

CHAPTER II

BACKGROUND AND LITERATURE SURVEY

Mixed wastes are defined as wastes that contain both toxic organic and heavy metal contaminants. Mixed wastes have been generated from various sources such as power generating plants, petroleum refining industry, gas manufacturing plant, industrial/municipal incinerators and leachate from underground tank or waste disposal site. Toxic organics commonly found in mixed wastes are chlorinated compounds (such as carbon tetrachloride, trichloroethylene, and polychlorinated biphenyls etc.), polyaromatic hydrocarbons and hydrocarbon solvents (benzene, toluene, xylene, acetone, chloroform etc.). Several heavy metals, such as Cd, Cr, Hg and Pb, are the inorganic constituents frequently found in mixed wastes.

2.1 Current Techniques for Contaminants Removal

Ion exchange/adsorption, precipitation, ultrafiltration and reverse osmosis are techniques currently used for the removal of dissolved heavy metals. Activated carbon and microbial degradation are extensively used to remove organic contaminants. The adsorption technique is one of the most simple, economical and efficient techniques. For several years, various natural adsorbents, such as clay, activated carbon and zeolite, have been used to remove heavy metal and organic contaminants. However, those adsorbents have a serious limitation due to their low capacity for removal of toxic organic contaminants from mixed wastes. To enhance the sorption capacity, various modification techniques have been studied, including the surface modification of clay or zeolite using surfactants. The modification not only increases the sorption capacity for organic compounds but also improves ability of the adsorbent for mixed waste treatment.

Consequently, numerous studies have been carried out to investigate the modification of the surface of natural adsorbents such as clay minerals. Organoclays can be formed by replacing natural inorganic cations on the surfaces of clay minerals with organic cations via simple ion exchange reactions (Xu and Boyd, 1995).

The uptake of organic compound by organoclays (surfactant-modified clay) is found to increase due to their hydrophobicity (Lo *et al.*, 1997).

Surfactant-modified clays have been used not only to remove organic contaminants but also to remove toxic metals such as chromium, cadmium, copper etc. Malakul *et al.* (1998) investigated the mechanism for sorption of metal on surfactant-modified clay complexes. The results revealed metal bind to the chelating agent on modified clay complex. Unlike unmodified clay which through purely ion exchange.

In addition to clay minerals, natural zeolite has also been studied in their ability for heavy metal and organic removal. Upmiere and Czurda (1997) investigated the adsorption behavior of the four natural zeolites and clay for different pollutants. The clay and the zeolite showed similar adsorption capacities for Cd^{2+} and phenol while the adsorption capacity of the zeolites for Tl^{2+} are up to 50 times higher than that of the clay. This demonstrated that the natural zeolite has higher potential to remove heavy metal than natural clay.

Recently, the surface modification technique has also been applied to natural zeolite such as clinoptilolite. In 1994, Cadena and Bowman studied the simultaneous removal of anion, cationic and neutral hazardous pollutants from aqueous solutions by surfactant-modified zeolite (SMZ). The results indicate that SMZ has significant potential for treating waters contaminated with mixtures of pollutants of various types.

2.2 Clinoptilolite

Clinoptilolite is the most common natural zeolite found mainly in sedimentary rocks of volcanic origin. When volcanoes spewed their ash on ancient lakes a few thousand millennia ago, the resulting chemical reaction of the ash and alkaline water altered the ash into various forms of zeolite crystal. Significant clinoptilolite deposits exist throughout the world. Clinoptilolite is used in many applications such as a chemical sieve, a gas absorber, a feed additive, a food additive, and an odor control agent, as a water filter for municipal and residential drinking water and aquariums. Clinoptilolite is well suited for these applications due to its

large volume of pore space, high resistance to extreme temperatures and chemically neutral basic structure.

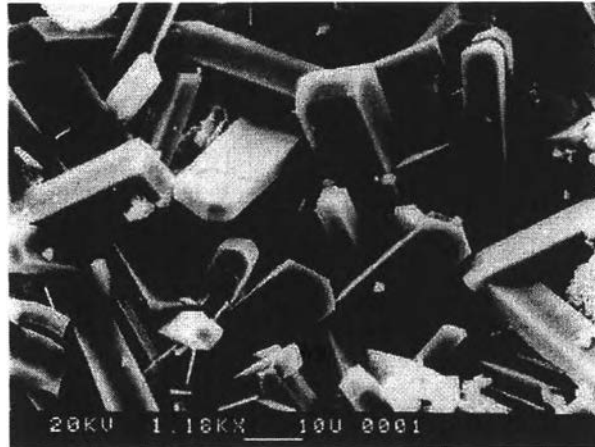


Figure 2.1 SEM image of clinoptilolite (Armbruster, 1996).

The simplified formula of clinoptilolite is, $(\text{Na,K})_6\text{Si}_{30}\text{Al}_6\text{O}_{72}\cdot n\text{H}_2\text{O}$. Structural of clinoptilolite is Si and Al ordering within the tetrahedral framework structure. Every oxygen is connected to either a silicon or an aluminum ion (at a ratio of $[\text{Al} + \text{Si}]/\text{O} = 1/2$), producing a sheet-like structural organization. A few bonds that are relatively widely separated from each other connect the sheets to each other. The sheets contain open rings of alternating eight and ten sides. These rings stack together from sheet to sheet to form channels throughout the crystal structure. The size of these channels controls the size of the molecules or ions that can pass through them and therefore a zeolite like clinoptilolite can act as a chemical sieve, allowing some ions to pass through while blocking others. The excess oxygen in the alumina molecules gives the framework a negative charge. This charge and the open framework allows the clinoptilolite to trap positively-charged ions (cations) such as sodium (Na^{+1}), potassium (K^{+1}), calcium (Ca^{+2}) and/or Magnesium (Mg^{+2}).

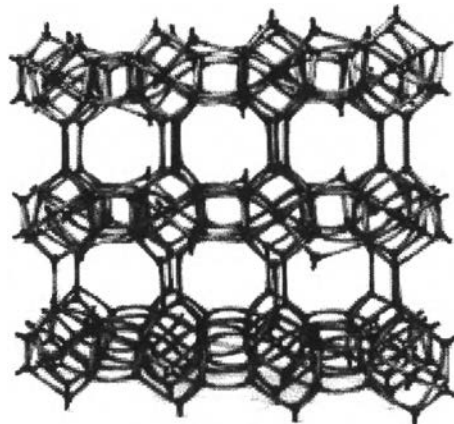


Figure 2.2 Clinoptilolite framework model view along cleavage plane of crystal plates.

2.3 Adsorption Properties of Clinoptilolite

Clinoptilolite has high cation exchange capacity that permits an efficient removal of heavy-metal cations. The high cation exchange capacity results from the unique crystal structure of zeolite minerals which is basically formed by a framework of SiO_4^- tetrahedral, wherein all oxygen atoms are shared by two adjacent tetrahedra resulting in an overall oxygen/silicon ratio of 2:1. The substitution of silicon by aluminum in the tetrahedral-sites results in a net negative charge of the framework, which is, balanced by loosely bound, exchangeable, extra framework cations, mainly of the alkali and alkaline earth elements. The cation exchange capacity (CEC) for the clinoptilolite and clay are 2.6 and 0.8 meq/g, respectively.

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. The study revealed that clinoptilolite is highly selective for lead (Pb), copper (Cu) and cadmium (Cd).

The pH of the solution affects the removal efficiency of the heavy metal. Mier *et al.* (2001) studied the interactions of Pb (II), Cd (II) and Cr (II) competing for ion exchange sites in naturally occurring clinoptilolite. The higher removal

efficiencies (>95%) occurred in the acidic pH range while in the higher pH range (>10) the efficiency declined.

Clinoptilolite has also been applied to remove toxic organics. Sismanoglu and Pura (2001) have studied the adsorption of ortho-, meta- and para-nitrophenols on clinoptilolite. The study observed that the adsorption of aqueous nitrophenols on clinoptilolite is a function of the solution concentration and temperature. That manifest clinoptilolite has potential to remove both toxic organic and heavy metal contaminants. However, problems of using natural zeolites for this purpose are; products contain a variety of impurities and has low sorption capacity for organic compounds. So the enhanced organics sorption capacity by surfactant modified clinoptilolite was investigated.

2.4 Study of Cationic Surfactant Sorption on Clinoptilolite

Cations (Na, K) adsorbed on the surface of clinoptilolite can be replaced by cationic 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 of the zeolite is accessible for the large surfactant molecules, the external surface becomes electrically neutral or even positively charged as a consequence of the surfactant loading as either a monolayer or a bilayer, respectively. However, the internal surfaces still remain an active cation exchanger (Li and Bowman, 1994).

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 carbon content of the zeolite to increase. The positive surface charge provides sites for sorption of anions such as chromate and nitrate. 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 metals such as Pb^{2+} and Hg^{2+} .

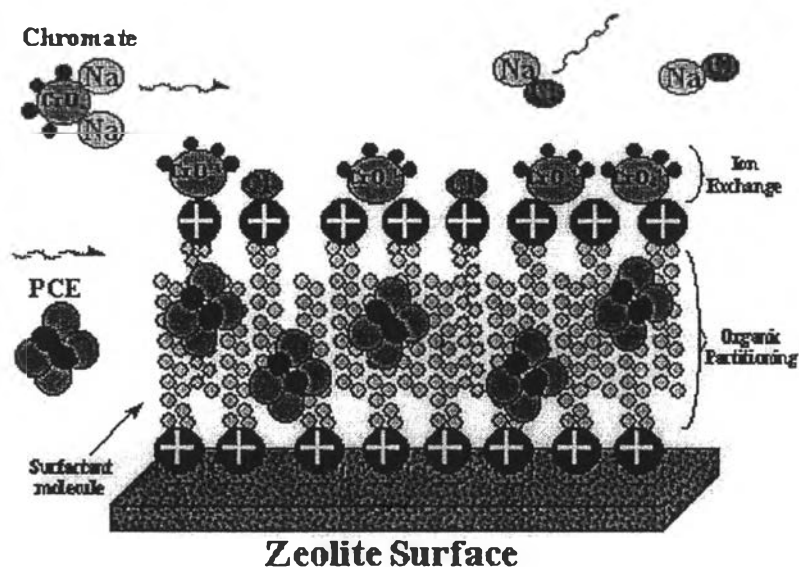


Figure 2.3 Sketchy drawing of HDTMA forming bilayer (tail to tail) on the surface of clinoptilolite (Bowman, 1994).

Li (1999) investigated the sorption kinetics of hexadecyltrimethylammonium (HDTMA) on natural clinoptilolite. The amount of sorbed HDTMA is a function of the initial HDTMA input and the sorption time. When the initial HDTMA input is less than the external cation-exchange capacity of the clinoptilolite, the HDTMA sorption is fast and equilibrium can be established in 1 hour. As the initial HDTMA input greater than the external cation-exchange capacity of clinoptilolite, which will result in more than a monolayer HDTMA surface coverage, the time for HDTMA sorption to reach equilibrium increases exponentially. The counterion solution concentration data suggest that at the initial stage HDTMA molecules sorb on the zeolite via micelle forms, which is manifest by a decrease in chloride solution concentration with time. When HDTMA solution concentration is depleted to less than its critical micelle concentration, the adsorbed micelles rearrange themselves to a more stable monolayer or bilayer configuration, which is reflected by an increase in counterion solution concentration due to desorption of chloride from admicelles.

In addition, the Tapping-Mode Atomic Force Microscopy (TMAFM) and High-Resolution Thermo gravimetric (HR-TGA) have also been used to study the

patterns of hexadecyltrimethylammonium bromide (HDTMA) sorption on the treated surface. The results indicate that the buildup of HDTMA bilayer, or some form of a bilayer, begins before full monolayer coverage is complete (Sullivan *et al.*, 1998).

The chemical and biological stability of SMZ was studied by Li *et al.* (1998). Under acidic conditions, desorption of HDTMA was negligible. Under basic conditions, desorption was negligible when Cl^- was the HDTMA counterion, while desorption was 15% when Br^- was the counterion. This indicated that more desorption occurred when Br^- was the counterion than when Cl^- was the counterion, except for the low ionic strength cases. Because of more HDTMA desorbed at low ionic strength system. The result also suggested that only monomer desorbed from the sorbed bilayer and the amount of monomer desorbed depends on the anion concentration in solution. This would explain why more HDTMA desorbed when SMZ was equilibrated with water than with higher ionic strength solutions. The results of the SMZ toxicity experiments indicated that the bacteria remained viable in all the microcosms with SMZ. In those microcosms containing aqueous HDTMA without zeolite, HDTMA inhibited the growth of the microorganism.

2.5 Use of SMZ to Adsorb Toxic Organics and Heavy Metals

Cadena and Bowman (1994) investigated the mechanism of anion sorption (e.g. chromate) by hexadecyl-trimethylammonium-modified zeolite. The results showed that the maximum chromate sorption appears to occur when zeolite is treated to 100% of its external cation exchange capacity. Bromide was used as counterion for HDTMA-modified zeolite in their study. Desorption of bromide was found to be approximately linear with increasing chromate sorption. The proportion of bromide desorbed was almost twice the quantity of chromate sorbed. Moreover, they also found that the presence of inorganic pollutants such as Pb^{2+} and organic pollutant such as BTX (Benzene, Toluene and Xylene) together in the same solution did not diminish HDTMA-zeolite ability to retain either class of compound. The results indicated that HDTMA-zeolite can treat waters contaminated with mixtures of pollutants of widely varying chemistries.

Counterions have significant effects on the HDTMA sorption on zeolite, chromate on cationic-treated zeolite and also affect in stabilizing the sorbed cationic bilayer. The HDTMA sorption capacity on zeolite follows $\text{Br}^- > \text{Cl}^- > \text{HSO}_4^-$. In contrast, the chromate sorption capacity follows $\text{HSO}_4^- > \text{Br}^- > \text{Cl}^-$. That indicated, the exchangeability of the counterion is more important than the total HDTMA loading in controlling the amount of chromate adsorbed by HDTMA-treated zeolite. HDTMA- HSO_4^- -treated-zeolite showed the greatest chromate sorption but industrial grade HDTMA- HSO_4^- is not currently available. Thus, it may not be economical to prepare HDTMA- HSO_4^- -zeolite for environmental application. That means HDTMA- Br^- -treated-zeolite is more practicability (Li and Bowman, 1997).

Sorption of ionizable organic solutes by SMZ was studied by Li *et al.* (2000). The results of this study demonstrate that sorption of organic contaminants increased when increased surfactant loading up to equivalent monolayer coverage (100mmol/kg). Beyond monolayer coverage, further increases in surfactant loading did not enhance sorption of organic contaminants at neutral pH. On the other hand, the sorption of the ionizable organic compounds such as phenol and aniline varied as a function of both pH and surfactant loading on the zeolite. When solution pH is such that the neutral form of an ionizable species dominates, no sorption enhancement occurs in treating the SMZ beyond monolayer coverage. At pH values where ionized species are important, sorption to SMZ at bilayer coverage will be enhanced or depressed depending upon the ionic charge.

Li and Bowman (1998) studied the sorption of Perchloroethylene (PCE) by SMZ as controlled by surfactant loading. Sorption of PCE on SMZ occurred through partitioning of PCE into the organic phase formed by the surfactant on the zeolite surface. The PCE sorption coefficient on SMZ is a function of the surfactant loading and resultant organic phase density. At below full monolayer coverage and higher surfactant loading levels, the PCE sorption is most effective. In bilayer PCE sorption the efficiency decreased due to increased density of the hydrophobic core of the sorbed surfactant bilayer. The results revealed the greater hydrophobicity of the monolayer- versus the bilayer-modified surface might be a result of the greater PCE sorption efficiency exhibited by the monolayer systems.

2.6 Regeneration of SMZ

SMZ has demonstrated its ability to remove a variety of contaminants. However, SMZ has a finite sorption capacity for different contaminants. Successful regeneration of SMZ appears to be the key factor for its applications in waste treatment. Li and Bowman (1999) studied the regeneration of SMZ after saturation with contaminants. They have shown that chromate-saturated SMZ can be treated with a carbonate solution, where the chromate was replaced by carbonate and/or hydroxide anions. By rinsing with HCl solution, the carbonate sorbed on surfactant bilayer reacts with protons to form CO₂ that escape from the surface and solution, leaving Cl⁻ as the counterion. However, the production of CO₂ gas decreased the hydraulic conductivity, resulting in no further drainage under gravity, indicating that this method was not a practical regeneration scheme. An alternative method was also studied by using sodium dithionite solution to reduce Cr (VI) to Cr (III). Reduction of chromate to Cr (III) frees up anion exchange sites for further chromate sorption. The cationic Cr (III) is likely strongly bound to the SMZ by cation exchange and/or precipitation as hydroxides. Early breakthrough was found after regenerated by sodium dithionite solution. The behavior of the dithionite-regenerated material suggests a decrease in chromate sorption affinity and/or change in hydraulic properties of the SMZ that result in increased hydrodynamic dispersion. The results also showed that PCE-saturated SMZ could be fully regenerated by air stripping.

Changing the pH of the solution is an alternative method to regenerate surfactant-modified adsorbents. Malakul *et al.* (1998) found that the adsorption of metal ions into modified-clay complexes has a strong pH-dependent. For the cadmium adsorption by the modified-clay complexes, it was found that high metal adsorption capacity could be obtained at pH 7, while there is negligible metal adsorption at pH 3. For the copper adsorption, it was found that no uptake of copper at pH 3 while at pH 8 copper ions are adsorbed strongly. It is suggested that the adsorption of metal ions on surfactant-modified adsorbents is reversible mechanism. The shift of pH from high to low values can be used to transform the adsorbents from a state of “high” affinity for metal ions (adsorption) to one of “low” affinity

(desorption). Thus changing pH of the solution can conveniently be used to regenerate surfactant-modified adsorbents.