CHAPTER II
BACKGROUND AND LITERATURE REVIEW

2.1 Mixed Wastes

Mixed wastes are defined as wastes that contain both toxic organic components and heavy metal contaminants. Mixed wastes used to generate from various sources including national laboratories and various industries such as Power Generation Plants, Electronic processes, Petroleum refineries, and chemical manufacturing. Hazardous mixed waste stream are routinely disposed to the ground surface ponds, trenches, and other liquid discharge facilities. Thus heterogeneity makes characterization difficult to implement. The commonly classified contaminants found in mixed wastes are listed in Table 2.1.

Table 2.1 Primary Contaminants in Mixed Wastes

Organics
Hydrocarbon solvents: benzene, toluene, xylene, acetone, chloroform, phenols
Chlorinated compounds: methylene chloride, carbon tetrachloride, trichloroethylene
Polychlorinated biphenyls (PCBs)
Polyaromatic hydrocarbons (PAHs)
Inorganics
Heavy metal: Ag, As, Ba, Cd, Cr, Cu, Hg, Ni, Pb, Se, Zn
Radioactive components: ^{14}C, ^{60}Co, ^{137}Ce, ^{192}Ir, ^{90}Sr

The presence of toxic organics and heavy metals in the environment is of major concern because of their toxicity and threat to human life and environment. Chlorinated compounds, polyaromatic hydrocarbons and hydrocarbon solvents are the examples of toxic organics. Table 2.2 shows threshold limiting values (TLVs) and effects of poisoning of some important toxic organics and heavy metals.

Table 2.2 Threshold Limiting Value (TLVs) and Effects of Poisoning of some Organics and Metals

Organics	TLV*(ppm)	Effects of Poisoning
Acetone	750	Irritant; corneal clouding; damage to liver
Benzene	10	Cancer; nausea, vomiting, dizziness, narcosis, reduction in blood pressure
Chloroform	50	Cancer, irritant
Toluene	No TLV	Serious Irritant
Trichloroethylene	No TLV	Cancer, narcotic, severe irritant
Xylene	100	Irritant, narcotic

Metal	TLV*(mg/m^3)	Effects of Poisoning
Aluminium	2	Possibly related to Alzheimer's disease
Cadmium	0.05	Destructive to membranes; nausea, vomiting; cancer; damage to lungs; kidneys
Copper	1	Destructive to membranes; nausea, vomiting
Chromium	0.5	Irritant; nausea; vomiting
Iron	1	Possible irritant; nausea; vomiting
Mercury	0.1	Irritant; nausea; vomiting; damage to nervous system, liver, kidneys
Zinc	No TLV	Nausea; vomiting

*From material safety data sheets (MSDS)

It can be seen that the TLVs for Table 2.2 are extremely low, thus very hazardous. However, toxicity of metals can be greatly affected by various factors including form of metal, accessibility, presence of other metals or complexion agents, and physicochemical parameters such as pH, temperature, salinity, etc.

2.2 Treatment of Wastewaters

Water can be contaminated through contaminants including toxic metals and organic compounds. A pressing environmental problem is to devise clean-up strategies that can effectively remove mixed wastes.

Conventional technologies are available for removal of mixed wastes such as chemical precipitation, distillation, filtration, incineration, membrane, reverse osmosis, solvent extraction, plasma arc, ion exchange, and adsorption are the each technology is a differently of applicable, advantage and disadvantage as follows.

2.2.1 Chemical Precipitation

Chemical precipitation is applicable for mixed wastes for separating hazardous metals and/or hazardous metal radio nuclides from other constituents in wastewaters. Specific conditions of pH, temperature, and precipitating reagent addition are required to selectively remove part or all of the radioactive components as a precipitate. But such precipitation processes have inherent problems of solid-liquid separation, high cost, and slow kinetics.

2.2.2 Distillation

Distillation is applicable for treatment of wastes containing organics that are volatile enough to be removed by the application of heat. It requires a great deal of energy for the removal of organic compounds. If used simple distillation, the chemical contaminants with boiling points below water will be condensed along with the water.

2.2.3 Filtration

Filtration technologies may be used following precipitation and settling processes to separate low-level mixed waste from high-level mixed waste. Hence, filtration may concentrate the high-level waste components in the filter cake, leaving a relatively low-level filtrate. Filtration technologies used to separate solid and liquid and do not destroy toxic components.

2.2.4 Incineration

Incineration is applicable to wastes composed of solvents and other organics that to use high temperature. Therefore, it is varying expensive and energy intensive process. Further, by products obtained from incineration are also hazardous and disposal of these products through stack hazard the environment.

2.2.5 Membrane

Membrane separation processes also used widely in biochemical processing and in pharmaceutical application. Membrane technique has advantage of operational simplicity, low solvent inventory, and low energy consumption. However, limitations of membrane technique are the temperature control and sensitivity to pressure. Most membranes are stable at low pH values.

2.2.6 Reverse Osmosis

Reverse osmosis has become very popular for producing freshwater from brackish water and seawater. The technique has low capital and operating costs compared with other alter-native processes such as multistage flash.

2.2.7 Solvent Extraction

Extraction technologies may be used to separate a mixed waste into its radioactive and hazardous components if either the hazardous or the radioactive components can be selectively extracted by the extracting solvent. Selection of the extracting solvent depends on the solubility of the organic waste in the extracting solvent.

2.2.8 Plasma Arc

Plasma arc is electrically generated technique to destroy hazardous waste. The liberated atoms are then separated and maintain an electrical charge. It actually separates all chemical components of hazardous waste but it operates at extremely high temperature which makes it uneconomical.

2.2.9 Ion Exchange

Ion exchange is applicable for waste water where metals are present as soluble ionic species. This technique is a reversible process in which hazardous cation and/or anion removed from aqueous solution and replaced by non hazardous cation and/or anion such as sodium, hydrogen, chloride, or hydroxyl ion. But ion exchange cannot remove organic compounds. However, due to low levels of these metals, this technique may not cost effective.

2.2.10 Adsorption

Adsorption used to treat wastewaters containing dissolved organics at fewer concentrations and dissolved metal and other inorganic contaminants. The most effective metals removal is obtained with metal complexes. Adsorption is one of most simple, economical and efficient technique. Adsorption process occurs when contaminant has a low solubility in the waste and has a greater affinity for the adsorbents than for the waste, or a combination of the two. The adsorbents have many types for treating wastewater such as activated carbon, natural clay and zeolites. However, the adsorbents have a serious limitation because of their low adsorption capacity for removing toxic organic. To enhance the adsorption capacity, various modification of clay or zeolite by using surfactant (Bowman et al., 1995, Malakul et al., 1998 and Zhu et al., 2000) after saturation of eluate with heavy metals, and organic contaminants. It can be regenerated by adjusting pH and air-purge, respectively, which is a cost effective and an ecological method for heavy metals and organic contaminants removal from solutions (Sriwongjanya, 2004).

2.3 Natural Zeolite

Natural zeolite, generally, brittle, solid rock and thus its grain size distribution can be controlled freely by crushing and sieving. Thus hydraulic properties of natural zeolite material can be fitted to meet particular requirements. Furthermore, the availability of zeolites as a coarse grained material facilitate its application in subaqueous environment since coarse grains settle to ground readily and once sediment, are relatively resistive against erosion.

Zeolites are crystalline hydrated aluminosilicates of the alkaline and alkaline-earth elements. About 40 natural zeolites have been identified during the past 200 years. At present, ther are the most common of natural zeolite that are of commercial interest due to their favorable exchange properties along with an abundant occurrence in nature. These are analcime, chabazite, clinoptilolite, erionite, ferrierite, heulandite, laumontite, mordenite, and phillipsite (Mumpton, 1997). More than 150 zeolites have been synthesized. Some of the more common synthetic zeolites are zeolites A, X, Y, and ZMS-5. Natural and synthetic zeolites are used commercially because of their unique adsorption, ion-exchange, molecular sieve, and catalytic properties.

Clinoptilolite is one of the most useful natural zeolite. It is well swited for these applications due to its large amount of pore space, high resistance to extreme temperatures and chemically neutral basic structure. It has high cation exchange capacity up to 6 $mmol_{(eq)}/g$ and even exceeds for smectite clays and thus permits an efficient removal of heavy metal cations. The high cation exchange capacity results from the unique crystal structure of zeolite minerals which basically formed by a framework of SiO_4-tetrahedral, wherein all oxygen atoms are shared by two adjacent tetrahedral resulting in an overall oxygen/silicon ratio of 2:1. The characteristic isomorphic substitution of silicon by aluminium in the tetrahedral-sites results in a net negative charge of the framework which is balanced by loosely bound, exchangeable, extraframework cations, mainly of the alkali and alkaline earth elements. The zeolite framework is remarkably open. It shows infinite, three-dimensional systems of tunnels and cages where the exchangeable cations as well as water molecules can be situated. The crystal structure for clinoptilolite is shown in Figure 2.1.
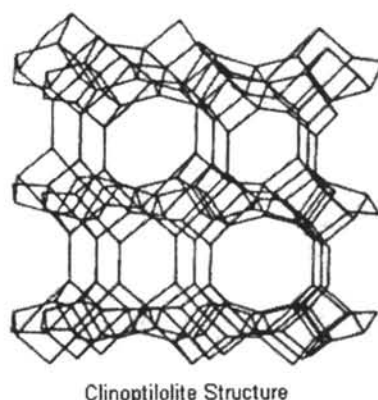
Clinoptilolite Structure

Figure 2.1 Crystal Structure for Clinoptilolite Structure.

The clinoptilolite can trap positively charged ion (cations) such as sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), iron (Fe^{2+}) and magnesium (Mg^{2+}). The cation exchange behavior, which controls the selectivity for particular cations in exchange processes, depends on the charge and size of the cations and the structural characteristics of the particular zeolite mineral e.g. channel dimensions. (Jacobs and Forstner, 1999).

Recently, great interest has been shown for this kind of materials due to its great ability to adsorb different types of pollutants at relatively low cost. The pre-treatment of zeolite surfaces with cationic surfactants additionally facilitates the retention of non-polar contaminants, e.g. chlorinated hydrocarbons, and anionic contaminants, e.g. chromate and arsenate (Haggerty and Bowman, 1994; Bowman *et al.*, 1995)

Clinoptilolite thus has the potential to remove both toxic organic and heavy metal contaminants. However, the problems in using natural zeolites are as follow; products contain a variety of impurities and low organics sorption capacity. So enhanced organics sorption capacity by surfactant-modified clinoptilolite was investigated.

2.4 Surfactant Adsorption onto Solid Surfaces

The adsorption isotherm of an ionic surfactant onto an oppositely charged substrate is typically S-shaped when plotted between the log of adsorbed surfactant

density and the log of the equilibrium concentration of surfactant (Scamehorn *et al.*, 1982). The isotherm can be divided into four regions, as shown in Figure 2.2.
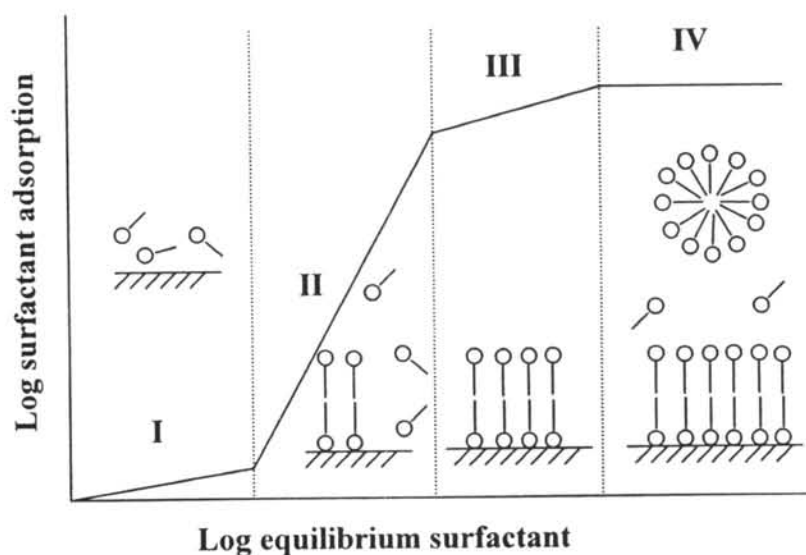

Figure 2.2 Schematic presentation of a typical surfactant adsorption isotherm.

Region I is low adsorption of surfactant on the substrate. The surfactant adsorbs mainly by ion exchange, possibly with the hydrophobic group more or less prone on the substrate. This region does not have lateral interactions between the adsorbed surfactant molecules.

In region II there is a rapid increase in adsorption of surfactant, resulting from interaction of the hydrophobic chains of oncoming surfactant ions with those of previously adsorbed surfactant and with themselves. The aggregation of these adsorbed surfactants has been called hemimicelle or admicelle, depending on their morphology. The hemimicelle is a monolayer structure having the head group adsorbed on the surface while the tail is in contact with the aqueous phase. In this adsorption region the original charge of the solid is neutralized by the adsorption of oppositely charged surfactant ions. The admicelle is a bilayer structure with a lower layer of head groups adsorbed on the substrate surface and an upper layer of head groups in contract with solution, so that solid surface has acquired a charge of the same sign as the surfactant ion. The point of transition from region I to region II, representing the first formation of adsorbed surfactant aggregates, is called the hemimicelle concentration (HMC) or critical admicelle concentration (CAC).

In region III, the adsorption of surfactant increases more slowly with concentration than in region II because adsorption now must overcome electrostatic repulsions between the oncoming ions and the similarly charged solid.

Region IV is a region where the adsorption reaches a plateau either because the surface has become saturated with admicelles or because the surfactant concentration in the solution has reached the CMC of the surfactant. At the CMC, the first micelle forms at the same chemical potential as the last admicelle forms. When the surfactant concentration is increased further, the chemical potential is the same as the first micelle to form and thus produce more micelles without an increase in the adsorption of more surfactant.

2.5 Adsorption of Contaminants by Natural Zeolite

Natural zeolites are unique economical, physical and chemical properties which are availability at low cost, retention of cationic contaminants by cation exchange and retention of non-polar and anionic contaminants after appropriate modification. (Jacobs and Forstner, 1999).

Previous studies have shown that Clinoptilolite has high selectivity for certain heavy metal ions such as Pb^{2+}, Cd^{2+}, Zn^{2+} and Cu^{2+}. A number of researchers have determined different selectivity sequences of natural zeolites for a range of various metalsand they found that Clinoptilolite shows a strong affinity for lead and cadmium. Most of them have suggested that pretreatment of natural zeolites enhances their ion-exchange ability (Malliou *et al.*, 1994; Semmens and Martin, 1988; Wark *et al.*, 1994; Zamzow *et al.*, 1990).

Natural zeolite has high cation exchange capacity that permits an efficient removal of heavy metal cations. Upmeier and Czurda (1997) investigated the adsorption behavior of the four natural zeolites and the clay towards different pollutants. The clay and zeolite showed similar adsorption capacities for Cd^{2+} and phenol while the adsorption capacity of the zeolite for Tl^{2+} was approximately 50 times higher than that of the clays. It demonstrates that the natural zeolite has a high potential to remove heavy metal than natural clay.

The cation exchange behavior, which controls the selectivity for particular cations in exchange processes, depends on the charge and size of the cations and the structural characteristics of the particular zeolite mineral e.g. channel dimensions. Ouki and Kavannagh (1999) studied the selectivity and removal performance of clinoptilolite. Study revealed that clinoptilolite is highly selective for lead (Pb^{2+}), copper (Cu^{2+}) and cadmium (Cd^{2+}).

The pH of the solution also has significant effect on the removal efficiency of natural zeolite for heavy metals. Mier et al. (2001) studied the interactions of Pb^{2+}, Cd^{2+} and Cr^{2+} competing for ion exchange sites in naturally occurring clinoptilolite. Their found that higher removal efficiencies (>95%) occurred in the acidic pH range while at high pH range (>10) the efficiency declined dramatically.

The temperature of solution also is demonstrated that the natural and modified zeolites have effective potential to remove toxic metal from waste water. Curkovi et al. (1997) studied the lead and cadmium removal from wastewaters where natural and pretreated zeolites were examined by using a batch-type method. Lead and cadmium removal results using natural zeolites and treated zeolites showed that treatment improved both the exchange capacity and the removal efficiency. The lead was more selectively removed than cadmium. The influence of the temperature on the ion-exchange process was also examined. It was found that the metal uptake was increased with increasing temperature during the ion-exchange process.

Clinoptilolite has also been applied to remove toxic organics. Sismanoglu and Pura et al. (2001) studied the adsorption of ortho-, meta- and para- nitrophenols on clinoptilolite. They found that the solution concentration and temperature are a factor on the adsorption of aqueous nitrophenols on clinoptilolite. They also concluded that clinoptilolite can remove both toxic organic and heavy metal contaminants. However, natural zeolites has some problem for adsorption contaminants such as has low sorption capacity for organic compounds. Therefore, enhanced organics sorption capacity by surfactant modified clinoptilolite was investigated.

2.6 Modification of Adsorbents Using Surfactant

Cationic surfactants, showing a strong affinity to the exchange sites at the zeolite surfaces, take the place of exchangeable metal cations and thereby form a layer covering the zeolite surface. Since only the external surface, and not the internal cage and tunnel structure, of the zeolite is accessible for the large surfactant molecules, the internal surface remains an active cation exchanger, while the external surface becomes electrically neutral or even positively charged as a consequence of the surfactant loading either in a mono-layer or in a bi-layer, respectively.

Cationic surfactants, as long chain quaternary ammonium cations such as hexadecyltrimethyl ammonium (HDTMA) are too large to enter zeolite channels or access internal cation exchange positions. Thus, the sorption of long chain quaternary ammonium cations is limited exclusively to external surfaces of zeolite particles. This HDTMA is essentially irreversibly bound to the zeolite's external surface. (Haggerty and Bowman, 1994)

Bowman et al. (1995) studied stability of surfactant-modified zeolite, indicated that the SMZ was stable when immersed in a variety of aggressive solutions. Extremes in solution pH, ionic strength, or organic solvents failed to remove surface-bound surfactant. The surfactant's affinity for the zeolite surface may be due to a combination of van der waals associations among the adsorbed surfactant hydrocarbon chains and entropic effects.

Sorption of the quaternary amine in bilayer or admicelle form are causing the charge on surface to change from negative charge to positive and the organic carbon content of the zeolite to increase. The organic-rich surface layer provides a partitioning medium for sorption of nonpolar organics such as chlorinated solvents and fuel components. Some of the zeolite's original cation exchange capacity is retained for sorbing positively charged species such as Pb^{2+} and Hg^{2+}. Thus, surfactant-modified zeolite (SMZ) can simultaneously sorbs the three major classes of water contaminants: inorganic cations, inorganic anions, and nonpolar organics as shown in Figure 2.3.
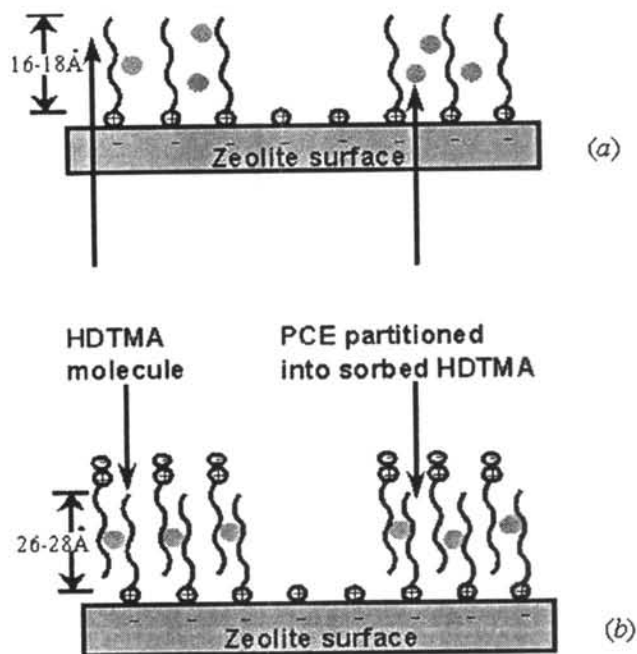
Figure 2.3 Diagrams of HDTMA sorbed as a monolayer and as a bilayer on the zeolite surface (Li and Bowman, 1998).

Malakul *et al.* (1998) investigated surfactant-clay complexes were prepared using cationic surfactant, cetylbenzyldimethyl-ammonium (CBDA) and anionic surfactant, palmitic acid (PA) adsorbed on montmorillonite. Found that the amount of CBDA in clay-CBDA complex is quite close to the CEC of the base clays. The XRD patterns of the modified clays also confirm exchange of the Na^+ cations by CBDA.

Koh *et al.* (2001) studied nonionic organic contaminants NOCs such as benzene, phenol, and toluene from contaminated wastewater can be effectively sorbed by organo-modified minerals. Organo-minerals were prepared from Na-montmorillonite, sericite, and zeolite by exchanging quaternary ammonium cations with various molecular weights such as Benzyl dimethyl tetradecyl ammonium (BDTDA), Hyamine 1622, and Benzyl trimethy lammonium BTMA. The adsorption capacity of these organic cations onto these minerals is in the order of montmorillonite > zeolite > sericite, which is mainly dependent on the Ca/Mg cation exchange capacity CEC of each mineral. The interlayer expansion of the basal spacings of BDTDA- and Hyamine-montmorillonite increases as the amount of

interlayer organic cation increases. BTMA montmorillonite is characterized by less interlayer expansion.

David and Jorge (2001) investigated the adsorption of sodium dodecylbenzene sulfonate (SDBS) in aqueous solution, over a bentonite and modified with quaternary ammonium salts such as tetramethyl ammonium bromide (TAB), hexadecyl trimethyl ammonium bromide (HDTMA), hexadecyl benzyldimethyl ammonium chloride (CDAC), and alkylbenzenyl dimethyl ammonium chloride (BTC) to 50% and 100% of its cationic exchange capacity (CEC). The result of adsorption of SDBS over organophilic bentonites is a relatively fast process. When the bentonite was modified at 100% of its CEC, it is modified at 50% which TAB is greater all the sites of cationic exchange are covered. The adsorption process of SDBS over the organophilic clays was the best described by the Langmuir isotherm.

You *et al.* (2002) studied clay-based adsorbents were synthesized by incorporating anionic surfactants, sodium octylsulfate (SOS), sodium dodecylsulfate (SDS), sodium 4-octylbenzenesulfonate (SOBS), and sodium dodecylbenzenesulfonate (SDBS), into magnesium aluminum layered double hydroxide (Mg–Al LDH) via ion exchange. The maximum surfactant adsorption occurred in the order: SDS > SOBS > SDBS > SOS. The maximum adsorption of SDS on Mg–Al LDH is slightly higher than the theoretical anionic exchange capacity of the Mg–Al LDH (TAEC), Adsorption of higher molecular weight surfactants, SDS, SDBS and SOBS, was significantly greater than the lower molecular weight surfactant, SOS. This suggests that the intercalation of lower molecular weight surfactants can be more difficult than that of the higher molecular weight surfactants. The adsorption coefficients for both organic compounds ranked in the following order: SOBS-LDH > SDBS-LDH > SDS-LDH > SOS-LDH. This order suggests that some anionic surfactants could form a more effective organic phase than others. The presence of benzene rings in SDBS and SOBS clearly increased adsorption due to enhanced hydrophobicity.

Nonionic organic contaminants (NOCs) can be effectively adsorbed by organo-zeolites. Organo-zeolites were prepared from synthetic ZSM-5 and natural zeolites, by exchanging the quaternary amines i.e. hexadecyltrimethylammonium

HDTMA-Br and n-cetylpyridinium bromide (CPB) were investigated by Ghiaci *et al.* (2004). Found that the maximum adsorption of CPB onto these zeolites is in the order of clinoptilolite > ZSM-5-88 > ZSM-5-31. Which is mainly dependent on the external cation exchange capacity (ECEC) of each zeolite, the hydrophobic nature of the zeolite might have some effect on adsorption. Maximum adsorption on clinoptilolite was more than twice of the ECEC of ZSM-5. Therefore, should expect that a bi-layer formation be completed at high concentration. Shows that the adsorption of surfactant on the clinoptilolite surface may be happen as hemimicelle aggregates more than bi-layer.

Karapanagioti *et al.* (2005) investigated surfactant-modified sorbents, one cationic (HDTMA) and three anionic (DOWFAX-8390, STEOL-CS330, and Aerosol-OT) surfactants were tested for their sorptive behavior onto different sorbents (alumina, zeolite, and Canadian River Alluvium (CRA)). The result that the sorption partition coefficient (Kp) increases in the following order STEOL-CS330–alumina (SA), Aerosol-OT–alumina (AA), and DOWFAX- 8390–alumina (DA).

2.7 Adsorption of Contaminants by Surfactant-Modified Adsorbents

Recent studies on the properties of surfactant-modified zeolite (SMZ) indicate that SMZ is an effective sorbent for multiple types of contaminants, such as the sorption of oxyanions by SMZ was attributed to anion exchange on the positively charged surfactant bilayer which the soption of hydrophobic organic contaminants was due to partitioning of the organics into the organic pseudo phase created by the surfactant tail group.

Ghiaci *et al.* (2004) studied the adsorption of benzene, toluene and phenol by CPB and HDTMA surfactant-modified ZSM-5-31, ZSM-5-88, and clinoptilolite besides as-synthesized MCM-41 molecular sieve. The increase in NOCs (benzene, toluene and phenol) concentration or initial concentrations of surfactants resulted in an increase in the NOC adsorption. Sorption capacity of NOCs were in the order of MCM-41 > organo-natural clinoptilolite > organo-ZSM-5-88 > organo-ZSM-5-31. Benzene and toluene almost showed similar sorption capacity on the organo zeolites, whereas phenol showed the lowest sorption capacity among them.

Li and Bowman (1997) studied the effects of the counterion Br⁻, Cl⁻, and HSO₄⁻ on the sorption of HDTMA onto clinoptilolite zeolite and the effect of the initial counterion on the sorption of chromate onto HDTMA–modified zeolite and found that counterious have significant effects on the HDTMA sorption on zeolite and chromate sorption HDTMA-treated zeolite. The HDTMA treated effectively to order: HDTMA-HSO₄ > HDTMA-Cl > HDTMA-Br. The lowest HDTMA surface coverage and that the effect of counterious in stabilizing the HDTMA bilayer follows the lyotropic series Br⁻ > Cl⁻ > HSO₄⁻.

Li and Bowman (1998) studied the surfactant-modified zeolite-clinoptilolite as an effective sorbent for removal of PCE from water. The PCE sorption on SMZ is a function of the surfactant loading and resultant organic phase density. PCE is most efficiently sorbed by SMZ when surfactant is present at or below full monolayer coverage; at higher surfactant loading levels, PCE sorption appears limited by a reduced effective volume and an increased density of the hydrophobic core of the sorbed surfactant bilayer, resulting in a decreased K_{oc}. The greater hydrophobicity of the monolayer- versus the bilayer-modified surface may also add to the greater PCE sorption efficiency exhibited by the monolayer system.

Bowman *et al.* (2000) investigated the sorption of HDTMA by zeolite, and solute sorption by the resultant surfactant-modified zeolite (SMZ). At low loading levels, HDTMA exchanges with charge-balancing cations on the zeolite's external surface. At sufficient HDTMA loading, greater than the external cation exchange capacity of 100 meq/kg for the St. Cloud zeolite, a bilayer or patchy bilayer of HDTMA molecules forms. The formation of this bilayer reverses the charge on the zeolite from negative to positive, and provides sites for exchange of anions such as chromate. The HDTMA bilayer forms an organic-solvent-like coating on the surface into which nonpolar organic solutes such as PCE can partition. Inorganic cations such as Cs^+ can bind to cation exchange sites on the internal zeolite surfaces, or be selectively bound on external surface sites as shown in Figure 2.4.
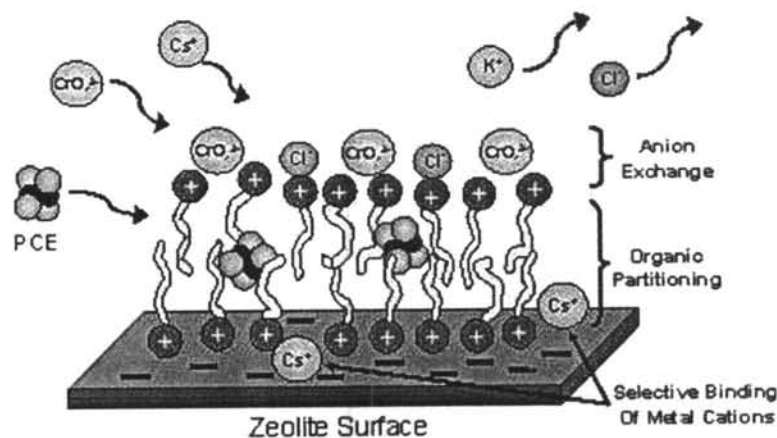
Figure 2.4 Schematic diagram of sorption mechanisms for anions, cations, and nonpolar organics on SMZ.

Koh *et al.* (2001) investigated the potential of three quaternary ammonium cations as surfactants and three minerals for sorbents of NOCs that are common contaminants of wastewater. The results indicate that BDTDA-montmorillonite has the most potential for adsorbent for three NOCs, benzene, toluene and phenol. Because of the BDTDA-montmorillonite 200% of CEC complex is the best one tested because of the high CEC and the large surface area. Its sorption effectiveness for benzene and toluene continued to increase with each increase in the surfactant to montmorillonite ratio.

Li and Bowman (2001) studied the removal of anionic species from water using surfactant-modified kaolinite. After modification with HDTMA, the sorption maximum of kaolinite for these oxyanions increased by at least two orders of magnitude. The sorption of chromate by organo-kaolinite was not affected by pH changes in the range of 5–9, but was greater at pH 3. At high pH and/or high ionic strength, sorption of chromate decreased due to competition from other anions in solution. Competitive effect, along with observed counterion balances, indicates that retention of oxyanions by organo-kaolinite is due to anion exchange. After treatment with more than 40 pore volumes of chromate solution, the chromate concentration in column effluents remained less than 10% of the influent concentration. Ninety percent of the original HDTMA remained on the organo-kaolinite after the column treatment.

Cortes-Martinez *et al.* (2004) investigated the modified zeolitic material with the surfactant (HDTMA) for the removal of cadmium from aqueous solutions. The effects pH and contact time on the adsorption process were examined. The optimum pH for adsorption was found to be 7. Cadmium retention reached equilibrium in 32 h and the rate of cadmium adsorption by the zeolites was rapid in the first 10 h. Elovich's model best described the reaction rate and the adsorption pattern followed the Langmuir-Freundlich isotherm model.

Lin and Juang (2002) investigated removal of Cu^{2+} and Zn^{2+} from aqueous solutions by sorption on the montmorillonite modified with sodium dodecylsulfate (SDS). Experiments were carried out as a function of solution pH, solute concentration, and temperature (25°C–55°C), found that the SDS-modified clay showed a much more negative zeta potential and a higher affinity for metal cations when comparation with the raw clay. In addition, the amount of sorption of both metal ions on modified clay increased with increasing solution pH.

Zhu and Chen (2000) studied a series of anion-cation organobentonite prepared by incorporating both cationic surfactant, bromide dodecyltrimethylammonium (DTMAB), and anionic surfactant, sodium dodecyl sulfate (SDS), to bentonite. The results indicate that the organic carbon contents of the organobentonites are proportional to the amounts of anionic and cationic surfactants in bentonite. The amount of organic pollutant removed from water depends greatly on the amount of SDS and DTMAB in the bentonite. Partition and adsorption contributions to the sorption amount of p-nitrophenol on organobentonites are described quantitatively. The mixed surfactants on anion-cation organobentonites excellently created partition mediums for organic pollutants in water. The removal rate of organic pollutants from water is improved by synergistic solubilization in both anionic and cationic surfactant moieties of the organobentonites. The effect of synergistic solubilization results mainly from partition at higher concentrations or adsorption at lower concentrations.

Recently, there have been studies on the preparation of surfactant-modified adsorbents by a two-step surface modification technique and examined their capability in the adsorption of heavy metal ions and organic pollutant separately and simultaneously. For example, the surfactant-clay complexes were prepared using

hectorite or montmorillonite as the base clay by Malakul *et al.* (1998). A simple two-step approach had been used to synthesize these modified-clay complexes through ion exchange and hydrophobic anchoring of several surfactants, using cadmium as a model metal and montmorillonite-cetylbenzyldimethylammonium-palmitic acid (M-CBDA-PA) as a model modified-clay complex. The results showed that the adsorption of metal ions onto modified-clay complexes had a strong pH-dependent characteristic and the uptake of metal ions by both modified-clay complexes increased with an increase in pH. Thus, pH can act as a molecular switch to regenerate the modified-clay complexes.

Saengchote (2003) studied the preparation of surfactant-modified zeolite (SMZ) through a simple two-step surface modification technique by adsorbing CTAB and palmitic acid (PA) to form the mixed bilayer on the zeolite surface as shown in Figure 2.5. The adsorption characteristics of surfactant-modified zeolite (SMZ) for heavy metal such as cadmium (Cd^{2+}) and organic contaminant such as toluene were examined. The results show that pH has significant effect on the adsorption of cadmium by SMZ. The adsorption capacity of cadmium by SMZ was found to increase with increasing pH. Moreover the ionic strength has insignificant effect on the cadmium adsorption by SMZ. In the mixed-solute systems, the presence of toluene slightly affected the cadmium adsorption by SMZ whereas the presence of cadmium was found to enhance the adsorption of toluene.
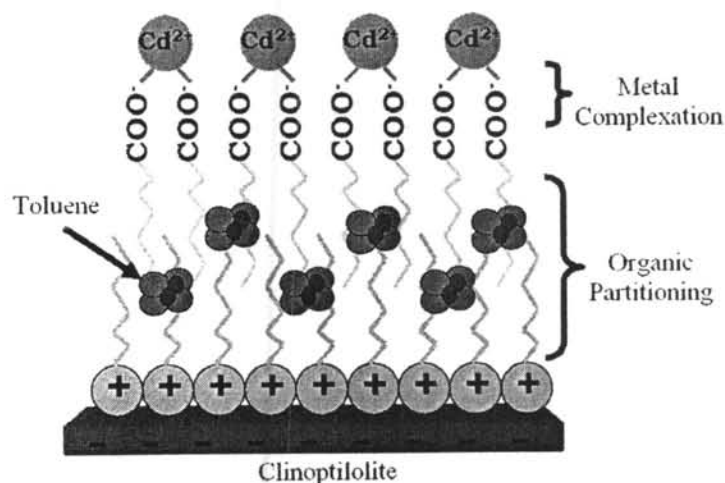

Figure 2.5 Schematic diagrams of sorption mechanisms for cadmium and toluene on SMZ.

Sriwongjanya (2004) further investigated SMZ adsorbents for their adsorption characteristics for heavy metal and organic contaminants as a function of metal ligand to surfactant loading ratio. The results showed that the adsorption of cadmium by SMZ was strongly affected by PA/CTAB loading on SMZ. The cadmium uptake increased with increasing PA/CTAB loading ratio in the range of 1:1 to 4:1. In contrast, the adsorption of toluene slightly decreased with increasing PA/CTAB loading on SMZ. In the mixed-solute systems where cadmium and toluene were adsorbed simultaneously, higher adsorption was observed in case of toluene but not in cadmium adsorption. The regeneration of SMZ was also demonstrated and the regenerated SMZ was shown to be reusable for several adsorption cycles with an acceptable loss in the adsorption capacity.

Sriplad (2005) studied the preparation of surfactant-modified zeolite (SMZ) by forming a mixed bilayer of cationic and anionic surfactants (CTAB and DOWFAX 8390, respectively) on its surface. The results showed that the adsorption of both heavy metals was well described by the Langmuir isotherm. In single-component system, the maximum adsorption capacity was found to be 0.28 mmol Pb^{2+}/g SMZ and 0.32 mmol Cd^{2+}/g SMZ. For the multi-component system (mixed Cd^{2+}/Pb^{2+}), although metal adsorption decreased, SMZ was shown to preferentially adsorb Cd^{2+} than Pb^{2+}. SMZ also effectively adsorbed organic contaminants such as toluene where the adsorption exhibited a linear-type isotherm. The mixed-solute systems clearly demonstrated that both heavy metal and organic contaminants could be adsorbed simultaneously by SMZ.