CHAPTER II
BACKGROUND AND LITERATURE SURVEY

Mixed wastes are defined as wastes that contain both heavy metal and toxic organic contaminants. Electronic processors, petroleum refining, wood preserving and chemical manufacturing are some of the leading sources of mixed wastes. Copper, zinc, chromium, cadmium and lead are common heavy metals found in mixed wastes. The adverse health effects of these heavy metals are well documented (Castiglia, 1995; Hansen, 1998; and Graeme and Pollack, 1998). Each metal has its own particular chemistry and toxicity patterns. Birth defects, cancer and a number of chronic diseases have all been linked to heavy metals. Toxic organic compounds commonly found in mixed wastes are chlorinated compounds, polyaromatic hydrocarbons and hydrocarbon solvents. These compounds are priority pollutants that affect human in various ways such as irritant, vomiting, narcotic and cancer.

2.1 Treatment Techniques for Wastewaters

Distillation, extraction, ion-exchange and adsorption are examples of treatment techniques for waste streams. Distillation technique is a thermal treatment technology applicable to the treatment of wastes containing organics that are volatile enough to be removed by the application of heat. Extraction technologies are used to treat a variety of organic constituents. The selection of an extraction fluid is dependent on the solubility of the organic waste in the extraction fluid. Ion-exchange is a treatment technology applicable to metals in wastewaters where the metals are present as soluble ionic species. This technique is a reversible process in which hazardous cation and/or anion are removed from aqueous solution and replaced by nonhazardous cation and/or anion such as sodium, hydrogen, chloride, or hydroxyl ions. But ion-exchange cannot remove organic compounds. Activated carbon adsorption is a treatment technology used to treat wastewaters containing dissolved organics at concentrations less than about 5 percent and, to a lesser extent, dissolved metal and other inorganic contaminants. The most effective metals removal is achieved with metal complexes. The adsorption technique is one of the most simple,

economical and efficient treatment techniques. The adsorption process occurs because the contaminant has a low solubility in the waste, has a greater affinity for the adsorbent than for the waste, or a combination of the two. However, the adsorbents have a serious limitation because of their low adsorption capacity for remove toxic organic. To enhance the adsorption capacity, various modification techniques have been studied, such as the surface modification of clay or zeolite by using surfactant (Bowman *et al.*, 1995, Malakul *et al.*, 1998 and Zhu *et al.* 2000). Recently, several research studies have shown that the surfactant-modified zeolite has the potential for the treatment of groundwater and wastewater containing a mixture of various types of contaminants (Bowman *et al.*, 1995; Neupane and Park, 2000; Lee and Kim, 2002 and Sriwongjanya, 2004).

2.2 Natural Zeolite

Natural zeolite minerals can be defined as crystalline, hydrated alumino-silicates of alkaline and alkaline-earth cations that consist of infinite or finite three dimensional crystal structures of $(Si, Al)O_4$ tetrahedral, which are linked together by the sharing of oxygen atoms as shown in Figure 2.1. Their structure contains channels and pores filled with a certain amount of water and exchangeable cations. This water can evaporate when the zeolite heated to about 250°C and is regained at room temperature; also some of cations constituent may be exchangeable from the zeolite inner cavities and pores without any major change of zeolite structure.
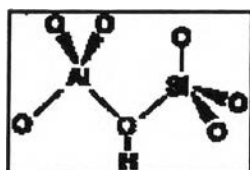

Figure 2.1 Primary building units of SiO_4 and AlO_4 tetrahedral.

Although clinoptilolite is not the most well known, it is definitely one of the most useful natural zeolites. Clinoptilolite exists in extensive deposits throughout the world. It has long been used in many applications such as a chemical sieve, a gas

absorber, a feed 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 amount of pore space, high resistance to extreme temperatures and chemically neutral basic structure. The crystal structure for clinoptilolite is shown in Figure 2.2.
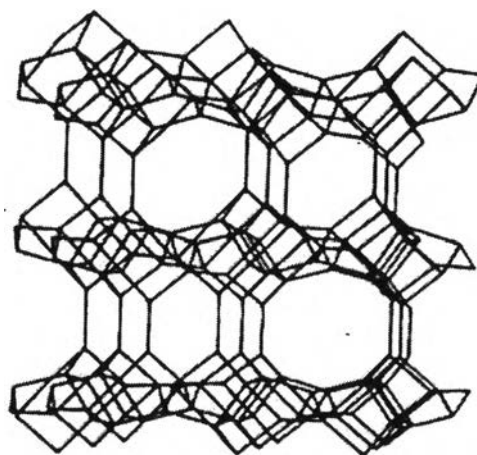

Figure 2.2 Crystal Structure for Clinoptilolite.

Clinoptilolite has a high cation exchange capacity, thus allowing an efficient removal of heavy-metal cations. The high cation exchange capacity results from the unique crystal structure of zeolite minerals, which basically is 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 excess oxygen in the alumina molecules gives the framework a negative charge. This charge and the open framework allow the clinoptilolite to trap positively charged ions (called cations) such as sodium (Na^{+1}), potassium (K^{+1}), calcium (Ca^{+2}) and/or 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. Clinoptilolite thus has the potential to remove both toxic organic and heavy metal contaminants. However, the problems for using natural zeolites are as follow;

products contain a variety of impurities, poor selectivity for heavy metal adsorption and low organics sorption capacity.

2.3 Adsorption of Contaminants by Natural Zeolite

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. This demonstrated that the natural zeolite has a higher potential to remove heavy metal than natural clay. Ouki and Kavannagh (1999) studied the selectivity and removal performance of clinoptilolite. They found that clinoptilolite was highly selective for lead (Pb^{2+}), copper (Cu^{2+}) and cadmium (Cd^{2+}). The selectivity could be the result of various factors, which influence ion exchange behavior in zeolite. One factor is the framework structure of the zeolite itself. The dimensions of the channel of zeolite must be large enough to allow passage of hydrated metal ion.

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. The higher removal efficiencies (>95%) occurred in the acidic pH range while at high pH range (>10) the efficiency declined dramatically.

Clinoptilolite has also been applied to remove toxic organics. Sismanoglu and Pura (2001) studied the adsorption kinetics and the adsorption isotherm of ortho-, meta- and para-nitrophenols on clinoptilolite. They found that the adsorption of ortho-, meta- and para-nitrophenols on clinoptilolite was a function of the solution concentration and temperature. The adsorption rates were observed to be equal to the first-order kinetics. The equilibrium was established in 3 hours. The rate of adsorption of ortho-, meta- and para-nitrophenols decreased with time at constant temperature. At constant concentration, the rate of adsorption increased sharply on increasing the temperature for all there nitrophenols. The adsorption isotherm could

be explained by the Langmuir equation. From the Langmuir parameter, the ortho- and meta-nitrophenol were less adsorbed when compared to para-nitrophenol

2.4 Modification of Natural Clay and Zeolite using Surfactant

The adsorption isotherm of an ionic surfactant onto an oppositely charged substrate is typically S-shaped when plot 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 2.3.
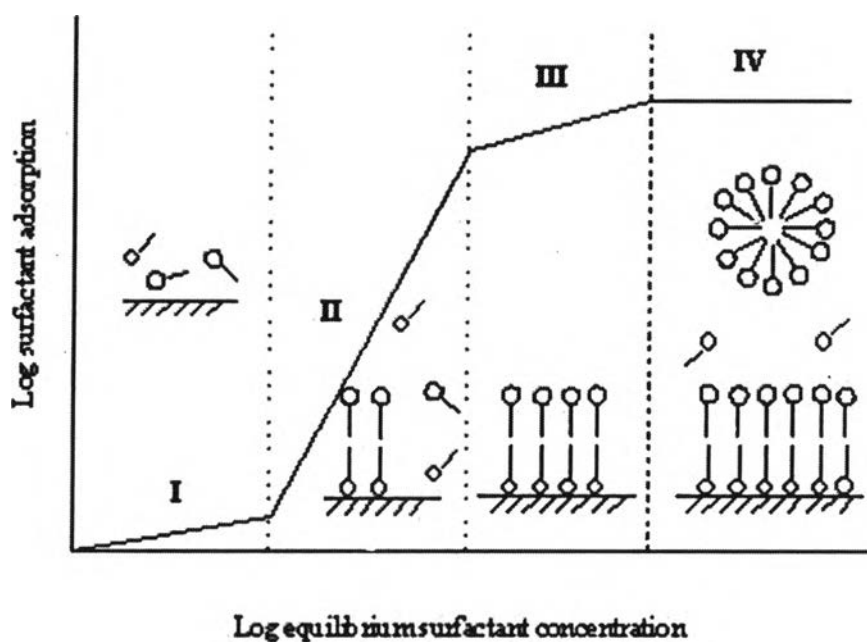

Figure 2.3 Typical adsorption isotherm of surfactant on solid oxide surface.

In region I low levels of surfactant adsorption occur 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 contact with solution, so that the 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 repulsion 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.

Cations (Na^+, K^+) adsorbed on the surface of natural adsorbents can be replaced by cationic surfactant. Haggerty and Bowman (1994) investigated the sorption of hexadecyltrimethyl ammonium (HDTMA) on clinoptilolite. HDTMA was exchanged with extrastructural cations of the zeolite up to the external cation-exchange capacity because it is too large to enter onto the internal portion of the zeolite thus sorption of the amine only occurred on the zeolite's external exchange site. And showing a strong affinity to the exchange sites at the zeolite surface due to HDTMA adsorbed to zeolite by Coulombic interactions with the surface. This HDTMA is essentially irreversibly bound to the zeolite's external surface.

Bowman *et al.* (1995) studied the stability of surfactant-modified zeolite. The result 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 Waal's associations among the adsorbed surfactant hydrocarbon chains and entropic effects.

Sullivan *et al*. (1998) examined adsorption of the HDTMA to clinoptilolite. They used Fourier transform (FT) Raman spectroscopy and batch sorption methods to elucidate the structure of adsorbed HDTMA. At high HDTMA loading or HDTMA's concentration above the zeolite's external cation exchange capacity (ECEC), the Raman spectra indicated that adsorbed HDTMA was similar in conformation to solution micelles and thus may contain anion exchange sites. At the HDTMA's concentration below the zeolite's external cation exchange capacity, the adsorbed HDTMA tail groups tended to have more disorder, similar to solution monomer.

Malakul *et al*. (1998) developed surfactant-modified clay complexes for metal adsorption. In their study, they used cationic surfactant, cetylbenzyldimethyl-ammonium (CBDA), as organic compounds in clay surface modification and the modified clay surface can be further used to anchor metal ligands such as palmitic acid through hydrophobic interaction. The results suggested that the amounts of CBDA in clay-CBDA complexes are 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.

The adsorption kinetics of hexadecyltrimethyl ammonium (HDTMA) on natural clinoptilolite was investigated by Li (1999). The amount of adsorbed 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 is 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 increase exponentially. The counterion concentrations suggested that at the initial stage of adsorption, HDTMA molecules adsorbed on the zeolite via micelle forms, which was manifested by a decrease in chloride solution concentration with time. When the

HDTMA solution concentration was depleted to less than its critical micelle concentration, the adsorbed micelles rearrange them 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.

Zhu and Chen (2000) studied the simultaneous incorporation of an anionic surfactant, sodium dodecyl sulfate (SDS), and a cationic surfactant, dodecyl trimethylammonium bromide (DTMBA), onto bentonite. The results indicated that the organic carbon contents and interlayer spacing of these organobentonites were greatly different from those of the natural bentonite. The organic carbon contents and interlayer spacing of modified bentonite changed regularly with the amount of mixed anionic-cationic surfactants coated onto the bentonite, which is the base of improving sorption properties of organic compounds to anion-cation organobentonites.

David and Jorge (2001) investigated the adsorption of sodium dodecylbenzene sulfonate (SDBS) in aqueous solution, over a organophilic bentonite which prepared to 100% and 50% of CEC of natural bentonite by cationic surfactant such as tetramethyl ammonium bromide (TAB), hexadecyl trimethyl ammonium bromide (HDTMA), hexadecyl benzyldimethyl ammonium chloride (CDAC), and alkylbenzyl dimethyl ammonium chloride (BTC). The result of adsorption kinetic for the different adsorption showed a same behavior. The equilibrium was reached at approximately 20-30 min. The adsorption process of SDBS over organo-bentonite was described by the Langmuir isotherm. The effects of the substitution of exchange cations by the quaternary ammonium ion on SDBS adsorption were explained. When the bentonite was modified at 100% of its CEC, it adsorbs approximately two times more SDBS than what it adsorbs when it is modified at 50%. The stability of SDBS onto organo-bentonite described by the Gibbs's energy change of adsorption for process: adsorbate over the adsorbent → adsorbate in the solution. These ΔG values indicated that the SDBS molecules are more stable in the adsorbed phase than in the aqueous phase.

2.5 Adsorption of Contaminants by Surfactant-Modified Zeolite

Bowman *et al.* (1997) used a one-step modification to prepare surfactant-modified zeolite by cationic surfactant such as hexadecyl trimetyl ammonium. The sorption of the quaternary amine in bilayer or admicelle form is causing the charge on surface to change from negative charge to positive and the organic 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. 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.
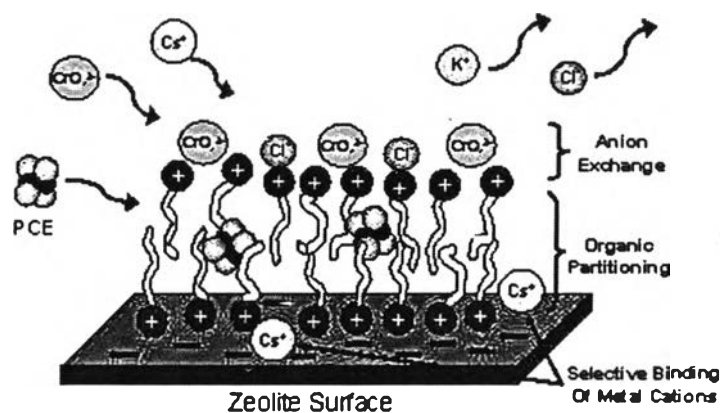

Figure 2.4 Schematic diagrams of sorption mechanisms for anions, cations, and nonpolar organics on SMZ. (Bowman *et al.*, 1997)

Bowman (1995) studied the sorption of nonpolar organic compounds, inorganic cation, and inorganic oxyanions by surfactant-modified zeolite. In result, for organic compound adsorption shown that untreated zeolite has not affinity for the organics (benzene, toluene, and p-xylene) but the modified zeolite can be adsorbed. The all adsorption isotherms are likely linear isotherm. For the inorganic cation such as lead (Pb^{2+}), the result shown that the untreated and modified zeolites have affinity for Pb^{2+}. This can be understood by recalling that HDTMA only occupy the zeolite's

external cation exchange sites. The Pb^{2+} can be accessible into internal exchange sites due to Pb^{2+} are smaller than zeolite's pore size. The modified zeolite also adsorbed anion (chromate, selenate, or sulfate) from solution. All of the anion displayed Langmuir isotherm behavior on modified zeolite.

Counterions can have a significant impact on the HDTMA adsorption on zeolite, the chromate adsorption on cationic-treated zeolite, and the stabilizing of the adsorbed cationic bilayer. The HDTMA sorption capacity on zeolite follows Br->Cl->HSO4-. In contrast, the chromate sorption capacity follows HSO4->Br->Cl-, thus indicating that 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-Br-treated-zeolite was shown to be more practicable (Li and Bowman, 1997).

Neupane and Park (2000) examined that adsorption of naphthalene onto anionic surfactant (SDBS) modified alumina. Adsorption of naphthalene to adsorbed surfactant phase is a partitioning-dominated process and linear regression lines were fitted through the all the data points at surfactant concentration. The result indicated that the adsorbed surfactant phase with more organic carbon content provides more efficient partitioning medium for naphthalene per mole of surfactant. Lee and Kim (2002) studied adsorption of naphthalene by HTDMA modified kaolinite. Naphthalene was partitioned into the organic phase created by the surfactant tails of the HDTMA modified kaolinite. The adsorption isotherms for naphthalene were nearly linear. The result suggested that the efficiency of the naphthalene of the naphthalene partitioning is strongly dependant on the surfactant configuration rather than on surface coverage of adsorbed HDTMA.

Zhu et al. (2000) studied the mechanism and characteristics of polar or ionizable solute adsorption by dual-cation organobentonites. Their was synthesized by replacing the metal ions in bentonite with both long-chain alkyl quaternary ammonium cations, such as dodecyltrimethyl ammonium (DTMA), benzyldimethyltetradecyl ammonium (BDTDA), cetyltrimethyl ammonium (CTMA), octodecyltrimethyl ammonium (OTMA), and short-chain alkyl quaternary ammonium cations, such as tetramethyl ammonium (TMA).The sorption isotherms of p-nitrophenol, phenol, and aniline are typically nonlinear and properties was

affected by treatment conditions, such as pH, amount of organobentonite, and shaking time.

Zhu and Chen (2000) studied the sorption of p-Nitrophenol by anion-cation organobentonite, which were prepared by incorporating both cationic surfactant bromide dodecyltrimethyl ammonium (DTMAB) and anionic surfactant sodium dodecyl sulfate (SDS) onto bentonite. The results indicated that the amount of p-Nitrophenol removed from solution depends greatly on the amount of SDS and DTMAB in the bentonite. The removal rate of p-Nitrophenol from solution was improved by synergistic solubilization in both anionic and cationic surfactant moieties of the organobentonites and the effect of synergistic solubilization results mainly from partition at higher concentrations or adsorption at lower concentrations. The sorption characteristics of the organo-modified soil for aqueous phase neutral organic compounds (NOCs), toluene, was studied by Chen *et al*. (2002). In their study, the modified soil prepared by replacing the cation of loess soil with both cationic surfactant, hexadecyl trimethyl ammonium bromide (HDTMA-Br) and anionic surfactant, sodium dodecylbenzene sulfonate (SDBS). The results showed the sorption isotherm of toluene appeared likely linear and increased gradually when the added amount of HDTMA was increased. When compare the sorption isotherm of the toluene on single-cation and anion-cation organo-soil is same trend.

Recently, Saengchote (2003) studied the modification of clinoptilolite using a two-step surface modification technique by adsorbing CTAB and palmitic acid (PA) to form the mixed bilayer on the zeolite surface. The resulting surfactant modified-zeolite (SMZ) has hydrophobic region for adsorbed metal ions and hydrophilic region for absorbed organic compounds as shown in Figure 2.5. SMZ prepared by using this technique was shown to selectively adsorb heavy metal ions such as cadmium (Cd^{2+}) from aqueous solution. Moreover the highly hydrophobic surface of SMZ also provided effective sorption sites for organic contaminants such as toluene. It was found that the adsorption capacity of SMZ decreased slightly in mixed-solute system where both Cd^{2+} and toluene were removed simultaneously.
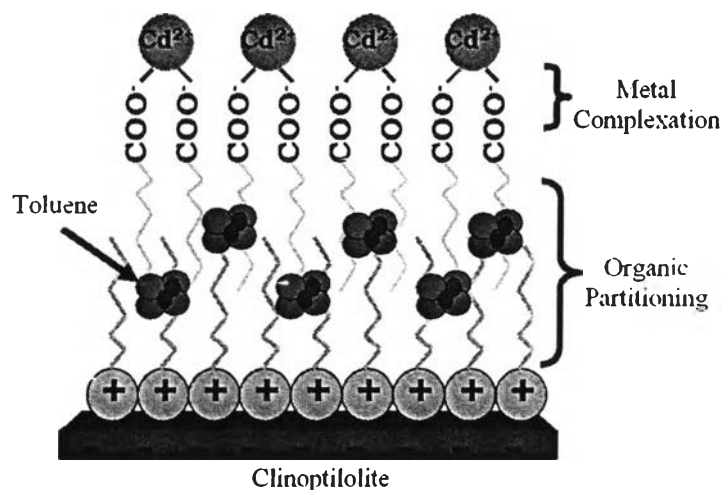
Figure 2.5 Schematic diagrams of sorption mechanisms for cadmium and toluene on SMZ.

Sriwongjanya (2004) investigated the preparation of surfactant-modified zeolite (SMZ) by a two-step surface modification technique and examined its capability in the adsorption of heavy metal ions and organic pollutant separately and simultaneously. These SMZ adsorbents were further evaluated 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.