

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Adsorption of Organic Compounds by Activated Carbon

Adsorption process has been widely used as a separation technique in various industries, particularly its applications in the removal of organic compounds from either gas or liquid phase stream by various adsorbents. Commercially available adsorbents are for example, zeolites, polymeric resins, and activated carbon (Garcia-Delgado *et al.*, 1992; Lin *et al.*, 2002; Wilhelm *et al.*, 2002). It has been known that there are different adsorption mechanisms for different adsorbent-adsorbate systems, depending on properties of the adsorbate and the adsorbent. In this perspective, four important features of the adsorbents should be considered. The first is adsorbent selectivity which adsorbent must selectively adsorb one or more components from others, second is adsorption-desorption reversibility which important for regeneration the adsorbent, third is capacity and finally, stability that have good stability during the operation and non-reactive.

Adsorption beds containing activated carbon are widely used to remove dissolved organic pollutants from industrial wastewater or gaseous emission streams. Activated carbon is a derivative form of variety of carbon containing raw materials, such as coconut shells, lignite, pitches, agricultural waste, coal and wood. These materials are activated at high temperature to enhance their surface area. The effectiveness of activated carbon for removal the organic compound from fluid by adsorption is dependent upon its importance properties which is surface area. Most of the activated carbon usually has surface area in order of 450-1800 m²/gram, depending on its origin (Sirisithichote, 1996). Examples of some typical activated carbons are shown in the Table 2.1.

In terms of application, activated carbon can be divided into two classes. The first class is gas-phase 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 liquefiable materials such as waxes.

Table 2.1 Surface areas of typically available activated carbons

Origin	Surface area (m ² /gram)
Bituminous coal	800 – 1,400
Coconut shell	1,100 – 1,150
Pulp mill residue	550 – 1,100
Wood	700 – 1,400

The main distinction between gas-adsorbing carbons and liquid-phase carbons lies 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, 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 general, 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 with regard to their physical form: powdered form and granular form. Selection of carbon type for a given application depends on comparative economics, types of existing equipment, and the carbon usage rate, variability of flowrate, the impurity concentration and composition, nature of the application, cleanliness, and disposal ways.

The most parts of activated carbon surface are nonpolar or hydrophobic, making the adsorption of inorganic electrolytes difficult but easy for organic (Pendleton, 1997). The other relevant property is the pore structure of activated carbon. It was found that wide pore size distribution (including micropores and mesopores) is provided for activated carbon (Bardosz and Salame, 1999). This property influences the large surface-to-size ratio. They are classified into two classes with 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.

When selecting the suitable carbon for a particular 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 areas 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 (Sirisithichote, 1996).

The particle size of carbon is one of importance considerations. The relative coarse carbons (12×20 mesh or 8×30 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 (12×40 mesh, 20×40 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 (Sirisithichote, 1996). In this study, 4×10 mesh of bituminous coal-based was used. It has a particle and internal pore size distribution allowing for rapid adsorption kinetics at medium to low differential pressure drop across the carbon bed because of its surface area, density, and strength characteristics.

2.2 Regeneration of Activated Carbon

Many chemical engineers believe that the operating costs of activated carbon adsorption are high. This is due to the predominant industrial practice of using the activated carbon only once and disposal or thermal regeneration

(McLaughlin, 1995). Current regeneration methods of spent activated carbon are thermal regeneration including steam regeneration, hot inert gas regeneration, thermal regeneration, and thermal reactivation. These regeneration methods are energy intensive due to involving in heating the spent carbon at elevated temperatures. Some of these methods are unable to serve on site resulting in extra cost for unloading the spent carbon and transportation to regeneration site. In addition, during regeneration process, some part of the activated carbon is destroyed or even decomposed if the regenerating temperature is high. Steam regeneration and hot inert gas regeneration, which regeneration conditions are mild, can successfully be used for the volatile adsorbates with atmospheric boiling points up to about 120°C (McLaughlin, 1995). The recovery of the valuable desorbed organic compounds requires separation equipment, which increase energy consumption of the over all process. Thermal regeneration and thermal reactivation involve heating at serve condition. At this condition, the recovery of the valuable organic compounds is impossible. Moreover, the activated carbon is deteriorated resulting in requirement of make up activated carbon. For both latter methods, the additional cost is required for unloading the activated carbon from the adsorber and transporting it to the regeneration site. This indicates that the regeneration of spent activated carbon is a major cost of the use of activated carbon. Therefore, other alternative regeneration methods have been searched with attempt to decrease the regeneration cost and develop for practical use in industry. These methods are for example chemical regeneration, solvent regeneration, supercritical extraction, and microwave regeneration. However, these methods have not been settled for industrial use.

2.3 Surfactant – Enhanced Regeneration of Activated Carbon

Surfactant – enhanced carbon regeneration (SECR) is an in-situ, low energy process that utilizes surfactant to remove adsorbed organics from activated carbon in order to regenerate it for reuse (Blakeburn and Scamehorn, 1989; Roberts and Scamehorn, 1989). In this process, a concentrated surfactant solution is passed through the spent carbon bed, as shown in Figure 2.1. The organics adsorbate desorbs and is solubilized into micelles in the solution. Micelles are surfactant

aggregates typically composed of 50-150 surfactant molecules. The micelle has a hydrocarbon - like interior into which organic molecules will dissolve or solubilize. A concentrated surfactant solution can contain large concentrations of dissolved organics because of solubilization (Blakeburn and Scamehorn, 1989). Therefore, a small volume of concentrated surfactant solution can potentially solubilize all of the adsorbed organic in a spent carbon adsorption bed, resulting in a small stream that has a high concentration of the organic adsorbate.

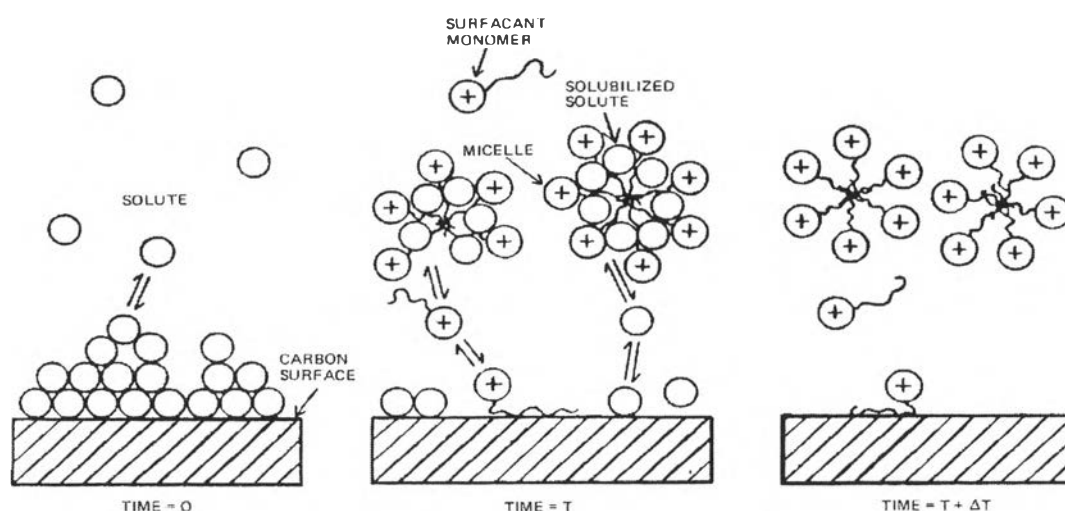


Figure 2.1 Equilibria present at the various stages of surfactant-enhanced carbon regeneration.

The surfactant can be removed from the regenerant solution exiting the adsorber by a precipitation process using monovalent or multivalent counterions. Ultimate recoveries of 95% were shown to be attainable for using divalent calcium and trivalent aluminum cations to precipitate anionic dodecyl sulfate (Brant *et al.*, 1989). This allows the surfactant to be recycled to the feed, which greatly improves the economics of this process. The desorbed organic may now be present at concentrations greater than saturation, resulting in a separate organic-rich phase splitting out for direct reuse. After that when done flushing, the carbon is ready for use for liquid phase applications or needs to be dried for gas phase applications. The process for use of SECR is shown in Figure 2.2. The conclusions concerning the flushing step is similar to that concerning the regeneration step, namely, that the

removal of the bulk of the residual of the adsorbed material can be achieved with a relatively small volume of solution. However, removal of the last portion of the residual material can require large quantities of flushing water (Thamtharai *et al.*, 2003).

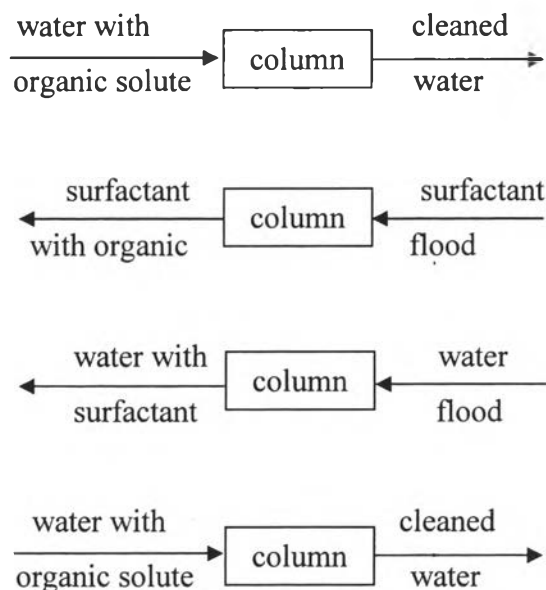


Figure 2.2 Process strategy in surfactant – enhanced carbon regeneration.

Previous works on 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 critical micelle concentration (CMC) passed through a spent carbon bed. Roberts and Scamehorn (1989) conducted the early work 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. They 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. In another related work from the same group, it was found that in the first 80% of TBP could be removed by treating with regenerant solution containing with a cationic surfactant (Blakeburn and Scamehorn, 1989). The removal of 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 (1995) studied SECR 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 equilibrium limited, while a mass transfer was the second effect. In this study, 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. The low concentration of the same model adsorbed solute (phenol) effect on using the SECR method was predicted (Sirisithichote, 1996). It was found that at low concentration of phenol, the adsorption was mainly affected by equilibrium limit, but when the concentration of phenol increased, the mass transfer limit tended to increase the effect on adsorption. More than 26% of adsorbed phenol was removed from the bed when applied with a moderate amount of surfactant regenerant solution.

It was found that when the desorption/solubilization process is complete, the carbon could contain some residual adsorbed surfactant and the water flushing had significant effect on the adsorption capacity of regenerated activated carbon. With water flushing at ambient temperature, the adsorption capacity of the regenerated carbon was approximately two items of that without water flushing. However, for both cases, the adsorption capacity of activated carbon after regeneration was drastically decreased. This is possibly due to residual surfactant remaining on the carbon after regeneration (Thamtharai *et al.*, 2003).

2.4 Adsorption of Surfactant on Hydrophobic Surface

Surfactant adsorption has been studied extensively on a number of materials, including layered double hydroxides (Pavan *et al.*, 2000; Mckay, 2001), zeolite (Pavan *et al.*, 1999; Garcia-Delgado *et al.*, 1992), silica (Kipling, 1965), mineral oxide (alumina) (Scamehorn *et al.*, 1982; Huang and Somasundaran, 1996;

Sikiric *et al.*, 1999), polymer (Brown and Zhao, 1993; Gupta *et al.*, 2001; Matinez *et al.*, 2002; Ladisch *et al.*, 2002), natural and synthetic fibers (Yoshio and Suzawa, 1970), and activated carbon (Garcia-Delgado *et al.*, 1992; Chern and Chein, 2001; Gonzalez-Martin *et al.*, 2002).

The adsorption of surfactants on solid surfaces is the basis for many technical applications because of their remarkable ability to influence the properties of surfaces and interfaces. For example in the *wetting* application, the surfactant adsorption increases the ability of aqueous solution to spread on the hydrophobic surface (Figure 2.3).

A characteristic property of surfactants is their tendency to aggregate at interfaces. This property results in an increase in surfactant concentration at solid/liquid interface in comparison to the bulk concentration.

The adsorption of surfactants at the solid-liquid interface is strongly influenced by a number of factors (Rosen, 1988): (1) the nature of the structural groups on the solid surface—whether the surface contains highly charged sites or essentially nonpolar groupings, and the nature of the atoms of which these sites or groupings are constituted; (2) the molecular structure of the surfactant being adsorbed (the adsorbate) —whether it is ionic or nonionic, and whether the hydrophobic group is long or short, straight-chain or branched, aliphatic or aromatic; and (3) the environment of the aqueous phase —its pH, its electrolyte content, the presence of any additives such as short-chain polar solutes, and its temperature. Together these factors determine the mechanism by which adsorption occurs, and the efficiency and effectiveness of adsorption.

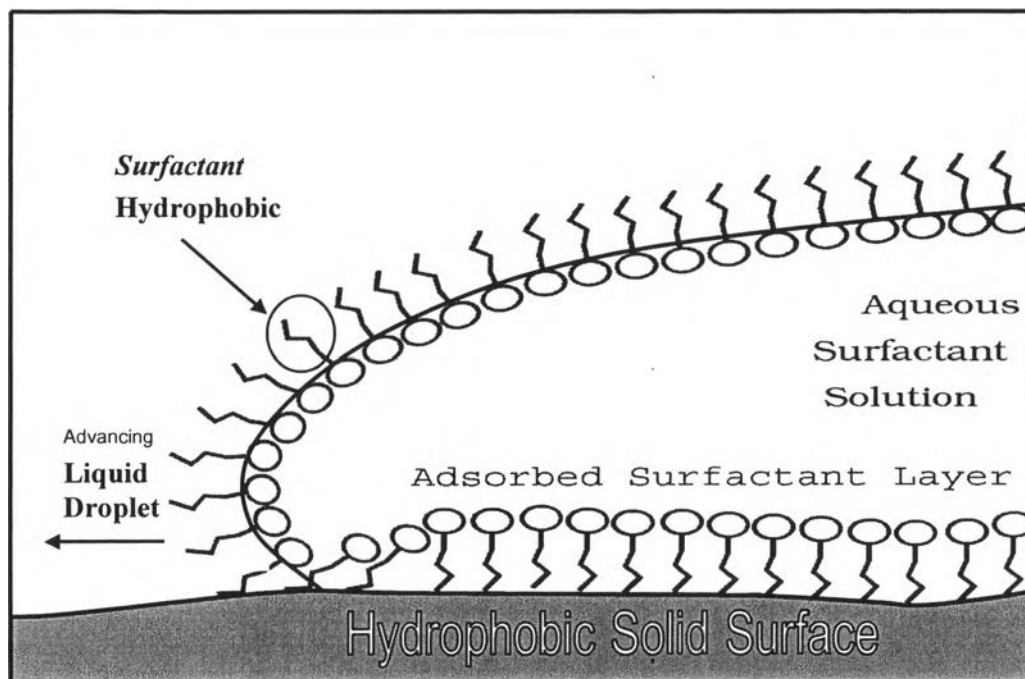


Figure 2.3 The role of adsorption in wetting.

2.4.1 Mechanisms of Surfactant Adsorption

Because of the variables mentioned above, there are several different adsorption mechanisms, which influence the enrichment of surfactants at the solid/liquid interface. Rosen (1988) classified the adsorption mechanism of the surfactants as follow:

1. Ion exchange
2. Ion pairing
3. Acid-Base Interaction
4. Adsorption by Polarization of π Electrons
5. Adsorption by Dispersion Forces
6. Hydrophobic Bonding

The mechanisms that involve with the adsorption on hydrophobic surface mainly are “*Adsorption by dispersion forces*” and “*Hydrophobic bonding*”.

2.4.1.1 Adsorption by Dispersion Forces

Adsorption by this mechanism occurs via London-Van der Waals dispersion forces acting between adsorbent and adsorbate molecules (Figure 2.4). Adsorption by this mechanism generally increases with increase in the molecular weight of the adsorbate (Rosen, 1988).

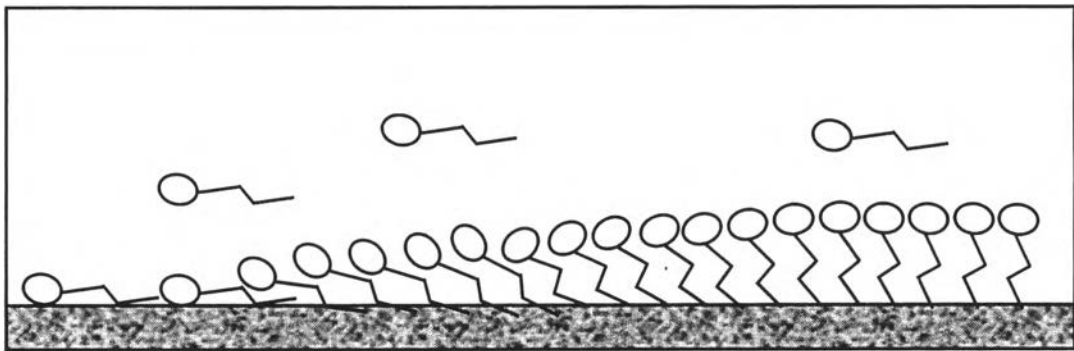


Figure 2.4 Surfactant adsorption via dispersion force on non-polar surface.

2.4.1.2 Hydrophobic Bonding

This mechanism occurs when the combination of mutual attraction between hydrophobic groups of the surfactant molecules (Figure 2.5) and their tendency to escape from an solution environment becomes large enough to permit them to adsorb onto the solid adsorbent by aggregating their chains (Rosen, 1988). These interactions may become stronger when more surfactant molecules are adsorbed (Zollars, 2001). Adsorption of the surfactant molecules from the liquid phase onto or adjacent to other surfactant molecules already adsorbed on the solid adsorbent also may occur by this mechanism (Rosen, 1988).

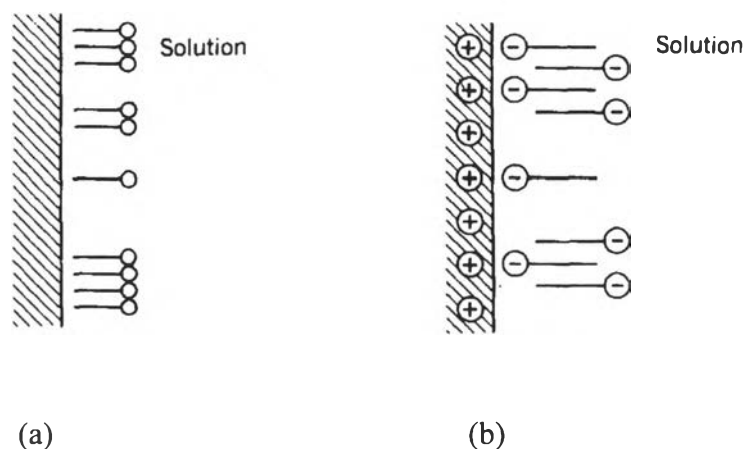


Figure 2.5 Adsorption from aqueous solution via hydrophobic bonding on (a) uncharged surface, (b) charged surface.

2.4.2 Adsorption Isotherm

Typically, adsorption isotherms for both non-ionic and ionic surfactants on the hydrophobic substrate, e.g. polyethylene, polypropylene, are the Langmuir type (Rosen, 1988). Figure 2.6 shows surface saturation near the CMC of the adsorbate. Adsorption onto these substrates is mainly by dispersion forces (Rosen, 1988).

In the beginning the orientation of the adsorbate may be parallel to the hydrophobic surface or slightly tilted, with hydrophobic group close to surface of the solid and hydrophilic part pointed toward the aqueous phase. Subsequently the adsorbed molecules may become oriented more and more perpendicular to the surface with hydrophilic portion pointed toward the aqueous phase (Zollars, 2001), the concentration of charged groups at the outer edge of the adsorbed layer becomes great enough to block any further adsorption due to electrostatic repulsion between the adsorbed surfactant and the surfactant molecules approaching the surface. In some cases, the adsorption isotherm shows an inflection point (Figure 2.6) as a result of changing in direction of the surfactant from parallel to perpendicular. An increase in the length of the hydrophobic group increases efficiency and slightly increases effectiveness of adsorption. The increase in efficiency is due to the increase in the magnitude of the $-\Delta G$ of adsorption with increase in the number of units in the hydrophobic chain; the increase in effectiveness may be due to tighter packing of the

hydrophobic chains. Also, addition of neutral electrolyte increases both the efficiency of adsorption of ionic surfactants, by decreasing the electrical repulsion between the similarly charged adsorbed ions and oncoming ions, and the effectiveness of adsorption, probably by decreasing the electrical repulsion between the similarly charged adsorbed ions, permitting closer packing (Rosen, 1988; Stuart *et al.*, 1999).

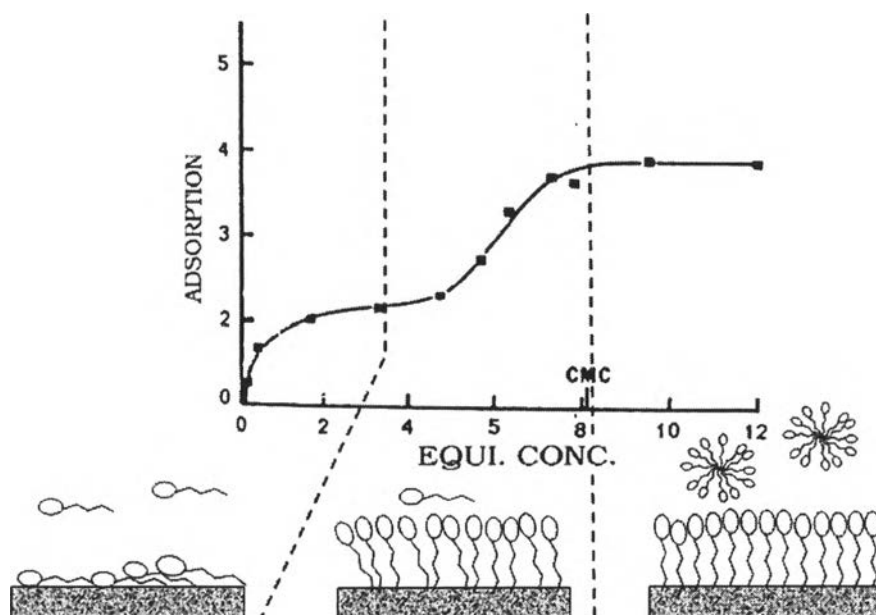


Figure 2.6 Adsorption isotherm of surfactant adsorption on hydrophobic surface.

2.5 Hydrophobic Polymeric Resins

Recently, several studies have focused on the potential application of polymeric adsorbents for separation and purification problems. One clear advantage of polymers is the ability to control their pore structure and internal surface area by varying the polymerization conditions. Moreover, one of the main advantages of polymeric adsorbents is that the adsorption can occur by weak adsorption affinity in opposition to other well-known adsorbents such as activated carbon. Therefore, it is expected that the polymeric adsorbents are useful for treating solvent vapors by pressure swing adsorption (Chigara *et al.*, 1996).

Polymeric resins are available in a range of different functionality and thus can be used for selective removal from multicomponent systems. Besides, they can be easily regenerated in situ, and they have been found to have sorption capacities, which approach or exceed that of activated carbon in some cases (Rodríguez *et al.*, 2002). Since, adsorption processes can be used for a wide range of concentrations of organic compounds such as phenol (Moon *et al.*, 1991) and are cost-efficient, especially if the pollutants are to be recycled. In addition, when compared to the traditionally used active carbon, a smaller amount of polymeric adsorbent is required, longer residence times can be achieved (Wagner and Schulz, 2001). In this context, polymeric adsorbents have gained increasing interest in various industrial applications.

Because of their adequate physical properties, adsorption capacity, and relatively low cost, the polymeric divinylbenzene-styrene (DVB-S) resins are extensively used by food and pharmaceutical industries for purification (Iskandarani and Pietrzyk, 1981). Moreover, the chemically modified adsorbents of this type have shown to exhibit significant improvements in the capacity and selectivity for some compounds (Martinez *et al.*, 1995)

There are various types of commercial polymeric resins, which can be classified as:

Amberlite: Amberlite or XAD polymeric resin trademark is the name under which reputation by Rohm and Haas Co. has been built for over half a century. It is now so widely recognized; that all reference literature on ion exchange cites Amberlite resins as a first choice. These are unique products for the purification of antibiotics in the pharmaceutical industry, recovery of products from fermentation in the bioprocessing/ nutraceutical industry, and for the removal of phenol and chlorinated solvents from waste. And also generally used for color removal in water treatment.

Amberchrom: Amberchrom media are macroporous, polymeric reversed phase liquid chromatography resins. They are designed for laboratory and process scale purification of proteins, peptides, nucleic acids, antibiotics, and small molecular weight pharmaceuticals.

Amberjet: These uniform particle size resins offer definite advantages in water treatment, resulting in better-treated water quality, lower rinse volumes and ultimately higher capacity.

Duolite: Duolite resins are unique specialty products used in the food, pharmaceutical, and chemical processing industries. The example of Duolite resin is phenol-formaldehyde resins which have a unique capacity for the adsorption of large organic molecules in the food and chemical industries combined with outstanding osmotic stability.

IMACTMHP: These "high purity" resins are made specifically for the treatment of drinking water and for food processing.

Amberlyst: Widely used for chemical processing, particularly in the petrochemical industry, Amberlyst resins are without equivalents. Many resins of this very special product line have demonstrated their efficiency for many years, but we are constantly improving and bringing new, superior products to this particular market segment.

Polymeric adsorbents are highly porous structures whose internal surfaces can adsorb and then desorb a wide variety of different species depending on the environment in which they are used. For example, in polar solvents such as water, polymeric adsorbents exhibit non-polar or hydrophobic behavior and so can adsorb organic species that are sparingly soluble. This hydrophobicity is most pronounced with the styrenic adsorbents. In non-polar solvents, such as hydrocarbons, etc. most adsorbents exhibit slightly polar or hydrophilic properties and so will adsorb species with some degree of polarity. This polarity is most pronounced with the acrylic adsorbents and the phenolic adsorbents. Table 2.2 shows some physical properties of commercial polymeric resin AmberliteTM XADTM family whereas Figure 2.7 shows synthetic reaction of styrene-divinylbenzene copolymer (XAD-4) (Harland, 1994).

Table 2.2 Some physical properties of commercial polymeric resin Amberlite™ XAD™ family (Data from Rohm and Haas Co.)

Amberlite	Chemistry	Surface area (m ² /g)	Average pore diameter (Å)	Mean diameter (micron)	Applications
XAD4	PstyDVB*	750	100	640	Removal of solvents and low MW species
XAD16	PstyDVB*	800	150	700	Small molecules, antibiotic recovery
XAD1180	PstyDVB*	500	400	530	Plant extracts, large MW product recovery
XAD1600	PstyDVB*	800	150	400	Antibiotic recovery, chromatography
XAD7HP	Aliphatic ester	500	450	560	Plant extracts, enzyme purification, peptides
XA761	Formo-phenolic	200	600	700	Plant extracts, enzyme purification, peptides

*pStyDVB = Polystyrene Divinylbenzene

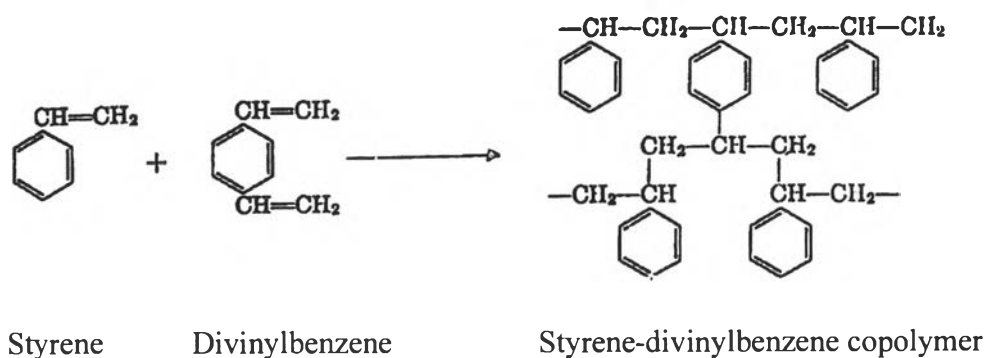


Figure 2.7 Synthetic reaction of polystyrene-divinylbenzene copolymer (XAD-4).