

## CHAPTER II

### THEORY AND BACKGROUND

#### 2.1 Activated carbon

The great advantages that activated carbons have over other recovery systems is the ability to recover the organic from low concentrations easily and inexpensively (Cheremisinoff, 1993). These low concentrations can not be readily removed by conventional treatment methods.

The effectiveness of activated carbon for removal the organic compound from fluid by adsorption is dependent upon its importance properties. The major significant is surface area. Most the activated carbon usually has surface areas in order of 450 - 1,800 m<sup>2</sup>/gram and example are shown in the table 2.1,

Table 2.1 Surface areas of typically available activated carbon

| Origin            | Surface area (m <sup>2</sup> /gram) |
|-------------------|-------------------------------------|
| Bituminous coal   | 1,200 - 1,400                       |
| Bituminous coal   | 800 - 1,000                         |
| Coconut shell     | 1,100 - 1,150                       |
| Pulp mill residue | 550 - 650                           |
| Pulp mill residue | 1,050 - 1,100                       |
| Wood              | 700 - 1,400                         |

The other property of which is less significance is the chemical nature of the carbon surface. It also influences on adsorption process by applying the principle of "like dissolves like" or can be said that "like adsorbs like". This chemical nature varies with the carbon types and can influence attractive forces between molecules. The most parts of activated carbon surface are nonpolar or hydrophobic (Keller et al., 1987), making the adsorption of inorganic electrolytes difficult but easy for organic. Eventhough, because of its high surface area, it can adsorb aromatic and unsaturated compounds better than some polar surfaces such as silica gel.

The third property is the pore structure of activated carbon. This property influences the large surface-to-size ratio. They are classified into two classes in respect to size. The important pore system is the small one called "micropore". It is involved nearly all the surfaces available for adsorption purposes. The micropores are developed primarily during carbon activation. They provide the large surface area for adsorption. The macropore contributes very small in adsorption. They do not add perceptibly to the surface area but provide a passageway to the particle interior and the micropores. The pore size distribution figures out the size distribution of molecule that can enter the carbon particle to be adsorbed. Large molecule can block off micropores, rendering useless their available surface areas. However, due to irregular shapes and constant molecular movement, the small molecules usually can penetrate to the micropores.

In application, activated carbon can be divided into two classes. The first class is Gas-adsorbent carbons that are used for purification application in the vapor or gas phase. The second class is Liquid-phase carbons that are used to decolorize or purify liquids, solutions, and liquifiable materials such as waxes.

The main distinction between gas-adsorbing and liquid-phase carbons lie in the pore size distribution. Gas-adsorbing carbons usually have the most pore volume in the micropore, 3 - 50 Å radius, and macropore, 1,000 - 50,000 Å radius, whereas with little pore volume in the range of 50 - 1,000 Å radius. Liquid-phase carbons have significant pore volume in the range of 50 - 1,000 Å radius, permitting ready access of liquids to the micropore structure and resulting in accomplishment of adsorption equilibrium for smaller adsorbate.

In generally, liquid-phase carbons have about the same surface area as gas-adsorbing carbons but larger total pore volume. Liquid-phase carbons are also divided into two types regarded to physical form including powdered form and granular form. In selection these two types for a given application depend on comparative economics, types of existing equipment, the carbon usage rate, variability of flowrate, the impurity concentration and composition, nature of the application, cleanliness, and disposal ways.

In this work, liquid-phase carbon in granular form is used. The commercial name is "Filtrisorb-300" that has mesh of 8x30 from Calgon company.

Adsorption capacity of the most important property of both powdered and granular carbon because it determines volume that liquid can be treated per weight of carbon and also the direct operating cost of carbon treatment and the sizing of equipment. Adsorptive capacity may be not related with surface area, high surface area does not have high adsorptive capacity because only wetted surface area that is effective and it never equals the total surface area.



To use granular activated carbon, pressure drop or bed expansion can be occurred. By operating downflow and confined upflow in column will generate pressure drop or head loss. In contrarily, for unconfined upflow column operation, the bed expansion is of primary importance.

In choosing the suitable carbon in system, the properties after it has been reactivated several times are more important than the properties of virgin carbon. After granular carbon is regenerated, the total surface area available for adsorption are significantly reduced. This is attributed to ash plugging of or inadequate removal of impurities from the small pores. For using the small pore in adsorption processes, the performance of the carbon will not be greatly affected by regeneration.

The particle size of carbon is one of importance consideration. The relative coarse carbons (12x20 mesh or 8x30 mesh, etc.) are generally used in systems with downflow, a high linear flowrate, relatively high suspended solids, relatively low impurity removal requirement, and high viscosity liquids. The finer pores (12x40 mesh, 20x40 mesh) are generally used with upward flow, a low linear flowrate, relatively low suspended level of solids, relatively high impurity removal requirement, and low viscosity liquids.

The Filtrasorb-300 was decided using in this research because of operation in countercurrent direction and adsorption of low organic concentration. However, it was not quite appropriate in upflow direction operating.



## 2.2 Adsorption of organic contaminant on activated carbon bed

Adsorption is a separation process in which certain components of a fluid phase are transferred to the surface of a solid adsorbent. When the water containing the organic contaminants is feed through the activated carbon bed, the organic solute will be adsorbed onto the carbon. In the ordinary temperature, the physical adsorption or physisorption is usually occurred, this adsorption process is provided by Van der Waal's force between the adsorbate and adsorbent. When the temperature increases, which is often higher than 200 °C or 400 °F, the chemical adsorption or chemisorption will be prevailed due to the activation energy increasing and will be available to make or break chemical bonds. Chemisorption can also be occurred by chemical interaction of adsorbate with surface molecules. This process is often irreversible.

The simple method, which is used for determining the feasibility of the activated carbon usage for the adsorption application, is plotting an adsorption isotherm. The adsorption isotherm expresses the distribution of adsorbate, between the adsorbed phase and solution phase at equilibrium by plotting of the amount of adsorbate adsorbed per unit weight of carbon versus the concentration of the adsorbate remaining in solution.

This equilibrium can be clarified by the Freundlich isotherm (Cheremisinoff, 1993; Suzuki, 1990),

$$x/m = k_1/n \quad (2.1)$$

where  $x$  = amount of adsorbate adsorbed, mg/L  
 $m$  = weight of activated carbon, mg

- $c$  = equilibrium concentration of adsorbate in solution  
after adsorption, mg/L
- $x/m$  = concentration in the adsorbate adsorbed per unit  
weight of activated carbon

By taking the logarithm of both sides, the following equation is achieved

$$\log x/m = \log k + (1/n) \log c \quad (2.2)$$

This equation is straight line which slope is  $(1/n)$  and intercept is  $\log k$ . It provides valuable information for adsorption expectation. However, there may be occasionally departure from linearity that is due to many effects for example the appearance of nonadsorbable impurity, several adsorbates that have difference degree in adsorption, or several adsorbates that some have difference rate and capacities in adsorption process. Isotherm test can be used to determine whether a required adsorbate is removed completely and the ultimate amount of activated carbon that should be used for each application.

Adsorption application in column can be operated in many ways such as fixed bed or pulse bed. Sometimes the beds can be connected together both in series and parallel which depend upon the condition used and operation objectives.

Fixed bed shows the efficient arrangement for conducting adsorption operation in the column. In this operating mode, a packed bed adsorbent is consisted in the column and the stream treated is passed through the bed. Firstly, the adsorbate is fully loaded at the inlet and then downstream. To plot

the relation between an effluent concentration and time profile is provided a called "Breakthrough curve".

At breakthrough, the effluent concentration begins to rise and eventually reaches nearby the influent concentration, it means that the bed is saturated. This concentration is termed "Breakthrough concentration" and this time is called "Breakthrough time". Alternately, this time can be described in terms of the amount of waste treated, expressed as the breakthrough volume or the breakthrough mass.

The part of the bed that displays the active portion where adsorption takes place is called "Mass Transfer Zone" or MTZ. It will travel downstream whether the saturated portion of bed increases along the bed.

Dynamic adsorption testing is also necessary to acquire some essential designed data involving the contact time required and the types of "Breakthrough curve". The usage rate also has been determined to reveal whether a single bed or staged system is preferred.

Adsorption on granular activated carbon in column is diffusion process consisting bulk diffusion of the adsorbate from liquid to the film around the carbon particle, diffusion through the film, internal pore diffusion to the adsorption sites, and competition for site due to displacement of previously adsorbed for multicomponent systems.

The important testing conditions for designing the adsorption in column system with activated carbon adsorbent are included column size, carbon types, particle size, velocity of liquid in the bed, operated temperature, and activated carbon pretreatment.

Carbon types and particle size are determined during isotherm testing. Particle size selection is a critical condition due to the overall diffusion in adsorption on carbon is contributed by the pore diffusion that can conclude that the smaller the particle, the faster the diffusion and the shorter the mass transfer zone.

In a low concentration of liquid level, systems at the higher linear velocity treat more liquid per volume and give the shorter mass transfer zone. In practice, column should be operated at the plant process temperature to make it economically in using. Prewetting carbon is also desired prior start adsorption to expel the air in the column since the air left can result in channeling, high pressure drop and premature breakthrough of adsorbate.

The adsorption of phenol was done by McKay et al. (1985). They found that the isotherm of phenol and also most organic from dilute aqueous solution adsorbed on carbon were Langmuir type. For EPA research entitled Carbon Adsorption Isotherm For Toxic Organic was done by Pobb and Cohen (1980) examined the value of  $K$  of 21 and  $1/n$  of 0.54 respectively for phenol adsorption on activated carbon.

### **2.3 Adsorption of surfactant on activated carbon**

Surfactant adsorption at the solid-liquid interface depends on the nature of the structural groups in the surfactant molecule, the nature of the structural groups on the solid surface, and the environment of the aqueous phase such as, pH, electrolyte, and temperature:

In the system that concentration of the surfactant is higher than CMC, the adsorption is dependent only on the monomer concentration. Consequently,



the surfactant adsorbed on the carbon surface will be in equilibrium with the inlet surfactant monomer concentration in solution that indicates that the surfactant adsorption is constant above CMC.

Because activated carbon acts as heterogeneous adsorbent, so there are many ways of surfactant adsorption on carbon surface. The hydrocarbon tails can lie down on the carbon. For the surfactant has an ionic head group, it can adsorb onto an opposite charge site of the carbon surface.

The adsorption of the surfactant solution is commonly observed by the Langmuir isotherm. Eventhough, there are many factors that can effect on the shape of it involving micellization of surfactant, surface potential, heterogeneity of the solid adsorbent, and the lateral interaction.

Schwuger and Smolka (1977) and Yusuji (1992), described that the adsorption of sodium dodecyl sulfate (SDS), which is used as surfactant in this work, appeared to be the Langmuir isotherm type. The adsorption of nonionic surfactant on the solid adsorbent shows the higher concentration adsorbed than of the ionic surfactant with the same hydrocarbon length. This is due to the strong electrical repulsion of the similarly charged hydrophilic surfactant groups.

In contrast, the saturation adsorption of ionic surfactant may be higher than of the nonionic this cause by smaller space requirement and higher packing density of ionic surfactant as shown in the case of SDS adsorption.

## 2.4 Surfactant and micellization

“Surfactant” or “surface-active-agent” is a substance that at low concentration adsorbed at some or all of the interface and significantly changes the amount of work required to expand that interface (Rosen, 1978). The surfactants have an amphipathic structure or there are both of lyophobic and lyophilic part in the molecule.

In aqueous solution, micelle provides a non-homogeneous environment for the solubilization. The lyophobic group is called hydrophobic, and the lyophilic group is called hydrophilic. The hydrophobic group is usually a long chain hydrocarbon residue whereas the hydrophilic group is an ionic or highly polar group. The surfactants are classified into two groups by the difference of the hydrophilic nature included, anionic surfactant containing the anionic charge groups, cationic surfactant containing the cationic charge groups, zwitterionic surfactant carrying both positive and negative charges, and nonionic surfactant bearing no apparent ionic charges.

At low concentration of surfactant solution, it presents in monomer form when the concentration rises until reaching to a specific concentration, then the aggregation molecules will be observed. This aggregation molecule is called micelle and the concentration that first micelle is formed called “Critical Micelle Concentration” or CMC. Micelle property affects on many interfacial phenomena, such as surface or interfacial tension. Moreover, it affects on many physical properties of the system, for example, electrical conductivity, light scattering, and refractive index.

In aqueous solution, the hydrophilic groups orient themselves to outside of the micelle and contact with the bulk solution whereas the hydrophobic

groups try to rearrange themselves away from the bulk solution by directing toward the interior of micelle molecule. They form oil-like liquid droplet. Figure 2.1 shows this micelle orientation in aqueous solution.

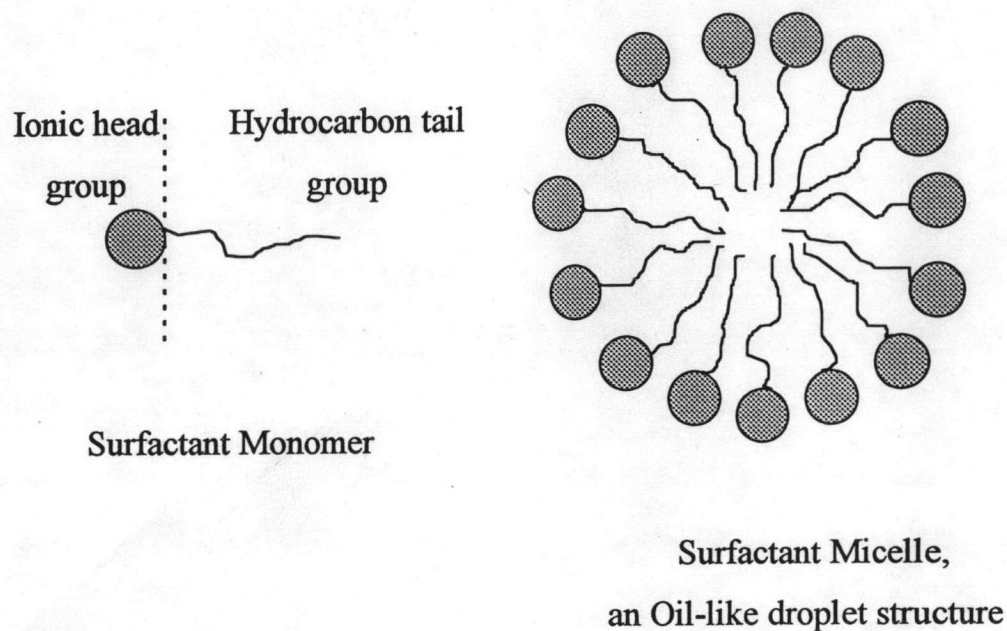


Figure 2.1 Micelle orientation in aqueous phase.

In the micelle formation, there are two major opposing forces present make up with an electrostatic repulsion between the charge head groups of hydrophilic in the outer shell of micelle and a hydrocarbon chain attraction in the hydrophobic tail groups. Accordingly, the micelle is formed better when there is increasing in hydrocarbon attraction or decreasing in electrostatic repulsion. Figure 2.1 shows this micelle orientation in aqueous solution.

Adding some neutral electrolyte of ionic surfactant can increase aggregation number and then increase micelle size. Increasing of hydrocarbon chain length results in rising of hydrocarbon attraction and then increase micelle size. Furthermore, these two effects can cause of CMC reduction too.

There are two main models that explained micelle formation including Pseudo-phase separation model and Mass action model. The pseudo-phase separation model establishes that above CMC the monomer concentration is constant even the surfactant is added. It indicates that all of added surfactants are formed micelles above CMC. The mass action model provides the difference explanation from the previous one. It predicts that the monomer concentration will slowly increase or decrease with increasing in concentration of surfactant. Eventhough, the mass action model also predicts that the monomer concentration is constant above CMC when the micelle aggregation number is large enough.

In ordinary, the aggregation number of micelle formation is about 20 to 200 monomer molecules (Rosen, 1978). Micelle structures and shapes are in many different types depend upon the their nature, the environment, and also the aggregation number of surfactants. The major types appear to be spherical micelle, elongated cylindrical or rod-like micelle, lamellar micelle, and vesicle micelle.

For surfactant used in this work, sodium dodecyl sulfate, has the CMC of  $8.3 \times 10^{-3}$  M at 25°C in aqueous solution (Mukerjee and Mysels, 1971; Christian and Scamehorn, 1995) by forming roughly spherical micelles containing about 70 surfactant monomers (Mukerjee and Mysels, 1971; Nguyen and Christian, 1989; Rosen, 1978; Turno and Yekta, 1978; Almgen and Swarmup, 1983).

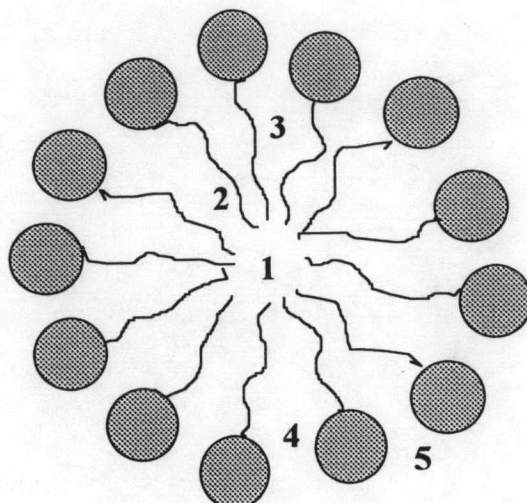


Micelle size, shape, and aggregation number can be changed by vary in temperature, concentration of surfactant used, and structural groups in the surfactant.

## **2.5 Solubilization of organic contaminants in micelle**

Solubilization is an important property of surfactant that concerns directly with the micellization. It is defined as the spontaneous dissolving of a substance be reversible interaction with a micelle of the surfactant in a solvent (Rosen, 1978). Therefore, when the surfactant is presented in an aqueous solution with concentration above the CMC, the solubilization of substances will be enhanced. The solubility of an organic can be much higher in a surfactant solution above CMC than in water due to solubilization (Rosen, 1978; Tadros, 1984; Hal and Tiddy, 1981; Adamson, 1967).

In spite of the characteristic of micelles that have both of hydrophilic and hydrophobic portion, there are five exact sites in the micelle at which solubilization occurs, inclusion into the inner core of micelle, deep penetration into the palisade layer, short penetrate into the palisade layer, between the hydrophilic head group, and on the micelle surface or at micelle-solvent interface. Figure 2.2 illustrates the sites of solubilization in surfactant solution.



- 1 - Inner core of micelle
- 2 - Deep penetrate in palisade layer
- 3 - Short penetrate in palisade layer
- 4 - Between the hydrophilic head groups
- 5 - In the micelle solvent interface

Figure 2.2 The sites in micelle provided for solubilization.

### 2.5.1 Solubilization in ionic surfactant solution

In the present of ionic surfactant solution, three modes of solubilization have been proposed (Shick, 1966).

- Non-polar molecule are dissolved in the inner core of micelle where the hydrocarbon tail of the aggregate molecule acts as the solvent.
- Polar molecule consisting of a hydrocarbon chain and a weakly hydrophilic group are solubilizes into the micelle with the hydrocarbon tail in the palisade layer and the hydrophilic protruding into the aqueous medium on the micelle periphery. Phenol molecule is proposed in this case.

- The solubilizates that are insoluble in hydrocarbon or in water are believed to be adsorbed on the surface of the micelle.

These three solubilization characteristics are shown in figure 2.3.

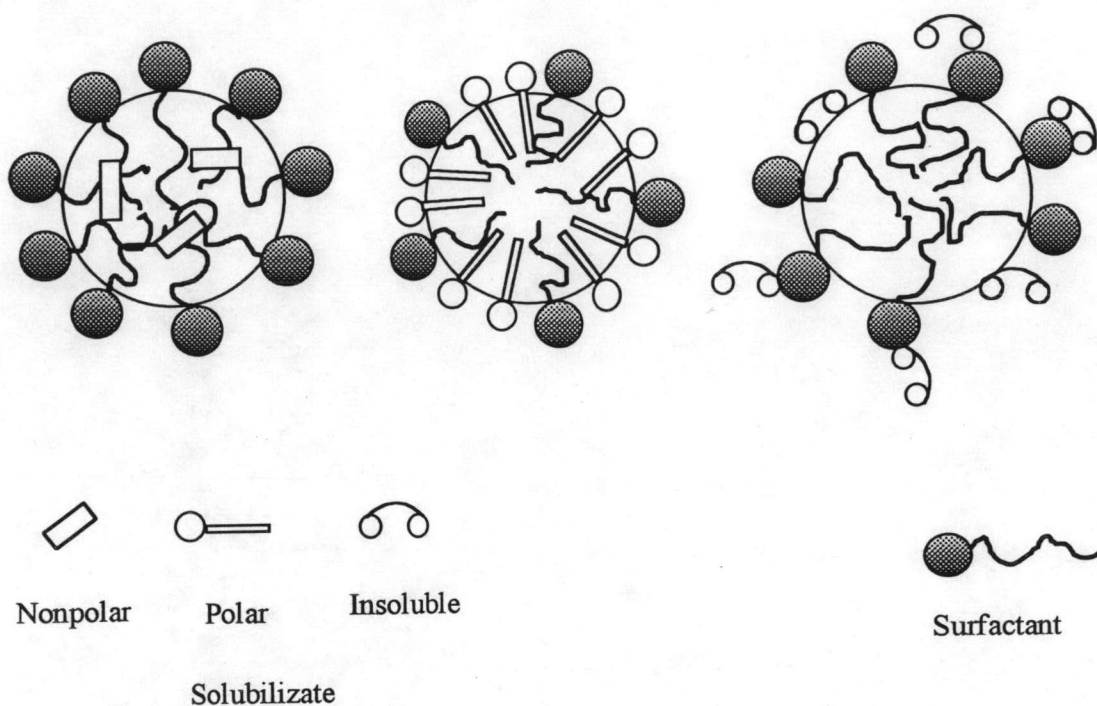


Figure 2.3 Schematic in solubilization of three different solubilizates.

### 2.5.2 Solubilization in nonionic surfactant solution containing polyoxyethylene chain

In this case, the location for solubilization is separated into two parts comprising with an inner core of hydrocarbon tails and an outer shell of hydrated polyoxyethylene.



The organic that have strong affinity between polyoxyethylene group will be solubilized in the outer shell of hydrated polyoxyethylene, such as phenol and its homologous.

The solubilization capacities or solubilizing power of the micelle is defined as the number of moles of solubilize per mole of micellized surfactant and can be identified by the equation 2.3.

$$\text{Solubilization capacities} = (C - \text{CMC}) \times V \quad (2.3)$$

where  $V$  is the volume of solution, L

$C$  is the molar concentration, mol/L and

CMC is the critical micellization concentration, mol./L

## 2.6 Previous works of SECR

The properties of solubilization and micellization are directly used for removing organic in the SECR technique by applying the surfactant with concentration above its CMC passed through a spent carbon bed. The previous work was done by Roberts and Scamehorn (1989) in a vapor phase application. They studied with the carbon bed containing either toluene or amyl acetate and used SDS as the regenerant solution. The adsorption capacities of the carbon bed reduce slightly after regeneration. Roberts and Scamehorn, (1989) also found that the regeneration of a higher molecular weight molecule (amyl acetate) was affected by mass transfer limited where the smaller one was affected by equilibrium limited.

Blakeburn and Scamehorn (1989) studied in liquid phase application. They presented that in the first 80% of TBP could be removed by treating with



regenerant solution containing with a cationic surfactant. The removal of the residual adsorbed surfactant could be achieved with a relatively small volume of flush water, but large quantities were required for more completely removal of the residual surfactant.

Bhummasobhana et al. (In press.) also studied in liquid phase application. They found that the higher of SDS concentration used, the more micelles formed, and the more adsorbed organic removed. When the more pore volumes of regenerant solution and flush water used, the carbon would perform the higher effective on subsequent adsorption. The regeneration of organic phenol was found to be mainly affected by an equilibrium limited, while a mass transfer was the second effect.

In Bhummasobhana et al. (In press.), the feasibility of applying the SECR process in a moderately high concentration of phenol loading was displayed by measuring the breakthrough curves for adsorption of phenol. In this study, the low concentration of the same model adsorbed solute (phenol) effect on using the SECR method was predicted, and also was shown by breakthrough curves.