



## CHAPTER I

### INTRODUCTION

#### 1.1 Introduction

Heavy metals, dyes and surfactants are found in the wastewater streams of industrial processes, including textiles, paper, paint manufacture, leather tanning, battery manufacture, dyeing, and others; their removal has attracted much practical and academic interest owing to increased concern with their environmental impact. (Ng *et al.*, 2002 and Ho *et al.*, 2002).

The presence of the toxic heavy metals contaminants in the treated or untreated wastewater from the industries either producing or using these metal bearing products introduces these metals into water bodies (Sudha Bai and Abraham, 2003). These released heavy metals through aquatic route; even at ultra trace metal imposes serious health risks via their bioaccumulation in living tissue throughout the food chain. Cadmium and copper are two very important elements as their release in the aquatic environment and accumulation could result in toxicity to both human and aquatic life. There are some conventional methods for treatment of liquid effluent for removal of traces of heavy metals such as ion exchange, chemical precipitation, adsorption reverse osmosis, coagulation, membrane filtration, electrochemical process and co-precipitation from the effluents encountered with few major disadvantages such as high energy requirements, incomplete metal removal and generation of toxic sludge which needs proper disposal in addition to financial constraints (Volesky, 2001).

Alkylphenol Polyethoxylates (APnEOs) comprise an important group of non-ionic surfactants that are widely used in household and industrial applications such as detergent production, textile industries, commercial laundries and tanning industries. It has been recently reported that APnEOs and their biotransformation products have estrogenic activity (endocrine disrupters) that may interfere with the normal functions of the hormonal systems of humans being, fish and wildlife. APnEOs make up the world's third largest group of surfactants in terms of production

and have been used for nearly 50 years. Every year about 500,000 metric tones of APnEOs are produced worldwide. Conventional biodegradation process cannot degrade APnEOs to a non-toxic form. It was estimated that 40% (calculated on a molar basis) of the total APnEOs loading into sewage treatment plants could reach natural water via secondary effluents in the form of metabolic products (Ahel *et al.*, 1996).

Dyes have long been used in dyeing, paper and pulp, textiles, plastics, leather, cosmetics and food industries (Gulnaz *et al.*, 2004). Colour stuff discharged from these industries poses certain hazards and environmental problems. These coloured compounds are not only aesthetically displeasing but also inhibiting sunlight penetration into the stream and affecting aquatic ecosystem (Tsai *et al.*, 2001). Dyes usually have complex aromatic molecular structures which make them more stable and difficult to biodegrade (Barragán *et al.*, 2006). Furthermore, many dyes are toxic to some microorganisms and may cause direct destruction or inhibition of their catalytic capabilities (Santhy and Selvapathy, 2006). Methylene blue (MB) is a heterocyclic aromatic chemical compound with molecular formula:  $C_{16}H_{18}ClN_3S$ . It has many uses in a range of different fields, such as biology and chemistry. At room temperature it appears as a solid, odorless, dark green powder that yields a blue solution when dissolved in water. The hydrated form has 3 molecules of water per molecule of MB. Methylene blue should not be confused with methyl blue, another histology stain, new methylene blue, nor with the methyl violets often used as pH indicators. Moreover, the total dye consumption of the textile industry worldwide is in excess of 107 kg/year, and an estimated 90% of this ends up on fabrics. Consequently, 1000 tones/year or more of dyes are discharged into waste streams by the textile industry only worldwide (Mark, 1996). Dye producers and users are interested in stability, fastness and consequently produce dyestuffs, which are more difficult to degrade after use (Wong *et al.*, 2004).

According to their limitations and among the inherent disadvantages of activated carbon are their wide distribution of pore size, heterogeneous pore structure, and low selectivity for adsorption. The recent discovery of mesoporous molecular sieves has stimulated a renewed interest in adsorbent and catalyst design (Lee *et al.*, 2001). Hexagonal mesoporous silicate (HMS) having been studied extensively in

adsorption and catalytic fields, has mesoscale pore and silanol as surface functional group. Hexagonal mesoporous silicate (HMS), which has been studied extensively in chemical engineering fields, has meso-scale pores and uniform surface functional groups. Silanol group on HMS surface is considered to have high affinity to various functional groups of pollutants molecule such as ethoxy groups in APnEOs molecules and O and N atom in dye molecular structure in aqueous phase.

Moreover, HMS surface can be modified by various methods to enhance specific characteristics by metal substitution or organic-ligand modification in crystalline structure. However, effects of crystalline structures, surface functional groups as well as pH on single and mixed pollutants removal from aqueous phase by adsorption have not been studied. In this study adsorption of single and mixed pollutants on four different types of surface functional groups; silanol, amino-, mercapto-, octyl- functional groups grafted onto HMS are investigated comparing with powdered activated carbon (PAC).

## 1.2 Objectives

The main objective of this research is to study the adsorptive selectivity characteristic of mixed pollutants; heavy metals, dye, and surfactant in single and bi-solute onto mesoporous silicate modified by various specific functional groups. The sub-objectives are as follows:

1. To investigate adsorption capacities of heavy metals, dye and surfactant on synthesized mesoporous silicates in single solute system.
2. To study effects of surface functional groups on single solute adsorption.
3. To study the effects of pH on adsorption mechanisms.
4. To study selective adsorption mechanism of mesoporous silicate materials in bi-solutes system.
5. To compare selectivity characteristic of synthesis adsorbents with PAC in single and bi-solute adsorption.

### 1.3 Hypotheses

The hypotheses for this study are:

1. Three types of pollutants might be adsorbed on uniform surface and crystalline structure of synthesized mesoporous silicate by different mechanisms.

For example;

- Heavy metals: Chemisorption
- Ionic dye: Electrostatic interaction, Hydrogen Bond,  
van der Waals force

- Non-ionic surfactant: Hydrogen Bond, van der Waals force

2. Selective adsorption efficiencies of three pollutants in single and bi-solute onto mesoporous silicate can be increased by surface modification with specific functional groups.

3. Surface characteristics and crystalline structures, for example; pore structure, surface charge, surface area, and pore size, etc. might affect to adsorption capacities.

### 1.4 Scopes of Study

The physical adsorption process formed by synthesis of mesoporous silicate materials was utilized to remove mixing three pollutants in “single, and bi-solute” from synthesis wastewater. Cd(II) and Cu(II) were used as heavy metals, TX-100 (APnEOs) was used as non-ionic surfactant, and Methylene blue was used as ionic dye. Pristine HMS, functionalized HMSs with surface functional groups, and PAC were used as adsorbents in this study.

The scope of this thesis contains 5 parts are follows:

Part 1: The synthesis of HMS and single-functionalization with organic-ligand.

A direct co-condensation method was performed for organic functionalization of mesoporous materials by using dodecylamine as a template and

tetraethoxysilane (TEOS) as a silica precursor. Aminopropyltriethoxysilane (APTES), Mercaptopropyltrimethoxysilane (MPTMS), and Dimethyloctylchlorosilane were used for surface functionalized modification on HMS.

Part 2: Physico-chemical characterization of synthesis Hexagonal Mesoporous Silicates (HMSs)

The physico-chemical characteristics of adsorbents including surface area, pore structure, pore size, surface charge, and surface functional groups were investigated by measure of nitrogen adsorption-desorption measurement, X-ray diffraction, acid-base titration, FT-IR spectroscopy, and elemental analysis, respectively.

Part 3: Adsorption Kinetic

The equilibrium contact times for single solute adsorption were investigated by varying contact time from 0 to 24 h under batch conditions with a suitable concentration and amount of adsorbent of 0.33 g/l. The adsorption rates of heavy metals (Cd(II) and Cu(II)), ionic dye (Methylene blue), and non-ionic surfactant (TX-100) onto pristine HMS, functionalized HMSs, and PAC were analyzed by using the pseudo-first-order equation of Lagergren and the pseudo-second-order kinetic model.

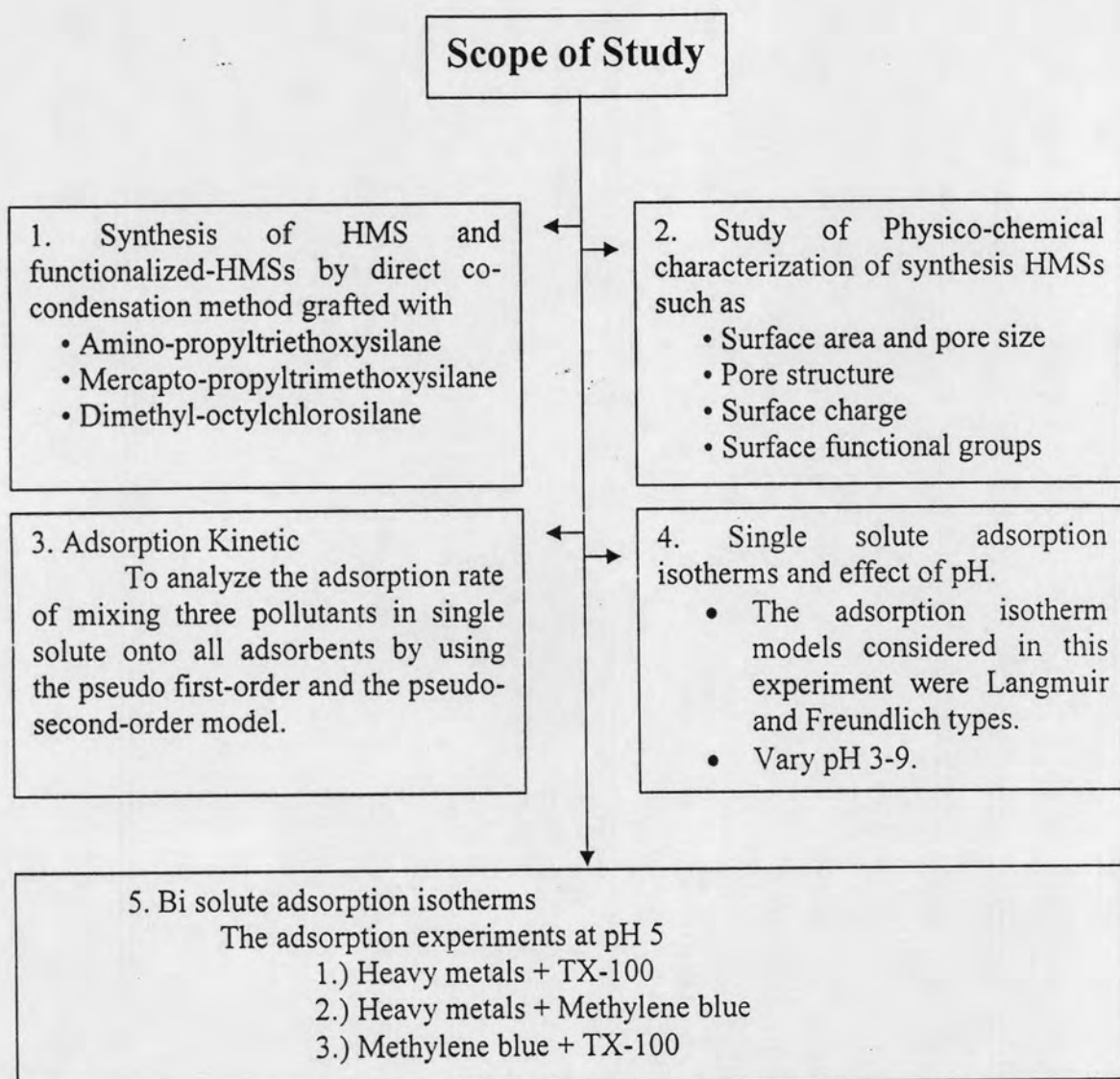
Part 4: Single solute adsorption isotherms and effects of pH

Adsorption isotherms of heavy metals (Cd(II) and Cu(II)), ionic dye (Methylene blue), and non-ionic surfactant (TX-100) for single solute were carried out by varying concentration of adsorbates and pH (3-9) under batch conditions with an amount of adsorbent of 0.33 g/l. The adsorption isotherm models consider in this experiment are Langmuir and Freundlich types.

Part 5: Bi solute adsorption

The experimental procedure was similar to that of single solute adsorption experiments at pH 5, except adding co-existing pollutants as following :

1. Heavy metals + TX-100
2. Heavy metals + Methylene blue
3. Methylene blue + TX-100



**Figure 1.1** Overall scope of study.