.3	Approx. 7
Biodegradable	yes	yes

## 3.2 Experimental Methods

### 3.2.1 Pumice pretreatment

Pumice was dried in an oven at 110°C for 6 hours and then was ground and sieved through a US standard sieve to sort into three sizes; 4.0-4.75 mm, 4.75-6.3 mm and 6.3-8.0 mm to study the effect of pumice's particle size on adsorption and extraction of pyrene.

### 3.2.2 Pyrene adsorption and extraction by toluene

- (1) Three sizes of pumice was prepared; 4.0-4.75 mm, 4.75-6.3 mm and 6.3-8.0 mm, 20 g for each size and then 5 g of pumice, varied in size, was placed into

the Erlenmeyer flask (250 ml), total 12 flasks were used.

- (2) Solutions of pyrene in toluene were prepared at concentrations of 1000, 4000, 7000 and 10000 mg/l, 30 ml each, and then 10 ml of each solution was placed in the flasks containing pumice. Pumice sizes and concentrations of pyrene solutions are varied.
- (3) The flasks were corked and then were shaken in the orbital shaker at 100 rpm for 3 hours, to let pyrene adsorb on the pumice.
- (4) Then the contaminated pumice was separated from the solution and was dried in an oven at 110°C for 6 hours in order to evaporate all toluene that may be left in pumice. The drained toluene solutions were collected and analyzed for pyrene concentration by a gas chromatograph in order to determine the quantities of pyrene loaded on pumice by mass balance equation. The procedure following The Standard Methods 6440 B. liquid-liquid extraction chromatographic method for polycyclic aromatic hydrocarbons including pyrene was used (American Public Health Association, 1998). SUS packed column was used with nitrogen carrier gas at 40 mL/min flow rate. Column temperature was set at 280°C. The detector was FID detector with 300°C temperature setting. Retention time for pyrene was set at 7-8 minutes.
- (5) The flasks containing different pyrene contaminated levels of pumice were contacted with toluene, 10 ml each, in the orbital shaker at 100 rpm for 3 hours to extract pyrene contaminated from pumice.
- (6) The supernatants of toluene were separated and analyzed to determine quantities of pyrene that was extracted from pumice. The results in relationship of pumice size and pyrene extraction were displayed in the graph form.

### **3.2.3 Effect of concentration and type of surfactant**

- (1) 20 Erlenmeyer flasks (250 ml) containing 5.0 g of pumice size 4.0-4.75 mm were prepared.
- (2) Solutions of pyrene in toluene were prepared at concentrations of 1000, 4000, 7000 and 10000 mg/l, 50 ml each, and then 10 ml of solutions was placed in the flasks containing pumice.
- (3) The flasks were corked and then shaken in the orbital shaker at 100 rpm for 3 hours, to let pyrene to be adsorbed on the pumice. Then the contaminated pumice was separated from the solution and dried in an oven at 110°C for 6 hours. The drained toluene solutions were collected and analyzed for pyrene concentration by a GC in order to determine the quantities of pyrene loaded on pumice by mass balance equation.
- (4) 40 ml of surfactant solutions of BioSolve and BioNonex, at concentrations of 1%, 3%, 5%, 7%, and 10% by volume were prepared. 10 ml of those solutions in each concentration was poured into the flasks containing different contamination levels of pumice. Then the flasks were shaken in the orbital shaker at 100 rpm for 3 hours to extract pyrene from pumice.
- (5) After extracted, pumice was separated and the surfactant solutions were centrifuged at 3000 rpm for 5 minutes to deposit all sediment. The supernatants of surfactant solutions were analyzed to determine concentrations of pyrene extracted. Pyrene removal efficiencies of different types and concentrations of surfactants were then compared.

### **3.2.4 Effect of extraction time on pyrene removal efficiency**

- (1) 33 Erlenmeyer Flask (250 ml) containing 5.0 g of pumice size 4.0-4.75 mm were prepared.
- (2) Solution of pyrene in toluene was prepared at concentration of 1000 mg/l and then 10 ml of this solution was poured in each flask containing pumice. Then

the flasks were corked and shaken in the orbital shaker at 100 rpm for 3 hours to let pyrene to be adsorbed onto pumice.

- (3) Then the contaminated pumice was separated from the solution and dried in an oven at 110°C for 6 hours. The drained toluene solutions were collected and analyzed for pyrene concentration by a GC to determine the quantities of pyrene loaded on pumice by mass balance equation.
- (4) 3 types of extraction solutions were prepared; BioSolve and BioNonex solutions at concentration 5% by volume, and water alone. 10 ml of those solutions was poured in each concentration into the flasks containing contaminated pumice. Then the flasks were shaken in the orbital shaker at 100 rpm at intervals ranging from 0.25 to 24 hours to extract pyrene from pumice.
- (5) After extracted, pumice was separated. The samples of surfactant solutions and water of the time interval were centrifuged at 3000 rpm for 5 minutes to deposit all sediment. The supernatants were analyzed to determine concentrations of pyrene extracted.

### **3.2.5 Pyrene removal on real soil containing organic matters**

Because the natural soil is not rigid in structure and some properties cannot be controlled, the real soil cannot be placed in the column. Batch experiment in the Erlenmeyer flask was done to study effect of organic matter consisting in the real soil on pyrene removal. All experimental procedures were the same as mention in 3.2.4 except 5 g of dry natural soil was used instead of pumice and BioNonex is the selected surfactant to test with the real soil.

### **3.2.6 Solubility experiments**

Batch experiments in Erlenmeyer flasks were performed at room temperature (25°C) to determine the pyrene solubility in water, BioNonex and BioSolve. For each surfactant, five concentrations were selected and solutions were prepared by adding 0.5 g of pyrene to 20 ml of the surfactant solution. This solution was stirred for 24 h to allow pyrene to equilibrate with the surfactant solution. The resulting solution was centrifuged

and analyzed for pyrene using GC.

### **3.2.7 Stability of colloidal gas aphron (CGA)**

As from the preliminary studies, BioNonex showed superior pyrene removal over BioSolve, so that BioNonex was used for the further soil flushing experiments in column to compare performance of soil washing with conventional surfactant solution and CGA suspensions. CGA generator adapted from Sebba F. (1987) was employed in our laboratory. In this experiment, CGA was generated from the spinning disc generator at the rotation speed of 5000 rpm for 9-12 minutes. The stability of CGA was investigated by varying surfactant concentration. Concentration of BioNonex solutions used was at 3% and 7% by volume. The stability was measured in terms of half-life, which was defined as the time required for half the amount of original liquid to drain.

1 L of CGA suspensions generated from BioNonex solution was poured in the measuring cylinder. Then the height of the clear liquid interface below the dispersion was measured with time. The half life of CGAs then could be determined. All data from these experiments are based on duplicated samples; the coefficient of the variation was expected to be less than +/- 1%.

### **3.2.8 Column flushing experiments**

1 L of pyrene in toluene solutions were prepared at the concentration of 1,000 and 10,000 mg/l to get two different levels of pyrene contamination. The solutions were divided into 4 parts in 4 of 500 mL-Erlenmeyer flasks, 250 mL each. 260 g of pumice was separated into 4 parts and each 65 g of that was put in each flask and then the flasks were shaken in the orbital shaker at 100 rpm for 3 hours to let pyrene to be adsorbed on the pumice. Then pumice was separated from the solution and dried in an oven at 110°C for 6 hours to evaporate all residual toluene. The drained toluene solution was analyzed for pyrene concentration to determine the amount of pyrene loaded on pumice. Dry contaminated pumice, estimated 260 g, was packed in the column to perform flushing experiments in column.



Acrylic column (55 cm long and 5 cm in inner diameter) was used for all soil flushing experiments. The outlet and inlet ends of the column were fitted with wire mesh to prevent pumice from being washed out of the column and to distribute the flow uniformly across the soil. Schematic diagram of the experimental column is shown in Figure 3.5.

All experiments were conducted in the upflow mode with conventional surfactant solutions and colloidal gas aphyron (CGA) suspensions generated from BioNonex at a flow rate of 100 ml/min. Concentrations of BioNonex were used at 3% and 7% by volume. The CGA generator was used in a continuous mode with CGA suspensions being withdrawn from one side and the surfactant solutions fed from the other. After column flushing, the duplicate effluent samples were collected in the time interval ranged from 0.5-20 hours and then analyzed for pyrene concentrations. Performances of soil flushing and pyrene removal efficiencies were then compared.

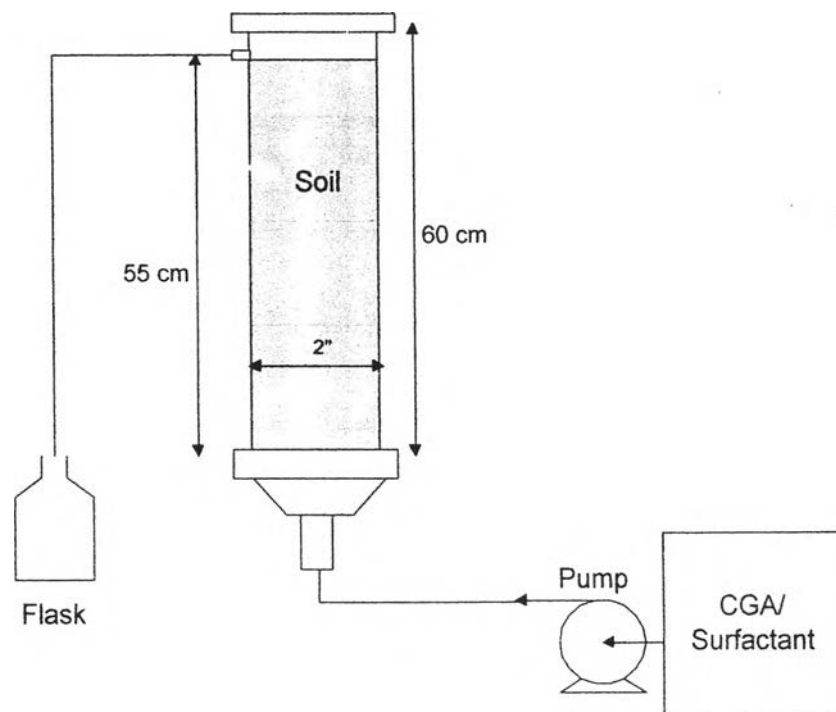


Figure 3.5 Schematic diagram of the experimental apparatus.

### **3.2.9 Surface area and pore size of pumice**

Because surface area and pore size of pumice influence pyrene adsorption and performance of surfactant washing, these properties should be studied. The specific surface area, pore volume and average pore diameter of pumice were analyzed by Brunauer, Emmett and Teller (BET) apparatus. Pumice was analyzed as purchased from the local market, 1300 mg pyrene/kg pumice loading and after washed with surfactant.