SURFACTANT MODIFIED ZEOLITE Y AS A SORBENT FOR SOME CHROMIUM AND ARSENIC SPECIES IN WATER

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To my beloved mother, father, brothers, sisters and my bestfriend

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ABSTRACT

The removal of some chromium and arsenic species from water by the surfactant-modified zeolite Y (SMZY) and unmodified zeolite Y was studied. Zeolite NaY was successfully synthesized from rice husk ash via seeding method involving the preparation of two separate gel formations. The synthesized and commercial zeolite NaY were characterized with XRD, FTIR, surface area and elemental analysis. The total cation exchange capacity (CEC) and external cation exchange capacity (ECEC) for the synthesis was higher than the commercial one due to the lower ratio of silica to alumina for the synthesized than the commercial zeolite Y. The zeolite NaY was subsequently modified with hexadecyltrimethyl ammonium (HDTMA) at the amount equal of 50%, 100% and 200% of ECEC of the zeolite. The study of Cr(III) removal showed the synthesized zeolite NaY effectively removed Cr(III) than the commercial one. The equilibrium sorption data fitted the Langmuir and Freundlich isotherm models and the kinetic study was followed the pseudo second order model. The slight decrease of the Cr(III) removal capacity for SMZY indicated that the sorbed cationic surfactant blocked sorption sites for Cr(III). While the unmodified zeolite had little affinity for the Cr(VI) and As(V) species, the SMZY showed significant removal of both species. The adsorption equilibrium data are best fitted to the Langmuir model. The removal of Cr(VI) was highest when the synthesized zeolite NaY was modified such that HDTMA achieved 100% of its ECEC. The SMZY-synthesis showed an adsorption of As(V) capacity higher than the SMZY-commercial. Because the As(III) exists form as neutral species in water, the removal of As(III) from water between unmodified and SMZY showed only a slight difference. The effects of different surfaces coverage of HDTMA-zeolite on the sorption of these species were insignificant. The SMZY was proven to be useful in removing cationic and anionic forms of arsenic and chromium in water simultaneously compared to the unmodified zeolite Y since it has the affinity for both cations and anions.

ABSTRAK

Penyingkiran beberapa spesies kromium dan arsenik daripada air oleh zeolit Y yang diubahsuai dengan surfaktan (SMZY) dan zeolit Y yang tidak diubahsuai telah dikaji. Zeolit NaY telah berjaya disintesis daripada abu sekam padi melalui kaedah pembenihan yang melibatkan penyediaan dua pembentukan gel yang berasingan. Zeolit NaY yang disintesis dan zeolit komersil dicirikan dengan XRD, FTIR, luas permukaan dan analisis unsur. Kapasiti penukaran kation (CEC) dan kapasiti penukaran kation luaran (ECEC) bagi zeolit yang disintesis didapati lebih tinggi daripada zeolit komersil disebabkan oleh nisbah silika kepada alumina bagi zeolit yang disintesis lebih rendah berbanding zeolit Y komersil. Zeolit NaY kemudiannya diubahsuai dengan heksadesiltrimetil ammonium (HDTMA) pada amaun 50%, 100% dan 200% daripada ECEC zeolit tersebut. Kajian menunjukkan penyingkiran Cr(III) oleh zeolit NaY yang disintesis adalah lebih berkesan berbanding zeolit komersil. Data penjerapan keseimbangan berpadanan dengan model isoterma Langmuir dan Freundlich manakala kajian kinetik mengikuti model pseudo tertib kedua. Penurunan sedikit terhadap kapasiti penyingkiran Cr(III) bagi SMZY menunjukkan surfaktan kationik yang dijerap menghalang tapak penjerapan bagi Cr(III). Zeolit yang tidak diubahsuai mempunyai sedikit sahaja afiniti terhadap Cr(VI) dan As(V) manakala SMZY menunjukkan penyingkiran yang ketara bagi kedua-dua spesies. Data penjerapan keseimbangan berpadanan dengan model Langmuir. Penyingkiran Cr(VI) adalah paling tinggi apabila zeolit NaY yang disintesis diubahsuai dengan HDTMA yang memenuhi 100% daripada ECEC zeolit tersebut. SMZY-sintesis menunjukkan kapasiti penjerapan As(V) lebih tinggi berbanding SMZY-komersil. Oleh kerana As(III) terbentuk dalam air sebagai spesies yang neutral, penyingkiran As(III) daripada air antara zeolit tidak diubahsuai dan SMZY menunjukkan perbezaan yang sedikit sahaja. Kesan perbezaan litupan permukaan bagi HDTMA-zeolit terhadap penjerapan spesies-spesies ini tidak terlalu ketara. SMZY terbukti berguna dalam penyingkiran logam yang membentuk kationik dan anionik dalam air secara serentak berbanding zeolit Y yang tidak diubahsuai kerana ia mempunyai sifat afiniti terhadap kation dan anion.

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LIST OF SYMBOLS

°C	-	Degree Celsius
C_o	-	Initial concentration
C_e	-	Equilibrium concentration
cm	-	Centi meter
dm	-	Deci meter
g	-	Gram
kg	-	Kilo gram
kV	-	Kilo Volt
L	-	Liter
m	-	Meter
M	-	Molar
mA	-	Mili ampere
meq	-	Mili equivalent
mg	-	Mili gram
min	-	Minute
mL	-	Mili Liter
mm	-	Mili meter
mmol	-	Mili mol
N	-	Normal
nm	-	Nano meter
ppm	-	Part per million
ppb	-	Part per billion
Å	-	Angstrom
µg	-	Micro gram
µL	-	Micro Liter

LIST OF ABBREVIATIONS

AAS	- Atomic Absorption Spectroscopy
APHA	- American Public Health Association
ASTM	- American Society for Testing and Materials
ATP	- Adenosine Tri-Phosphate
BET	- Brunauer, Emmet, and Teller
BTEX	- Benzene, Toluene, Ethylene and Xylene
CCA	- Chromated Copper Arsenate
CEC	- Cation Exchange Capacity
CHNS	- Carbon Hydrogen Nitrogen Sulphur
CMC	- Critical Micelle Concentration
CQ	- Chloroquin
CRM	- Certified Reference Materials
DDTMA	- Decadecyltrimethyl Ammonium
DHA	- Dehydroabietic Acid
ECEC	- External Cation Exchange Capacity
EPA	- Environmental Protection Agency
FAAS	- Flame Atomic Absorption Spectroscopy
FAU	- Faujasite
FTIR	- Fourier Transform Infrared
HDTMA	- Hexadecyltrimethyl Ammonium
ICDD	- International Centre for Diffraction Data
ICPMS	- Inductively Coupled Plasma Mass Spectrometry
IEC	- Ion Exchange Capacity
IR	- Infrared
LEDs	- Light Emitting Diodes

LOI - Loss on Ignition

LTA - Linde Type A

MCL - Maximum Contaminant Levels

MTDC - Malaysian Technology Development Corporation

NAA - Neutron Activation Analysis

NIOSH - National Institute for Occupational Safety and Health

NMR - Nuclear Magnetic Resonance

ODTMA - Octadecyltrimethyl Ammonium

OTS - Octadecyltrichlorosilane

PCE - Perchloroethylene

PDF - Powder Diffraction File

PFC - Plug Flow Combustor

PTFE - Polytetrafluoroethylene

QC - Quality Control

R&D - Research and Development

RHA - Rice Husk Ash

SIRIM - Standards and Industrial Research Institute of Malaysia

SMC - Surfactant Modified Clinoptilolite

SMZ - Surfactant Modified Zeolite

SMZY - Surfactant Modified Zeolite Y

TCE - Trichloro Ethylene

TDTMA - Tetradecyltrimethyl Ammonium

TEA - Tetraethyl Ammonium

TOC - Total Organic Carbon

UV-Vis - Ultra Violet-Visible

WHO - World Health Organization

XRD - X-Ray Diffraction

XRF - X-Ray Flourescence

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Water is not only ubiquitous in nature, but is a necessary ingredient for all forms of life. The human embryo is approximately 90 percent water, and adults are 65 to 70 percent water; the percentage of water then decreases in old age (McCaull and Crossland, 1974). Water is essential for life and no person can live more than a few days without it. There are many sources of water such as lakes, rivers, oceans, groundwater, rain and streams. In reality, water is not pure in nature because approximately half of the known chemical elements have been found dissolved in nature. A clean running stream, even in its unpolluted state, contains a complex mixture of organic and inorganic substances. Today, as the population expands and industry evolves, there are many different disease-causing microorganisms and complex human health hazards that can be related to the organic and inorganic substances i.e. toxic metals, dumped in the water in mammoth quantities by our fast-changing technological civilization. Because of this problem, the regulations and laws for standard limitation of contaminants in water have become the main priority for the environment institutional in every country and world organization to overcome the exceeding value of contaminants in water for the protection of human health. To ensure that wastewater treatment process in industrial facilities and the water purification process for drinking water comply with the regulations, these processes require the best technology to reduce the amount of contaminants. The method of treatment required for the removal of contaminants or their reduction to acceptable limits, depends in part on the fineness of the material. Therefore, the development of cost effective alternative sorbents material for treatment of contaminants in water is needed.

There are many sorbent materials exist in this world either occurring naturally or produced synthetically. Nowadays, alternative cost effective technologies or sorbents are greatly required to overcome the exceeding value of contaminants in water. The materials produced from natural materials that are available in large quantities or certain waste products from industrial or agricultural operations may have the potential to be used as inexpensive sorbents. One of the natural products that produced in abundance in Malaysia is the rice husk which can be used as a source of silica for the preparation of the zeolite; the material which has adsorption properties.

1.2 Rice Husk Ash as a Source of Silica

Rice husk ash is the natural sheath that forms on rice grains during their growth and it has no commercial value. In Malaysia, rice husk is produced in abundance after every paddy harvesting season and contributes to major agricultural waste. The husks are eliminated by burning them in the field at high temperature leaving behind a white blackish powder which is the constituents of silica. The presence of the silica ash causes a number of problems to the environment that causes pollution and disposal problems because of its nonbiodegradable property. Therefore, useful applications of the rice husk are desirable to solve this problem. The major constituent of rice husk after complete burning at high temperature is silica (SiO_2) in amorphous structure which formed as white powder and some amount of metallic impurities (Yalcin and Serinc, 2001).

The utilization of rice husk ash as an alternative source of silica towards the synthesization of zeolites has been reported nearly 20 years ago by Bajpal and Rao (1981). They have synthesized mordenite type zeolite using silica from rice husk ash. Besides that, rice husk ash was also used as a source of silica in the preparation of zeolite NaX (Dalal and Rao, 1985). Apart from that, zeolite Y was also successfully synthesized and was readily patented in Malaysia by Halimaton Hamdan and Yeoh Ann Keat (1993). There are two forms of silica; amorphous and crystalline. The amorphous form of silica is active towards the synthesis of zeolite but the crystalline form is inactive. The combustion of rice husk under controlled atmosphere and temperature less than 800 ^{o}C will generate the amorphous silica in the form of white powder and this silica ash which is transformed from the husk by complete burning constitutes 15 to 20% of the total weight of the husk. Hence, it is appropriate to employ rice husk ash from combustion of rice husk at temperature lower than 800 ^{o}C as a source of silica in the synthesis of zeolite.

It is important and essential to characterize rice husk ash before using it to synthesis zeolite because the successful synthesis of zeolite rely on the reactive source of raw materials especially silica. The main characterization methods of rice husk ash involves X-ray diffraction technique (XRD), Infrared spectroscopy (IR) and elemental analysis. The XRD diffractogram will indicate the phase of material, either crystalline or amorphous. Source of silica obtained from rice husk ash that will be used to synthesis zeolite must be in the complete amorphous form. This form of silica will be featureless in the XRD diffractogram and the appearance of diffused maximum at $2\theta = 23^{o}$ (Halimaton Hamdan *et al.*, 1997). The IR spectroscopy is also an imperative tool to characterize rice husk because the spectrum of material can support the data from XRD. The IR spectrum of amorphous silica is illustrated by the intense peaks at 1100, 800 and 470 cm^{-1} which are contributed from the asymmetric, symmetric and bending vibration frequencies for Si-O-Si bonds respectively (Cross and Jones, 1969). The information about the quantity of silica contained in the rice husk ash is crucial prior to synthesizing of the zeolite because one of the factors affecting the production of zeolite is the amount of raw material (Robson, 2001). Therefore, the percentage of silica enclosed in the rice husk ash must be determined.

1.3 Zeolite

Zeolite is a crystalline material and its structure consists of hydrated aluminosilicates of metals from group I and group II, in particular, sodium, potassium, magnesium and calcium. Structurally the zeolites are framework aluminosilicates which are based on an infinitely extending three-dimensional network of AlO_4 and SiO_4 tetrahedra linked to each other by sharing all of the oxygen. The structural formula of a zeolite is represented by the crystalline unit cell as:

$$M_{x/n}[(AlO_2)_x(SiO_2)_y].wH_2O$$

Where:

M : cation
n : valence cation
w : the number of water molecule
y/x : the ratio of the tetrahedral silica to alumina
portion [ ] : framework composition

The framework contains channels and interconnected voids which are occupied by the cation and water molecules. Zeolites consist of SiO_2, Al_2O_3, alkali cation, water and other substances with varying functions from one another. Table 1.1 summarizes the function of each element in zeolites. The cations are quite mobile and may usually be exchanged to varying degrees by other cations. Intracrystalline “zeolitic” water in zeolites can be removed continuously and reversibly.

The appropriate definition of zeolites by Smith (Breck and Flanigen, 1964) is:

> "A zeolite is an aluminosilicate with a framework structure enclosing cavities occupied by large ions and water molecules, both of which have considerable freedom of movement permitting ion exchange and reversible dehydration."

Table 1.1: Element sources in the zeolites and their function.

Source	**Function (s)**
SiO_2	Primary building units of the framework
AlO_2	Origin of the framework charge
OH^-	Mineralizer, guest molecule
Alkali cation	Counter ion of framework charge
Water	Solvent, guest molecule
Organic directing agent	Counter ion of framework charge, guest molecule, template

Zeolites are often termed as "molecular sieve" because the zeolitic pores are microscopically small with approximately molecular size dimensions. The windows and channels of a zeolite allow it to discriminate among guest molecules and cations on the basis of size. Zeolites are divided into two main classes, namely, mineral such as clinoptilolite, mordenite and garronite and the synthetic zeolite such as zeolite A, X and Y. The zeolite molecular sieve has three major functions, which are as catalyst, ion exchanger and adsorbent material. In view of the fact that silicon typically exists in a 4+ oxidation state, the silicon-oxygen tetrahedral is electrically neutral. However, in the framework of zeolite, aluminum typically exists in the 3+ oxidation state so that aluminum-oxygen tetrahedral form a centre that is deficient of one electron. Thus, zeolite framework is typically anionic and charge-compensating cations populate the pores to maintain electrical neutrality. These cations can participate in ion exchange processes and will yield important properties for zeolites. When charge-compensating cation are "soft" cations such as sodium, zeolites are excellent water softeners because they can pick up the "hard" magnesium and calcium cations as well as toxic metals cation in the water living behind the soft cation.

The fundamental properties and applications of molecular sieve zeolites involve many scientific disciplines and cross many of the traditional boundaries. Fields involved are inorganic and physical chemistry with emphasis on surface and colloid chemistry and catalysis, biochemistry, the geological sciences of geochemistry, geology, mineralogy and physics, including crystallography, spectroscopy and solid state physics (Breck, 1971). One of the main applications of zeolites is ion-exchanger. The ion-exchanger can be classified into organic and inorganic ion-exchanger. Resin is the organic form ion-exchanger while zeolites are classified as the synthetic inorganic ion exchanger. The major application of ion-exchanger is to remove toxic metals in the purification of water. The cation exchange behaviour depend on the nature of the cation species, the size of ion or complex cation, charge of ion or complex cation and type of zeolite structure (Breck, 1964). Thus, zeolites are capable for the removal of the toxic metals from water due to the ion exchange properties of zeolites.

Adsorption and ion exchange are the most common and effective processes for removing ions discharged into the environment, with resins being the most important group of ion exchange materials followed by zeolites. However, resins are expensive and must be regenerated and activated carbon is generally less effective for most metals and also requires regeneration. Therefore, alternative effective and economic sorbents are needed. Many authors have studied the application of both synthetic and natural zeolites as sorbents for the removal of metals cation from water. Some authors have reported the applications of the synthetic zeolite in removing heavy metals, for instance, Shevade and Robert (2004) used zeolite Y for arsenate removal from pollutant water, Veronica Badillo-Almaraz *et al*. (2003) used zeolite X for the adsorption of Zn(II) species from aqueous solution and the utilization of Zeolite NaY as an ion-exchanger for Co(II) and Fe(II) by Kim and Keane (2000). Among the natural zeolite, clinoptilolite is the naturally occurring zeolite that mostly used as an ion-exchanger and adsorption in the purification of water as clinoptilolite is probably the most abundant zeolite found in nature because of its wide geographic distribution and large size of deposits (Peric *et a*l., 2004). There are many papers reporting on the application of clinoptilolite as an adsorbent for toxic metals including the removal of lead and cadmium (Maliou *et al*., 1992), arsenate and arsenite (Elizalde-Gonzalez *et al*., 2001b) and copper, zinc, cobalt, nickel and mercury (Blanchard *et al*., 1984). Therefore, zeolite is one of the promising inorganic materials in removing toxic metals in the purification of water.

1.3.1 Zeolite NaY

Synthetic zeolite NaY is the synthesized zeolite Y of which sodium cation neutralize the framework structure of aluminosilicate and this material is in the same group with zeolite X. Both zeolites exhibit a structure similar to naturally occurring faujasite types. The differences between these zeolites are due to the composition and other physical properties brought about by the compositional differences. The Si, Al contents of zeolite Y are similar to that of faujasite whereas zeolite X is much more aluminous. Zeolite Y exhibits the FAU (faujasite) structure which has a 3-dimensional pore structure with pores running perpendicular to each other in the x, y and z planes similar to LTA, and is made of secondary building units 4, 6 and 6-6. The pore diameter is large at 7.4Ǻ since the aperture is defined by a 12 member oxygen ring, and leads into a larger cavity of diameter 12Ǻ. The cavity is surrounded by ten sodalite cages (truncated octahedral) connected on their hexagonal faces as shown in Figure 1.1. The unit cell is cubic (a = 24.7Ǻ) with Fd-3m symmetry. Zeolite Y has a void volume fraction of 0.48, with a Si/Al ratio of 2.43 (Bhatia, 1990).

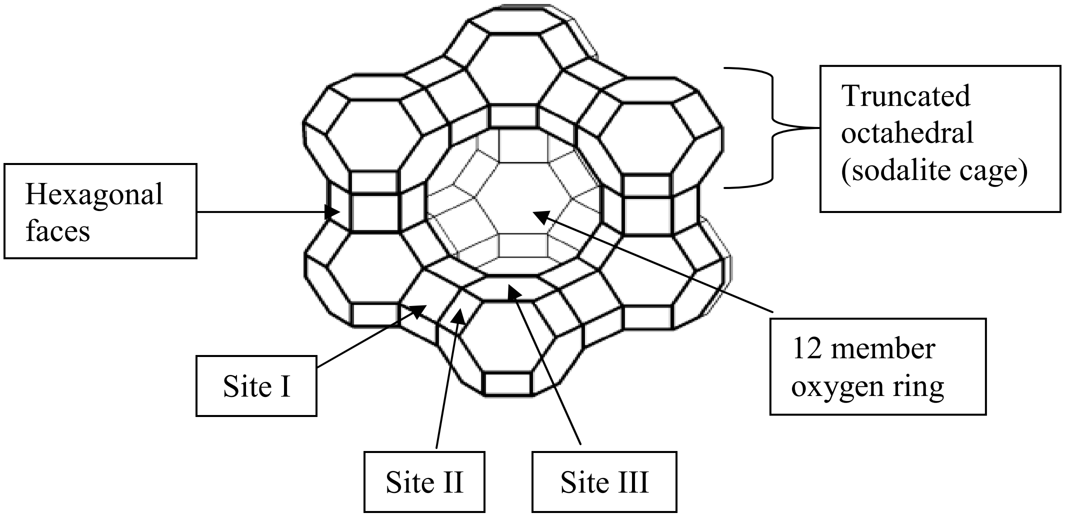


Figure 1.1 The truncated octahedral (sodalite cage) connected on the hexagonal faces in zeolite Y. The three types of cation sites are shown.

The framework of both zeolite Y and X consists of a tetrahedral arrangement of the truncated octahedral, i.e. the octahedral are joined to the octahedral faces by hexagonal prisms (Figure 1.1). The truncated octahedral is referred to as the sodalite unit or sodalite cage. The cations in the structure occupy three types of positions. These are type I, type II and type III which are in the centres of the hexagonal prism, on the six membered rings and on the walls of the channels, respectively. In the sodium form of a typical zeolite Y there are 56 sodium ions per unit cell while in the zeolite X, 86 cations per unit cell. These are distributed in the 3 different sites where for the zeolite Y, 16 in site I, 32 in site II and 8 in site III while for the zeolite X, 16 in site I, 32 in site II and 38 in site III. A major difference between zeolite X and Y is the non-occupancy of the type III sites for zeolite Y (Breck, 1964). Zeolites can be grouped into six categories according to the number of O-atoms in their largest ring. The faujasite family including zeolite Y are categorized into the 12-membered oxygen ring systems (Chen *et al*., 1994). Zeolites in this group system are also known as large pore zeolites.

Zeolite Y was discovered by Breck in 1961 when his group of researchers found that it should be possible to synthesize the zeolite X structure with silica/alumina ratios as high as 4.7 but his trial resulted in the zeolite that have a significant change in properties at a ratio above 3.0. Since zeolite X had been defined in reported patent as having silica/alumina ratios between 2.0 and 3.0, the isostructural zeolite with ratios above 3.0 and up to 6.0 were named and patented as zeolite Y (Robson and Occeli, 1988). The chemical formula for zeolite Y expressed in terms of moles of oxides may be written as (Breck, 1964):

$$0.9 \pm 0.2\ Na_2O : Al_2O_3 : w\ SiO_2\ ;\ x\ H_2O$$

Here w is a value greater than 3 up to about 6 and x may be a value up to about 9.

Among the numerous synthetic zeolite, the widely used in many field is the zeolite Y. One of the important applications of zeolites is as a cracking catalyst. Zeolite Y being more stable at high temperature due to the higher Si/Al ratio than other synthetic zeolites is useful as a catalyst for the cracking of petroleum. That is why zeolite Y had taken the place of zeolite X in the 1960s as a catalyst (Smart and Moore, 1993). Besides that, zeolite Y has also been used as the ion exchanger in order to remove heavy metals from water because of its high surface area, cation exchange capacity and stability. Kim and Keane (2000) reported the study on the ion exchange of divalent cobalt and iron by zeolite NaY. They concluded that sodium-based zeolite Y is effective in removing divalent iron and cobalt from aqueous solutions over the concentration range 0.005-0.05 mol dm^{-3}. Oliveira *et al.* (2004) had studied the removal of the metallic contaminants using magnetic-zeolite Y which is a physical composite of iron and zeolite Y, as a way of applying magnetic property to separate metals from water.

1.3.2 Synthesis of Zeolite NaY

The factors affecting the synthesis of zeolite Y is comparable to the synthesis of other synthetic zeolite. A few main parameters, conditions and materials related to the synthesis of zeolite must be recognized and moreover it is of utmost importance to know the source of the materials and technical grade materials to be assayed and analyzed for impurities before the synthesis of zeolite (Robson, 2001). The nature of the starting materials, overall chemical composition of the reactant mixtures, factors affecting nucleation, reaction time and pressure as well as temperature are also important in determining the zeolite species (Breck, 1974; Barrer, 1982). These variables and parameters do not necessarily determine the products obtained in hydrothermal reactions because the reactant mixtures may be heterogeneous and nucleation appears to be kinetically rather than thermodynamically determined and controlled (Barrer, 1982).

Breck and Tonawanda (1964) in their reported patent explained more about the condition on how to synthesis zeolite Y. One of the conditions that should be followed is when an aqueous colloidal silica sol or reactive amorphous solid silica is employed as the major source of silica, zeolite Y may be prepared by preparing an aqueous sodium aluminosilicate mixture having a composition, expressed in terms of oxide-mole-ratio, which falls within one of the ranges shown in Table 1.2. Crystallization occurs readily between 80 and 125 ºC. The temperature affects the size of the crystals, with the larger crystals forming at lower temperatures.

Table 1.2 : Composition ratio of synthesis Zeolite NaY

Ratio	Range 1	Range 2	Range 3
Na_2O/SiO_2	0.20 to 0.40	0.41 to 0.60	0.61 to 0.80
SiO_2/Al_2O_3	10 to 40	10 to 30	7 to 30
H_2O/Na_2O	25 to 60	20 to 60	20 to 60

In the synthesis of zeolite, source and starting materials are very crucial to determine the production of zeolite. Three major source materials that should be emphasized are the source of water, aluminium and silica according to the term zeolites as an aluminosilicate. Zeolite NaY can be synthesized by many sources of silica. Silica can be obtained from sodium silicate, silica gels, silicic acid, aqueous colloidal silica sols and reactive amorphous solid silica. The source of silica in the synthesis of zeolite Y can also be obtained from the natural products, for instance, from the coal fly ash (Zhao *et al.*, 1997) and rice husk ash (Halimaton Hamdan *et al.*, 1997; Zainab Ramli *et al.*, 1996). In this study, we have used rice husk ash as a source of silica to synthesize the zeolite NaY. There are researchers that have successfully synthesized zeolite NaY from rice husk ash whereby when the dried rice husk is burnt in controlled atmosphere and temperature below 800 ºC it will produce rice husk ash containing over 90% reactive amorphous silica (Halimaton Hamdan *et al*., 1997). According to the Breck and Tonawanda (1964), one of the conditions for successfully synthesized zeolite NaY is the reactive amorphous silica. In addition, the application for the production of zeolite NaY in this study is as a sorbent material less pure silica materials from rice husk ash can be employed in order to reduce the cost instead of using the costly commercial silica.

There are some problems that occur during the synthesis of zeolite NaY since the source of material used in this synthesis is amorphous silica and also the formation of zeolite NaY is metastable. It is possible to produce two or more crystalline phases from the same unreacted gel components. In the case of the formation zeolite Y, during the crystallization sequence, the initial formation of the desired faujasite phase (NaY) occur and subsequently followed by the evolution of a transient phase closely, gmelinite and finally by the production of garronite (Zeolite NaP) (Chen *et al*., 1994). Beside that, other phases identified to crystallize when the Na_2O/SiO_2 and H_2O/Na_2O were changed include herschelite, noselite and zeolites P and A (Szostak, 1992). In order to avoid such phenomena from occurring and to yield high purity of zeolite NaY, the seeding and ageing methods during the synthesizing of zeolite NaY from rice husk ash will be highlighted.

During the synthesis of the zeolite NaY, a number of parameters were emphasized in order to obtain the product with high purity of crystalline zeolite NaY and low impurities as well as the elimination of other undesirable phases. The synthesis of zeolite is also a typical inorganic reaction procedure, therefore, the parameters that have been highlighted and will affect the product are:

1) Type of starting materials.
2) Initial composition of the gel.
3) Alkalinity of the reaction.
4) Ageing period.
5) Crystallization temperature and time.

These parameters will be discussed below as all of them play important roles for successful synthesis of zeolite NaY with a Faujasite structure.

1) Type of starting materials

The starting materials used in the synthesis were rice husk ash as a source of amorphous silica (SiO_2), sodium aluminate as a source of aluminate and sodium hydroxide as a source for the alkaline condition. Hydrothermal synthesis of aluminosilicate zeolites involved a mixture of Si and Al species that were obtained from rice husk ash and sodium aluminate, respectively. The mixture was then converted via an alkaline supersaturated solution from sodium hydroxide (NaOH) solution into microporous crystalline aluminosilicates. Sodium hydroxide serves as a source of sodium ions and also assisted in controlling the pH. Zeolite Y is synthesized only from reactive amorphous silica while unreactive amorphous silica usually produces a mixture of zeolite Y and P (Zainab Ramli *et al*., 1996). Sodium aluminate was supplied by Riedel De Haen containing 50 to 56% of Al_2O_3 and rice husk ash containing 91.65% of amorphous silica. Sodium aluminate was used to introduce aluminium in the anionic form since alkali salts have a strong electrolytic effect on gel formation after addition of alkali silicate solution (Robson, 2001). The high percentage of raw material will yield high purity of product because the structure and properties of the molecular sieve product are highly dependent on the physical and chemical nature of the reactants used in preparing the reaction mixture, especially the composition of desired materials in the raw materials. In addition, according to the original patent for the synthesis of zeolite Y (Breck, 1964), amorphous silica from rice husk ash was indicated as one of the preferred sources of silica for obtaining Zeolite NaY.

2) *Initial composition of gel*

The initial composition for the synthesis of zeolite NaY from RHA followed the Na_2O-Al_2O_3-SiO_2-H_2O system. The overall composition of gel is 4.62 Na_2O: Al_2O_3: 10 SiO_2: 180H_2O when expressed in terms of oxide-mole-ratios, results in Na_2O/SiO_2 is 0.462, SiO_2/Al_2O_3 is 10 and H_2O/Na_2O is 45. This composition falls into range 2, referring to Table 1.2. Thus, the composition of initial gel was appropriate for the synthesis of zeolite Y from reactive amorphous silica as suggested by Breck *et al.* (1964).

3) *Alkalinity of the reaction*

The pH of the mixture was controlled by sodium hydroxide solution to provide the alkaline pH of generally between 8 and 12. The alkaline condition is important in the synthesis of zeolite because $[Al(OH)_4]^-$ is most abundant in alkaline solution. The oligomeric silicate species react with this monomer $[Al(OH)_4]^-$ to produce aluminosilicate structure. Furthermore, the increased pH will accelerate crystal growth by shortening the induction period (period before formation of viable nuclei) (Wetkamp *et al.*, 1994). The crystallization generally proceeds via the solution phase because the solubility of silicate, aluminate and aluminosilicate in the solution are important as crystallization mechanisms. Thus, the elevated pH is important since the solubility depends on the alkalinity. Besides that, the activity of SiO_2 in the aluminosilicate mixture also depends upon the alkalinity $[OH^-]$. The higher the $[OH^-]$ the lower the activity; therefore the synthesis of zeolite with low SiO_2/Al_2O_3 requires high $[OH^-]$. Hence, the increase of Al_2O_3 will provide more ion exchange sites necessary for ion exchange property.

4) *Ageing period.*

After the aluminosilicate gel was prepared, the hydrogel was kept for 24 hours at ambient temperature. This ageing process is crucial in obtaining a high purity product especially in the synthesis of zeolite Y. The important step during the ageing period is the dissolution or depolymeriztion of the silica sol that will increase the concentration of dissolved silica promoted by the alkaline. The ageing time of 24 hours was selected because Breck (1964) has proven that this period is optimum in producing a high yield of zeolite Y that is 92%. Bo and Hongzhu (1998) also reported that the rate of crystallization and composition of the crystalline products depend strongly on the ageing time and temperature in the synthesis of zeolite Y. This fact is also supported by another author, Zhao *et al*. (1997) which emphasized that ageing process was the important role in achieving the favorable hydrothermal aluminosilicate chemistry for zeolite formation. Along with this process and seeding method, they had successfully synthesized zeolite Y without marked presence of other impurities especially the absence of the formation of zeolite P.

5) *Crystallization temperature and time.*

The crystallization temperature in hydrothermal condition is around 100 ± 3 ^{o}C since the crystallization is most satisfactorily effective at a temperature from 80 ^{o}C to 125 ^{o}C. At lower temperatures (below 200 ^{o}C), the crystals which are formed are smaller in size than those generated at higher temperature (Breck, 1964). Whereas the increasing temperature of crystallization favours the formation of the zeolite P followed ultimately by analcime (Breck, 1974). The crystallinity of the product normally increases in time. However, this is only partially true because zeolite synthesis is governed by the occurrence of successive phase transformation (Ostwald rule of successive phase transformation). As a result, the thermodynamically least favorable phase will crystallize first and will be successively replaced in time by more stable phases. In case of the Zeolite Y formation, the crystallization sequence is: amorphous → Faujasite → NaP

(Gismondine type) (Wetkamp *et al*., 1994). Therefore, with the aim to avoid such formation from occuring; crystallization time was fixed for 24 hours.

In order to prevent contamination, Teflon and PTFE containers were used during the preparation of all solutions, for the reaction mixture and for the crystallization process. Glass vessels were not used and were avoided since glass participates in the reaction and silica, alumina and boron are known to be leached out of glass (Robson, 2001). These containers were washed with hydrofluoric acid (5%) before and after experiments to eliminate the silica and alumina as well as other contaminants contained inside the containers as the HF is known to able to dissolve these substances. After crystallization, it was necessary to filter the solid product immediately and washed with hot water because there was so much unreacted base left which can destroy the structure of the zeolite Y and reduce the degree of crystallinity. Washing with hot distilled water will eliminate these undesired substances (Bo and Hongzhu, 1998). During the synthesis, safety must be considered as the experiments involved hazardous materials. Measures taken include wearing gloves and face mask when handling the caustic materials. The reaction vessels were opened immediately after they were taken out from the oven (100 ^{o}C) in order to prevent damage to the vessel.

1.3.2.1 Seeding Technique

Seeding and ageing are two important techniques in zeolite synthesis in order to obtain a pure crystalline phase with high percentage of desirable product as well as low impurities. Seeding is a technique in which the supersaturated system (seed gel) is inoculated with small particles of materials to be crystallized. The seeding method necessitates the preparation of two separate gels; seed gel is about 5 percent from overall and the remaining is feedstock gel. These two gels will be mixed together in the final part of the synthesis. Adding seed crystals to a crystallization system will result in increased crystallization rate. The enhanced rate might be due to the increasing existing surface area but also might be the result of enhanced nucleation of new crystals (Robson, 2001). The secondary nucleation mechanism referred to as initial breeding results from microcrystalline dust being washed off of seed crystal surfaces in a new synthesis batch. These microcrystalline fragments grow to observable sizes and result in greatly enhanced crystallization rates due to the significantly increasing crystal surface area compared to the unseeded system. Consequently, it is to be expected that addition of seed to a synthesis system will introduce sub-micron sized crystallites into the system which will serve as nuclei. Finally, the same particulates which appear to catalyze zeolite nucleation in unseeded systems may remain in sufficient number to catalyze nucleation in seeded systems, since they are inherently present in the seed crystal sample and may be impossible to eliminate via typical filtration techniques. In the seeding technique, if the surface area provided by the seed crystals is larger than the one supplied by fresh nuclei, the seeding technique provides a favourable condition for measuring linear growth rates (Barrer, 1982).

1.3.2.2 Ageing

Ageing is a process in which the mixture of aluminosilicate is left for a period of time at room temperature or below the crystallization temperature. In case of the formation of zeolite Y, the appropriate period of time is 24 hours. Preliminary ageing of the reaction mixture at room temperature after gel formation followed by subsequent crystallization at a higher temperature of 100 ^{o}C improves the crystallization process because the ageing process will proceed more quickly than in the non aged case. During the gel aging, germ nuclei will be formed within the solution and they grow to observable sizes upon subsequent high-temperature synthesis (Cook and Thompson, 1988). After the initial gel formation, the aging step is necessary in order to equilibrate the heterogeneous gel mixture with the solution, resulted in the lower SiO_2/Al_2O_3 ratio in the gel necessary to form zeolite Y (Breck, 1974). Therefore, the ageing process will be emphasized during the synthesis progress as it can provide a major consequence in successfully synthesizing zeolite NaY from rice husk ash with high percentage of zeolite Y in resultant product.

1.3.3 Characterization

In general, the characterization of a zeolite has to provide information about structure and morphology, the chemical composition, the ability to sorb and retain molecules and the ability to chemically convert these molecules. Information on the structural, chemical and catalytic characteristics of zeolites is essential for deriving relations between their chemical and physicochemical properties on the one side and the sorptive and catalytic properties on the other. Such relations are of high importance, as they allow the rational development of sorbents, catalyst and advanced structural materials. In this study, the zeolite was synthesized from rice husk ash and the main uses are as cation exchangers and sorbent, thus only characterizations with respect to these applications are being dealt with in depth. There are many characterization techniques but the important ones in this study are X-ray diffractogram (XRD), infrared spectroscopy (IR), elemental analysis and ion exchange capacity (IEC). Each of the characterization techniques will be described below.

1.3.3.1 X-Ray Diffraction Technique

For zeolites produced in the laboratory, X-ray powder diffraction data is the most commonly used to validate the synthesized zeolite and to identify a newly synthesized material as well as to monitor the effects of a post-synthesis modification. X-ray powder diffraction data is also the most commonly used technique as a ‘fingerprint’ in the identification of a material because each crystalline solid has its own characteristic X-ray powder pattern (West, 1988). The measured pattern is compared to an existing one, whether it is a pattern in the Collection of Simulated XRD Powder Patterns for Zeolites, the Powder Diffraction File (PDF) of the ICDD or an in-house data file (Robson, 2001). In recent days, the use of X-ray diffraction technique is of utmost importance in identifying the synthesized zeolite because of the general availability of powder X-ray diffraction facilities and the increasing application of computers to automate sample scanning and data analysis as well as to enable rapid collection of data on a large number of samples essentially in the absence of an operator (Jarman, 1985). Besides for identification material, XRD diffractogram provides much information such as the degree of crystallinity, the presence of other phases or impurities and the determination of crystal structure.

The X-ray diffraction technique is based on the Bragg's Law. The Bragg approach to diffraction is to regard crystals as built up of layers or planes such that each acts as a semi-transparent mirror. Some of the X-rays are reflected of a plane with the angle of reflection equal to the angle of incidence, but the rest are transmitted to be subsequently reflected by succeeding planes. The derivation of Bragg's law is shown in Figure 1.3. The relation between lattice planes with a distance *d*, the angle of reflection, θ and measured at wavelength, λ can be described by Bragg's law in equation 1:

$$n\lambda = 2d\sin\theta \qquad (1)$$

The primary use of Bragg's law is in the determination of the spacing between the layers in the lattice for, once the angle θ corresponding to a reflection has been determined, d may readily be calculated.

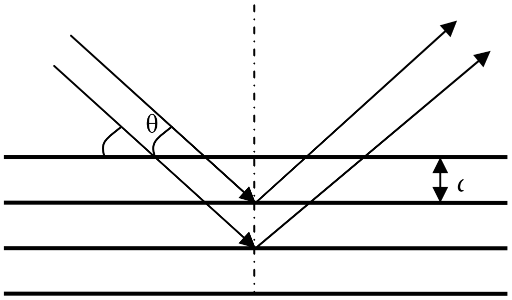


Figure 1.2 Derivation of Bragg's law for X-ray diffraction

The mostly used XRD technique for zeolites is the powder diffraction technique because zeolite is mainly in the powder form. Powder diffraction techniques are used to identify a sample of a solid substance through the comparison of the positions of the diffraction lines and their intensities with a large data bank which can be acquired from the powder diffraction file, maintained by the International Centre for Diffraction Data (ICDD) and contains information of about 50 000 crystalline phases. The principles of the powder diffraction technique are shown in Figure 1.4. A monochromatic beam of X-rays strikes a finely powdered sample that, ideally, has crystals randomly arranged in every possible orientation. In such a powder sample, the various lattice planes are also present in every possible orientation. For each set of planes, therefore, at least some crystals must be oriented at the Bragg angle, θ, to the incident beam and thus, diffraction occurs for these crystals and planes. The diffracted beams may be detected by surrounding the sample with a detector.

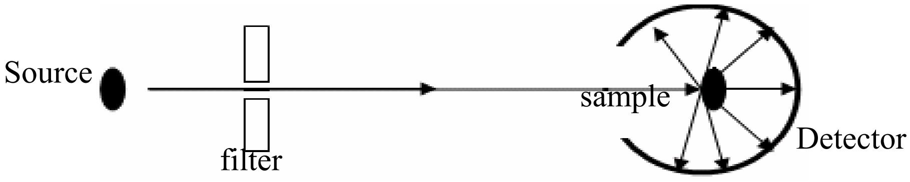


Figure 1.3 The illustration of the X-ray powder diffraction method

The most important use of the powder method is in the qualitative identification of crystalline phases or compounds. While most chemical methods of analysis give information about the elements present in a sample, powder diffraction is very different and perhaps unique that it tells which crystalline compounds or phases are present with no direct information about their chemical constitution.

The determination of the unit cell dimension of zeolites can also be obtained from the X-ray technique. Zeolites are in the form of crystal, thus its structure is built up of regular arrangements of atoms in three dimensions; these arrangements can be represented by a repeating unit or motif called the unit cell. The unit cell is defined as the smallest repeating unit which shows the full symmetry of the crystal structure (West, 1988). The unit cell dimension of a freshly synthesized faujasite-type zeolite is a sensitive measure of composition which, among other uses, distinguishes between the two synthetic faujasite type zeolite, X and Y. The unit cell dimension, a of the zeolite can be calculated from the equation:

$$a = \{(d_{hkl})^2 (h^2 + k^2 + l^2)]^{\frac{1}{2}} \tag{2}$$

where

hkl = the miller indices (Å)

d = distance between reflecting planes having the Miller indices.

The d-spacing can be derived from equation 1 as:

$$d_{hkl} = \frac{\lambda}{2\sin\theta} \tag{3}$$

The wavelength of X-ray radiation (λ) for CuKα_1 is 1.54060 Å (0.154060 nm). The value of unit cell dimension from this equation thus can be used to determine the Si/Al ratio of zeolite Y by Breck's equation (Breck, 1974):

$$\frac{Si}{Al} = \frac{1.66656}{a - 24.191} - 1 \tag{4}$$

Hence, it is useful to characterize the raw material, synthesized zeolite and the modified zeolite by the X-ray diffraction technique as it can give many valuable information about the materials that had been studied.

1.3.3.2 Infrared Spectroscopy

The fundamental basic theory of the infrared spectroscopy is that the infrared radiation will promote transitions in a molecule between rotational and vibrational energy levels of the ground (lowest) electronic energy state (Cross and Jones, 1969). The vibrational modes, involving pairs or groups of bonded atoms can be excited at higher energy states by the absorption of radiation of appropriate frequency. In the infrared spectroscopy technique, the frequency of the incident radiation is varied and the quantity of radiation absorbed or transmitted by the sample is obtained. The infrared spectra of solids are usually complex with a large number of peaks corresponding to each particular vibrational transition. In order for a particular mode to be active towards infrared, the associated dipole moment must vary during the vibrational cycle consequently centrosymmetric vibrational modes are infrared inactive.

Zeolites are crystalline aluminosilicates consisting of corner linked tetrahedral where the Al and Si atom lie at the centres of tetrahedral and oxygen atom lie at the corners. As a result, the vibrations of the framework of zeolites give rise to typical bands in the mid and far infrared. The usually used region of infrared for the characterization of zeolites is the mid-infrared region which is from 200 to 1300 cm^{-1} since it contains the fundamental vibrations of the Si, AlO_4 or TO_4 units in all zeolites framework (Rabo, 1976). In this region, there is a specific range for a typical band related to the zeolites structure that was studied by many earlier researchers in order to provide the information for the structural characteristics. Rabo (1976) reported that Flanigen, Khatami and Szymanski are the earlier researchers who studied the mid-IR spectroscopy in the characterizations of zeolite. The original assignments of the main IR bands were described in Table 1.3. (Robson, 2001). They classified the mid-IR vibrations for the zeolites structure into two types of vibrations which are related to the internal vibrations of the TO_4 tetrahedra and the vibrations primarily related to external linkages between tetrahedral. The internal vibrations mainly in the primary building unit in zeolite frameworks tend to be insensitive to variations in framework structure, while the external linkages are sensitive to the framework topology and to the presence of symmetrical clusters of tetrahedral in the form of larger polyhedra.

Table 1.3 : The assignments of the main infrared bands for zeolites

i)	Internal tetrahedral	(Structure insensitive vibrations)
a)	1250 – 920 cm^{-1}	Asymmetrical stretch of Si-O-T
b)	720 – 650 cm^{-1}	Symmetrical stretch of Si-O-T
c)	500 – 420 cm^{-1}	T-O bend
ii)	External linkages	(Structure sensitive vibrations)
a)	650 – 500 cm^{-1}	Double ring vibrations
b)	420 – 300 cm^{-1}	Pore opening vibrations
c)	1150 – 1050 cm^{-1}	Asymmetrical stretch of Si-O-T
d)	820 – 750 cm^{-1}	Symmetrical stretch of Si-O-T

T = Si, Al

The strongest band is in the region of 1250 to 920 cm^{-1} related to the T-O stretch and the next strongest band in the 420 to 500 cm^{-1} is from the T-O bending mode while stretching modes involving mainly the tetrahedral atoms are in the region of 650 to 820 cm^{-1}. A band in the 500 to 650 cm^{-1} region related to the presence of the double rings in the framework structures which is observed in all of the zeolite structures that contain the double 4- and double 6-ring that can be found in zeolite Y (Breck, 1974).

Although organic chemists are frequently concerned with the use of infrared spectroscopy data for the identification of compounds, it is also helpful for inorganic chemists to characterize the inorganic materials. However, the infrared spectroscopy data is barely used to support data from X-ray diffractogram which is the 'fingerprint' for the identification of zeolites and its new derivatives. Besides that, the spectra is also used to compare between raw material (silica) and the synthesized zeolite. Flanigen (Rabo, 1976) from Union Carbide Corporation reported that the infrared spectroscopy can yield information not only on short range bond order and characteristics but also on long range order in crystalline solid caused by lattice coupling, electrostatic and other effects and can serve as very rapid and useful structural techniques. Additionally, infrared spectroscopy is also a valuable technique for exploring and studying the nature of hydroxyl groups in zeolite, the interaction of cations with adsorbed molecules and the fundamental framework structure of zeolites (Gould, 1974).

In the infrared spectrum of zeolites in the range of 300 to 1300 cm^{-1}, for some of the structure sensitive and insensitive bands, a linear relation between the wavenumber and the number of lattice aluminum atoms (N_{Al}) is reported (Rabo, 1976). After calibration, it is possible to use this relation to derive the number of lattice aluminum atoms from the band positions. Since the structure insensitive asymmetric stretch (σ_1) (950 – 1250 cm^{-1}) and the structure sensitive symmetric stretch band (σ_2) (750 – 820 cm^{-1}) frequencies increase with decreasing Al content in a linear manner, these frequencies can be used in the determination of the number of lattice aluminum atoms (N_{Al}) for zeolite Y. The number of Al in the framework of zeolite NaY sample can be calculated according to the following equation derived by Kubelkova et al. (1988)

$$N_{Al} = [4.425 - 4.054^{-3}\sigma_1] \times [N_{Al} + N_{Si}] \qquad (5)$$

$$N_{Al} = [4.468 - 5.299^{-3}\sigma_2] \times [N_{Al} + N_{Si}] \qquad (6)$$

where $[N_{Al} + N_{Si}]$ for zeolite Y is equal to 192. The value of the number of lattice aluminium atoms from equation 5 and 6 can be used for the calculation of Si/Al and SiO_2/Al_2O_3 ratio according to the equation 7 and 8, respectively:

$$\frac{Si}{Al} = \frac{192 - N_{Al}}{N_{Al}} \qquad (7)$$

$$\frac{SiO_2}{Al_2O_3} = \frac{192 - N_{Al}}{\frac{N_{Al}}{2}} \qquad (8)$$

1.3.3.3 Elemental Analysis

The structure of zeolite NaY consist of a three dimensional framework of SiO_4 and AlO_4 tetrahedra with the sodium cation to balance the framework charge while the water molecule is enclosed in the large cavities of the framework. Thus, the determination of the bulk elemental composition of zeolites is important in many aspects of zeolite synthesis, characterization and applications. This information is used to verify the synthesis formulation, the bulk of silica and alumina ratio (Si/Al ratio), the cations concentration, degree of ion exchange and the detection of contaminant elements such as impurities and poison (Robson, 2001). Corbin *et al.* (1987) had studied the comparison of analytical techniques for the determination of silicon and aluminium content in zeolites. The techniques include atomic absorption spectroscopy (AAS), neutron activation analysis (NAA), proton inelastic scattering, X-ray fluorescence (XRF), wet chemical, inductively coupled plasma-mass spectrometry (ICP-MS) and nuclear magnetic resonance (NMR). They concluded that the effectiveness of each of the technique differs from each other and requires the appropriate modification of the sample preparation prior to measurements. From their study it can be summarized that there are many techniques for the determination of elemental composition in zeolites.

The elements and species that are important to be determined are sodium, aluminum, silica and water. The instrumental method to determine these elements involves inductively coupled plasma mass spectroscopy (ICPMS) for the determination of aluminium and flame atomic absorption spectroscopy (FAAS) for the determination of sodium cation. These instrumental techniques are the most common techniques employed for the determination of compositional metals because they offer the advantage of reducing interferences and matrix effects and have advanced accuracy, precision and speed well than "classical wet chemistry". In general, the sensitivity of ICP-MS is better than the conventional flame AAS. However, flame AAS has rather better sensitivity for group IA elements, including sodium, hence the reason for the determination of sodium using AAS and aluminum with ICP-MS. Both ICP-MS and AAS necessitate that the sample be introduced as liquid, thus decomposition is necessary prior to analysis and similar preparation schemes apply for both techniques. The approach for decomposition sample that are used in this research is the beaker digestion with hydrofluoric acid. The digestion requires the addition of hydrofluoric acid in order to solubilize the Si. Besides ICP-MS and AAS, the X-ray fluorescence (XRF) also can be used for the determination of composition in zeolites. As compared to ICP and AAS, the wavelength dispersive XRF had the benefit which include the ability to determine some non-metals, conceptually require simpler sample preparation and with improved precision. However, in many cases XRF cannot perform the complete characterization due to its poor sensitivity for light elements and sensitivity to changes in the matrix composition. While XRF has its greatest use in a controlled manufacturing environment, ICP and AAS is often the technique of choice in the research and development (R&D) environment. The determination of loss on ignition at a specified temperature and time will be used to determine the percentage of water.

The results from the elemental analysis can provide information to calculate the ratio of silica to alumina which determines the thermal and chemical stability of the zeolite, the hydrophilic nature of the zeolite, the numbers and strength of the acid sites in the acid form and the capacity of the ion exchange. Breck and Tonawanda (1964) who was the first person to discover the zeolite Y had patented the zeolite Y having silica/alumina ratio above 3.0 and up to 6.0 since zeolite X had been defined as having silica/alumina ratios between 2.0 and 3.0. Changing the Si/Al ratio also changes its cation content and the stability. Fewer Al atoms means that the zeolites are more siliceous, thus fewer exchangeable cations will be present and the thermal stability improves.

1.3.3.4 Ion Exchange Capacity

Because of zeolites are composed of crystalline aluminosilicates with the structure based on tetrahedral SiO_4 and AlO_4 units, connected by shared oxygen atoms, they are one of the synthetics inorganic cation-exchangers. This kind of three-dimensional structure has small pores where the exchangeable ions are located and where the ion exchange reactions take place. Silicon is tetravalent and aluminium is trivalent, which result in negatively charged framework structures. Thus each mole of aluminium produces one equivalent of cation exchange capacity for the zeolite framework. Ion exchange is a chemical reaction in which free mobile ions of a solid, the ion exchanger, are exchanged for different ions of similar charge in solution. The exchange reactions in typical zeolite can be written as follows:

$$M^+X^- + N^+ \rightarrow N^+X^- + M^+ \qquad (9)$$

Where:

M^+X^- = Zeolite with M^+ is framework and X^- is counterion.

N^+ = Cation in the solution

The ion exchange properties of zeolites are mainly based on the charge density and pore size of the materials (Breck, 1974). In zeolites where the internal void space consists of portions accessible only through smaller pores, the total ion exchange capacity may be available to the smallest ions but only part to larger ions. However, the majority of the total ion exchange capacity is available to the most common cations. Furthermore, the cation exchange behaviour also depends on the temperature, concentration of the cation species in solution, the anion species associated with the cation, the solvent, the structural characteristics of the particular zeolite and the nature of the cation species, size, both anhydrous and hydrated and cation charge (Breck, 1974). In addition, the chemical composition is also the factor governing the cation exchange of zeolite as a higher exchange capacity. This is observed with zeolites of low silica per alumina ratio since each AlO_4 tetrahedra in the zeolite framework provides a single cation exchange sites. Zeolite X exhibits higher cation exchange capacity than zeolite Y because it has lower silica to alumina ratio hence higher framework charge.

Cation exchange capacity (CEC) can be defined as the sum of the exchangeable cations that a mineral can adsorb at a specific pH, i.e. a measurement of the negative charges carried by the mineral (Wilson, 1994). The ion exchange capacity of zeolite ion exchanger is a function of their silicon oxide/aluminium oxide mole ratio, since AlO_4 tetrahedra in the zeolite framework provides a single cation exchange sites (Sherman, 1978) and its commonly measured in terms of moles of exchangeable cation per gram (or 100 grams) of zeolites, moles/g or in terms of equivalents of exchangeable cation per gram (or 100 grams) of zeolites, meq/g. Using CEC expressed in terms of miliequivalents per gram (meq/g) makes it easy to compare how much of any cation can be exchanged by a particular zeolite, without having to worry about the charge on the cation involved. The exchange process involves replacing one singly-charged exchangeable atom in the zeolite by one singly-charged atom from the solution, in this study; the singly-charged atom that is used to exchange sodium cations in zeolite NaY is ammonium cation, NH_4^+ which possesses single charged ion. So, it is of utmost importance to know and verify the ion exchange capacity of the synthesized zeolite because the main function of the zeolite in this study is for ion exchange with heavy metals in the aqueous phase.

The total cation exchange capacity is the sum of external cation exchange capacity (ECEC) and internal cation exchange capacity. Because of large molecule of hexadecyltrimethyl ammonium, HDTMA, this molecule cannot enter the angstrom size of pore zeolite and will exchange on the surface of zeolite. The measurement ECEC is to differentiate between internal and external cation exchange sites that would enable better investigation of changes in modified mineral properties as a function of surfactant loading and also to characterize the exchange capacity of the mineral surface for HDTMA (Li and Bowman, 1997). Therefore, it is essential to determine the external cation exchange capacity by using HDTMA cation as the exchanged cation before the modification of zeolite surface. From the measured external cation exchange capacity, the maximum uptake of the HDTMA will be known and will provide information for internal cation exchange capacity.

1.4 Surfactant Modified Zeolite

Some of the toxic metals may exist as cations, anions, non-ionized species and complex macromolecules in the aqueous phase (Sengupta, 2002), for instance, arsenic which is prominently carcinogen, can form anion as arsenate (As(V)) and non-ionized species as arsenite (As(III)). Another known toxic metal in water is chromium (Cr) which can also form Cr^{3+} cation (Cr(III)) and the anionic form as chromate, CrO_4^{2-} for Cr(VI). Therefore, the materials that can remove this kind of toxic metals simultaneously in the water body are of great importance with regards to the water purification or wastewater treatment. To achieve this result, the composite ion exchanger has to be developed, for which it shall contain the properties of cation and anion exchanger at the same time. In order to sorb anion and cation, the modified surface must possess positively and negatively charged exchange sites. However, a typical zeolite cannot remove or sorb the anion species as its surface is in the anionic charges. By treating the zeolite with a cationic surfactant, an organic covering is created on the external zeolite surfaces and the charge is reversed to positive charge. Therefore, the modification surface of zeolite by cationic surfactant (i.e. HDTMA) can be made according to the successful clinoptilolite modified with HDTMA by Li and Bowman (1997) and they called it surfactant-modified zeolite (SMZ). Laboratory batch and column tests demonstrate that SMZ can simultaneously remove multiple types of contaminants from water, including inorganic anions such as chromate and hydrophobic organics such as chlorinated solvents and fuel components (Li *et al.*, 1998b). Zeolite NaY resembles natural zeolite minerals that have permanent negative charges on their surface and large cation exchange capacity (CEC) which enables them to be modified by cationic surfactant to enhance their sorption of organic and anionic contaminants in water.

The surfactant that is commonly employed to be attached on the zeolite surface in the previous studies is HDTMA, the quaternary amine hexadecyltrimethylammonium cation which is a long chain cationic surfactant that possesses a permanent positive charge. The HDTMA is in the group of cationic surfactant where they have positively charged hydrophilic head group generally amine, attached to a hydrophobic tail of hydrocarbon moiety. The structure of the HDTMA is shown in Figure 1.5. The HDTMA structure consists of permanently charged trimethyl ammonium head group attached to a 16-carbon chain. It can be obtained as common salts such as HDTMA-bromide and HDTMA-chloride. Since the uses of this surfactant are mainly as hair conditioner, mouthwash and fabric softeners, it is assumed that low levels of HDTMA will not be harmful to the environment. The critical micelle concentration (CMC) is the minimum concentration of the surfactant needed to form a micelle and for HDTMA-Br is 0.9 mmol/L. The individual surfactant molecules will self associate into micellular clusters above the CMC.

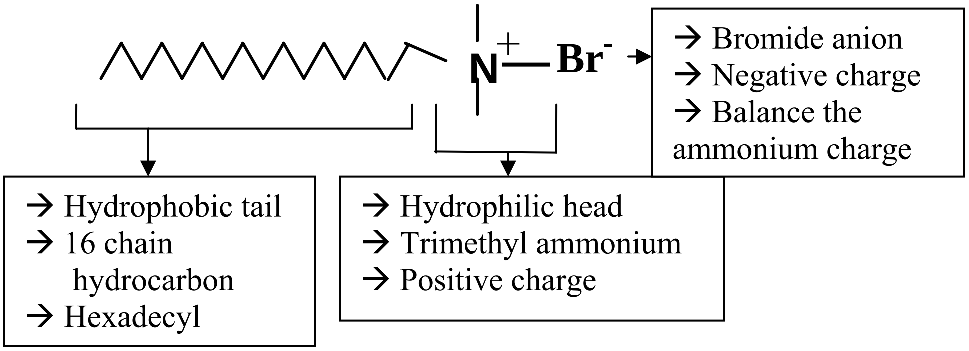


Figure 1.4 The structure of hexadecyltrimethyl ammonium bromide (HDTMA-Br)

Depending on the chemical structure of the cationic surfactant, it is possible to make a hydrophilic solid behaves as if it was hydrophobic or (less usual) to make a hydrophobic solid behave as if it were hydrophilic (Porter, 1994). When the adsorption of a surfactant onto a solid surface is considered, there are several quantitative points that are of interest. They include:

i) The amount of surfactant adsorbed per unit mass of solid.
ii) The solution surfactant concentration required to produce a given surface coverage or degree of adsorption.
iii) The surfactant concentration at which surface saturation occurs.
iv) The orientation of the adsorbed molecules relative to the surface saturation occurs.

v) The effect of adsorption on the properties of the solid relative to the rest of system

In all of the above, it is assumed that such factors as temperature and pressure are held constant. The maximum surfactant loading on zeolite surface is a function of surfactant type, chain length and counter ion type (Li and Bowman, 2001a).Thus, the surface properties of zeolite can be modified by using cationic surfactants HDTMA because the surface of zeolite is the net negative charged resulting from isomorphic substitution of cations in the crystal lattice.

Theoretically, when the zeolite contacting with HDTMA above the CMC in the aqueous phase, the HDTMA cation will selectively exchange with the inorganic cations on the external surface of zeolite framework. In the case of zeolite NaY, sodium cation (Na^+) will be exchanged and forms a surfactant bilayer with anion exchange properties. The equation of the exchange can be described below:

$$2M^-Na^+ \quad + \quad HDTMA^+ \quad \leftrightarrow \quad M^-Na^+HDTMA^+ \quad + \quad Na^+ \qquad (10)$$

where M is the framework of zeolite having negatively charge. The HDTMA molecule will be exchanged with the zeolite’s cation in the external framework and limited exclusively to external surface of zeolite particles because the HDTMA molecule is too large to penetrate the internal pore spaces of the zeolite or to access the internal cation exchange positions since it has a long chain quaternary ammonium cations.

The sorption of cationic surfactant onto a negatively charged surface of zeolite involves both cation exchange and hydrophobic bonding (Li and Bowman, 1997). It was suggested that at low loading levels of HDTMA exposed to a negatively charged zeolite surface, it will be retained by ion exchange and eventually form a monolayer at the solid-aqueous interface. At this stage, the surfactant molecules exist as monomers in aqueous solution at concentrations below the CMC which is typically below 1 mmol/L. When the surfactant concentration is greater than CMC, the surfactant molecules associate to form solution micelles in addition to monomers. As the amount of HDTMA increases and the initial surfactant concentration is greater than CMC, the interaction among the hydrocarbon tails causes the formation of a bilayer or patchy bilayer with the first layer retained by cation exchange and the second layer by hydrophobic bonding and stabilized by counter ions. The sorbed surfactant creates an organic-rich layer on the zeolite surface and the charge on the surface is reversed from negative to positive. The positively charged head groups are then balanced by counter ions. A model for the interaction of HDTMA on the external surface of zeolite is shown in Figure 1.6. This theoretical phenomenon shows that the anion that counterbalanced the positive charge from HDTMA will be exchanged by more strongly held counter ions while the organic partitioning will absorb organic substances and the outer cations will be replaced with cation that neutralizes zeolite from the internal pore.

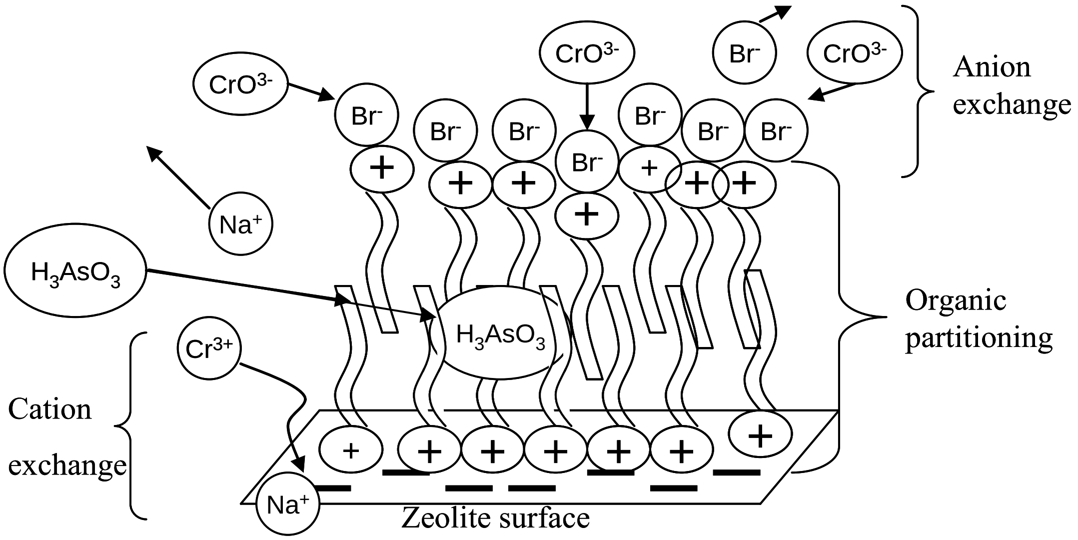


Figure 1.5 Schematic diagram of HDTMA micelle formation in solution and admicelle formation on the zeolite surface and the uptake substance onto surfactant modified zeolite.

Along with its unique properties, the resultant surfactant modified zeolite (SMZ) is capable of simultaneous sorption of anions, cation and non-polar organic molecules from water.

The advantages of surfactant modified material are that it can be used to eliminate multiple types of undesired contaminants elements in water which are inorganic cation (e.g.; Pb^{2+}, Cd^{2+}, Cr^{3+}) and inorganic anion (e.g.; chromate, selenate, arsenate) as well as organic substances (e.g.; perchloroethylene (PCE), trichloro ethylene (TCE), benzene, toluene, ethylene and xylene (BTEX)) all together. The surfactant modified zeolite proved to be chemically and biologically stable at a long term period. Li *et al*. (1998b) studied the long term chemical and biological stability of surfactant modified natural zeolite, and they concluded that the SMZ was stable in high ionic strength, high and low pH environments, under both aerobic and anaerobic conditions and moreover resistant to microbial degradation.

Recently, clinoptilolite is the natural zeolite that is mostly used in order to create the SMZ for the adsorption and removal of many types of contaminants in water and it has been working successfully. The studies on the use of SMZ from clinoptilolite for environmental remediation were limited to the removal of organic contaminants from water until Haggerty and Bowman (1994) showed that SMZ significantly increased the sorption of chromate. The sorption of chromate was attributed to anion exchange on the outermost surface created by the sorbed surfactant bilayer (Li *et al*., 1998a). Besides sorption of chromate, SMZ has also been proven to sorb other oxyanions such as sulphate (SO_4^{2-}) and selenate (SeO_4^{2-}) (Haggerty and Bowman, 1994), nitrate (NO_3^{2-}) (Li, 2003) and also dihydrogenphosphate ($H_2PO_4^-$) (Vujakovic *et al*., 2000). Li *et al*. (2002) also reported that cation exchange by SMZ is reduced compared to the unmodified zeolite. They observed that the reduction in metal cation uptake by the SMZ is controlled by the surfactant loading on the zeolite surface and by the type of metal cations. There are many papers which reported on the sorption of organic contaminants in water by SMZ. Bouffard and Duff (2000) applied SMZ as adsorbents for the removal of dehydroabietic acid (DHA) from a model process white-water, Li and Bowman (2001a) studied the regeneration of SMZ after saturation with perchloroethylene, Hayakawa *et al*. (2000) used zeolite P and X that had been attached with hexadecyl-, tetradecyl- and dodecyltrimethylammonium bromides as a drug carrier and the release of chloroquin (CQ), besides that, SMZ as the new efficient adsorbents for mycotoxins was studied by Tomasevic-Canovic *et al*. (2003). These literature reviews show that SMZ has many uses in the purification of water as the contaminants exist in many forms, cationic, anionic, neutral and organic form.

1.5 Toxic Metals in Water

Heavy metals are metallic elements that have a high atomic number and are toxic to living organisms. Because they are toxic, heavy metals are sometimes referred to as toxic metals (Young, 2000). There are approximately 30 different toxic metals that have impacts upon human health and each of them will produce different behavioral, physiological and cognitive changes in an exposed individual. Examples of toxic metals are chromium (Cr), arsenic (As), selenium (Se), cadmium (Cd), nickel (Ni), lead (Pb), mercury (Hg), manganese (Mn), cobalt (Co), zinc (Zn) and copper (Cu). Although arsenic (As) and selenium (Se) are the elements on the border between metals and non-metals and are known as metalloids, they are also considered as toxic metals because of their toxicity and well-known carcinogence since they exhibits some metallic properties.

Heavy metals in natural waters may be suspended (particles >100 nm in size), colloidal (particles in the intermediate range between suspended and soluble) or soluble (particles <1 nm) (Rubin, 1974). The suspended and colloidal particles may consist of individual or mixed metals in the form of their hydroxides, oxides, silicates, sulfides or as other compounds, or they may consist of clay, silica or organic matter to which metals are bound by adsorption, ion exchange and complexation. The soluble metals may be ions, simple or complex or un-ionized organometallic chelates or complexes.

Heavy metals enter the water systems; surface water, groundwater, supplied tap water and rain water from a variety of sources and can be divided into three major sources which are nature, human activities and agriculture. The largest natural source exposed to surface water is directly from rocks and soils. Dead and decomposing vegetation and animal matters, also contribute small amounts of metals to adjacent waters. Large quantities of metals in water are also contributed from wet and dry fallout of atmospheric particulate matters derived from natural sources, for instance, the dust from the weathering of rock, from volcanic eruption and the smoke from forest fires and micrometeorites dust (Young, 2000). The second major source of heavy metals in the water system is from human activities that pollute and contaminate the water bodies through direct discharge of various treated or untreated municipal, residential or industrial effluents. Many of the toxic metals discharged in surface and groundwater are from the industrial wastes such as from the industries of metal mining operations, metallurgical, electroplating industries and tanneries (Rubin, 1974) mostly from wastewater treatment process especially located in big town areas. The concentration of various metals in industrial discharges depends upon the type of industries, specific processes operations and the wastewater treatment system. Besides that, the contamination of heavy metals in water is also contributed from illegal disposal of industrial effluents. The source of heavy metals in the natural water by human activities also include land clearing which is primarily related to the lumbering industry and the construction industry as well as for agricultural purposes. The clearing of land can be subjected to extreme erosion particularly during the construction period; hence increasing the potential for the carrying of heavy metals to the aquatic environment. In the domestic sewage, the amounts of metals may vary according to water usage, quantity and types of food eaten, time of year, economic status and the sewage system (Rubin, 1974). In supplied tap water, heavy metals come from the corrosion of the metal pipes used to carry water to consumers (Bailey *et al*., 1999). Agricultural activities also affect the source of metals in water particularly in the rural region. The used of fertilizers by humans applied to the soil and the death and subsequent decomposition of plants can affect the distribution of metals in groundwater. In addition to these sources, the lowering of pH in rain and surface water and the increased and widely used surfactants in consumer and industrial product have greatly enhanced the mobility of heavy metals in the environment (Sengupta, 2002).

Toxic metals can be distinguished from other toxic pollutants, since they are non-biodegradable and can accumulate in living tissues, thus becoming concentrated throughout the food chain (Korngold *et al.*, 1996). It is well known that toxic elements and their discharge into receiving waters cause detrimental effects on human health and will constitute a great risk for the aquatic and environment system. The health hazards presented by heavy metals depend on the level of exposure which are generally divided into two classes: acute exposure and chronic exposure. Acute exposure refers to contact with a large amount of the heavy metals in a short period of time whereas chronic exposure refers to contact with low levels of the heavy metals over a long period of time (Young, 2000). The toxicity of heavy metals is attributed to harmful and even lethal effects on the human body, particularly on the central nervous system, causing mental disorders such as fatigue, insomnia, decreased concentration, aggressive behaviour, memory loss, learning deficits, depression, irritability, gastric symptom, sensory symptom and motor symptom, and to the physical manifestations such as liver and kidney dysfunction, infertility, gout, hypertension, headache and Candida (yeast) infections (An *et al.*, 2001). One of the papers reported from India, which is one of the countries having problems of increasing toxic metals in water system affecting many people; Singh *et al*. (2004) had studied the impact of the toxicants discharged from sewage treatment plants on the health, agricultural and environmental quality in the wastewater disposal area. The impact of the wastewater toxicants (metals and pesticide) on human health in the areas receiving wastewater was assessed through a standard questionnaire containing a total of 35 items, which cover eight neurobehavioral functions established to be affected by the chemicals exposures. The studied population was divided into exposed and unexposed groups. They found that there was a significant difference in the overall analysis between the exposed and unexposed population group. The levels of the metals in the human blood and urine samples of the exposed and unexposed groups were also studied to confirm the analysis of the questionnaire and they found that the levels of metals in the samples were higher in exposed population than those unexposed population groups. Thus, they concluded that there has been a considerable impact of these toxicants on human health in the exposed area.

The problems of toxic metals distribution and its toxicity in aquatic system are global problems which give pressure to the federal and state governments to overcome this issue. Growing levels of toxic metals pollution in the natural water system related to the evolution of the industrial and agricultural activities demand effective approach to overcome this problem.

1.5.1 Chromium

Chromium is a transition metal, one of the elements found between group II and III in rows 4 through 6 of the periodic table. Its atomic number is 24, its atomic mass is 51.996 and its chemical symbol is Cr. Chromium is one of the toxic metals that has been studied because it can be formed in both cationic and anionic in water. Chromium exists in oxidation states +2, +3, +4, +5 and +6, but the most common, stable and abundant forms are chromium (III) and chromium (VI) (Katz and Salem, 1994). Chromium (III) exists in the form of cation, Cr^{3+} and it occurs naturally in the environment while chromium (VI) exists in the anionic form (chromate) produced by industrial process for laboratory reagents and manufacturing intermediates. Each of both forms has a unique chemistry and behaviour; for example, the chemical form of chromium is largely determined by their potential toxicity as Cr(VI) is believed to be carcinogenic in humans while Cr(III) is actually an essential micronutrient (Katz and Salem, 1993). In the aqueous solutions, Cr(VI) is very soluble and exists in the form of chromic acid (H_2CrO_4) and in the form of dichromate ($Cr_2O_7^{2-}$) while in neutral solutions, Cr(VI) is present in the form of $HCrO_4^-$ and CrO_4^{2-} (Korngold *et al*., 2003).

Chromium is an ubiquitous element, not only because of its occurrence in nature, but also due to the many anthropogenic sources resulting from its widespread industrial application (Martinez-Bravo *et al*., 2001). Chromium and its compounds are used in refractories, drilling mud, electroplating cleaning agents in the metal finishing industry, mordants in the textile industry, catalytic manufacture, fungicides and wood preservatives, in the production of chromic acid and specialty chemicals. They are also used as a constituent of inorganic pigments, as a sensitizer in the photographic industry, as dyes and pigments and in medicinal astringents and antiseptics. Other uses for chromium and its compounds include organic chemical synthesis, leather treatment, photomechanical processing and industrial treatment, including treatment of cooling tower water (Katz and Salem, 1994). As chromium is very widely used, there are many sources of leaching the chromium into the natural water system and it should be removed practically.

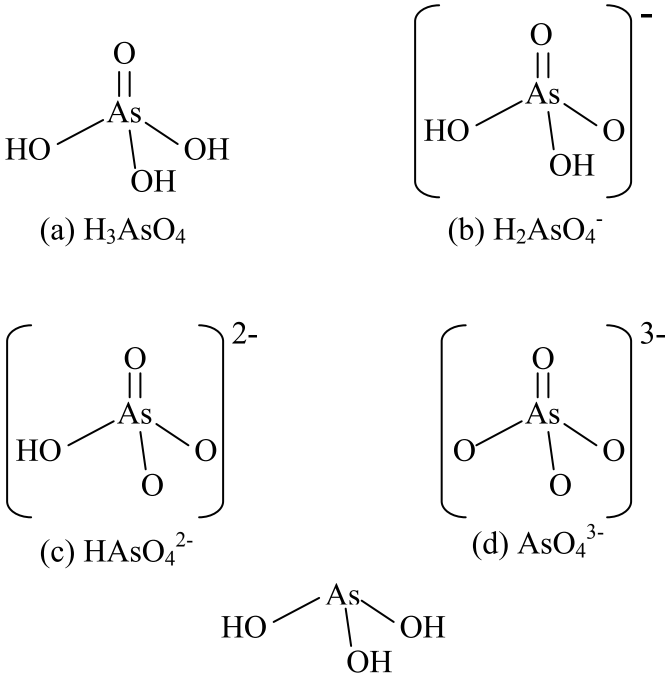
Cr(VI) is toxic and a carcinogenic. It is quite soluble in the aqueous phase almost in the entire pH range and mobile in the natural environment. The carcinogence and toxicity of Cr(VI) is based on its state where the chromate anion resembles the form of sulfates and phosphate (Costa, 2003). In addition, the toxic nature of the Cr(VI) ions is attributed to their high oxidation potential and their relatively small size, which enables them to penetrate through biological cell membranes (Balarama-Krishna *et al*., 2005). At physiological pH, Cr(VI) exists as an oxyanion, with an overall charge of minus 2 having borrowed electrons from oxygen. In this form, Cr(VI) resembles oxyanions, such as sulfates and phosphates, which are used extensively in humans for many diverse biochemical processes. The individual cells of the body need to take up sulfate and phosphate and have active systems that transport these nutrients. However, chromate fools the cell's anion uptake system into thinking that Cr(VI) is sulfate or phosphate and the cells transport chromate from the outside of the cell into its interior. Thus, if chromate is delivered to any cell in the body regardless of the route of exposure it will be taken up into the cell. In contrast, Cr(III) does not resemble any biological nutrient and has no similar way to enter the cell. However, it is possible that Cr(III) may be oxidized into Cr(VI) in the appropriate condition, hence the toxicity of Cr(VI) take place. Usually, Cr(III) is readily oxidized to the hexavalent state at high pH (Katz and Salem, 1993). Presently, Cr(VI) has been recognized as a probable agent of lung cancer and it also produces gastrointestinal disorders, dermatitis and ulceration of skin in man (Balasubramanian and Pugalenthi, 1999).

The regulation for the limitation of the chromium concentration in water should be highlighted and emphasized in every country due to the toxicity, reactivity and probable carcinogens of chromium. Acceptable limits for the chromium in water differ in almost every country. As a guideline, the World Health Organization (WHO) recommends a maximum level of 50 μg/L (ppb) for Cr(VI) in drinking water (Zu, 1993) and the National Institute for Occupational Safety and Health (NIOSH) recommends that the levels of chromium should be reduced to 10^{-3} mg/m^3 (Rengaraj *et al*., 2003). The Environmental Protection Agency (EPA) has set the MCL (Maximum Contaminant Levels) at 0.1 ppm in drinking water because EPA believes, given the present technology and resources, this is the lowest level where the removal of this contaminant can be achieved in drinking water.

1.5.2 Arsenic

Arsenic is the third member of the nitrogen family, which consists of elements in group 15 of the periodic table. Its atomic number is 33, its atomic mass is 74.9216 and its chemical symbol is As. Arsenic is characterized more by its ubiquity than by its abundance. Arsenic is a naturally occurring metalloid element, the 20th most abundant element in the earth's crust and is the 12th most abundant element in the human body (King, 1994). As a metalloid, arsenic has both metallic and nonmetallic properties. Arsenic displays various oxidation states that are -3, 0, +3 and +5. The commonly encountered oxidation states of arsenic in water are +3 (As(III) or arsenite) and +5 (As(V) or arsenate) of which the former mostly exist in the neutral form while the latter exist in the anionic form. The major chemical form in which arsenic appears to be thermodynamically stable is arsenate ion. At moderate or high redox potentials arsenic can be stabilized as a series of pentavalent (arsenate) oxyanions, H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}. However, under most reducing (acid and mildly alkaline) conditions and lower redox potential, the trivalent arsenite species (H_3AsO_3)

predominate (Mandal and Suzuki, 2002). The structures for arsenates and arsenite species are shown in Figure 1.6.



(a) H_3AsO_4

(b) $H_2AsO_4^-$

(c) $HAsO_4^{2-}$

(d) AsO_4^{3-}

(e) H_3AsO_3

Figure 1.6 The structure of the anion form of arsenate (a, b, c and d) and the neutral form of arsenite (e) species.

Arsenic is very widely distributed in nature with its abundance on earth is thought to be about 5 parts per million (Young, 2000). In waters, it occurs in rivers, lakes, streams, groundwater and in the seas and oceans. The arsenic concentration of most potable waters seldom exceeds 10 ppb, although values as high as 100 ppb have been reported (Cleseri *et al.*, 1989). Exposure to arsenic may come from natural sources, from industrial sources or from food or beverages. Arsenic is increasingly being found in water in many parts of the world such as Bangladesh, Taiwan, Chile, West Bengal-India, Mexico, Argentina, Canada, Hungary and some parts of USA; Utah, Western Oregon and California (Mandal and Suzuki, 2002). The arsenic polluted areas of the world can be geologically subdivided into areas made of sediments derived from water or volcanic rocks characterized by the presence of geysers, gold and uranium mining areas (Kundu, 2004). These elevated arsenic concentrations are mostly of natural origin.

Most arsenic is used in the form of compounds of which As_2O_3 is the sole basic material. The largest consumers of arsenic trioxide are the USA, Malaysia and the UK (Merian, 2004). The uses of arsenic are to make alloys mostly with lead, transistor and light-emitting diodes (LEDs) and also in wood preservatives as CCA (Chromated Copper Arsenate) (Young, 2000).

Arsenic and its compounds are toxic, poison and carcinogenic to animals and human with Arsenite (As(III)) is generally considered more acutely toxic than arsenate (As(V)). Arsenate and arsenite are thought to elicit acute toxicity via different mechanisms where arsenate mimicks phosphate and interfering with ATP production in the mitochondria while arsenite binds to and inactivates sulfhydryl-containing enzymes (Lantz *et al.*, 1994). In low doses, arsenic produces nausea, vomiting and diarrhoea while in larger doses, it causes abnormal heart beat, damage to blood vessels and a feeling of ‘pins and needles’ in hand and feet. Long term exposure to arsenic and its compounds can cause cancer where the inhalation can result in lung cancer and if swallowed, cancer is likely to develop in the bladder, kidneys, liver and lungs (Newton, 1999). Large doses of inorganic arsenic can cause death. The specific disease called arsenocosis that be related only if the doses of inorganic arsenic compounds are higher in the human body.

Since arsenic is well known as toxic and carcinogenic that affects many people around the world, the Safe Drinking Water Act requires Environmental Protection Agency (EPA) to revise the existing 50 ppb standard for arsenic in drinking water. On January 22, 2001 EPA adopted a new standard and public water must comply with the 10 ppb standard beginning January 23, 2006 (EPA, 2001). In addition, arsenic is the one substance that is considered to be potential occupational carcinogens by National Institute for Occupational Safety and Health (NIOSH). In addition, the provisional guideline value recommended by the World Health Organization is 10 ppb (WHO, 1993).

1.6 Removal of Toxic Metals in Water

As discussed in the previous sections chromium and arsenic are very toxic, carcinogenic and very harmful to human beings, in addition, the requirement to comply with the regulation made by the governments, the importance of removing both toxic metals in various sources before discharging them into surface water streams or for drinking water are very crucial. With the purpose to reduce or eliminate the concentration and quantity of both metals, the treatment of the affected water can be done by using many types of techniques and methods such as filtration, chemical precipitation, coagulation, ion exchange, adsorption, electrodeposition, reverse osmosis, cementation, solvent extraction and biological processing. All these approaches have their inherent advantages and limitation. The oldest and most frequently used method for removal those toxic metals from wastewater are precipitation. Although this process is effective to remove a large amount of toxic metals, it has some disadvantages. It produces a large amount of sludge which has a long settling time and harmful to the soil. For this reason, adsorption processes has been and actually are the most frequently applied method in the industries instead of precipitaion and consequently the most extensively studied.

Recently, a wide range of sorbent is available for the removal of chromium from water especially the hexavalent chromium (chromate) since the toxicity and solubility of chromate anion is well-known to be extremely higher than trivalent chromium. The surfactant modified zeolite from the natural zeolite, i.e. clinoptilolite, is widely used to remove chromate from water (Ghiaci *et al*., 2004; Li, 2004; Haggerty and Bowman, 1994; Vujakovic *et al*., 2000). The other sorbent used for the removal of chromate includes biosorbent, for instance, chitosan (Schumi *et al*., 2001; Bodu *et al*., 2003), hazelnut shell (Cimino *et al*., 2000), *sargassum sp.* biomass (Cossich *et al*., 2002), *Aeromonas cavidae* (Loukidou *et al*., 2004) and *bacillus sp.* (Nourbakhsh *et al*., 2002), the ion exchanger resins in the anionic form (Korngold *et al*., 2003), the activated carbon (Selvi *et al*., 2001; Babel and Kurniawan, 2004) and coals (Lakatos *et al*., 2002). Since the toxicity of trivalent chromium is greatly less than hexavalent chromium, only a little has been reported in the removal of trivalent chromium from water. The sorbent for the trivalent chromium includes biosorbent such as brown seaweed biomass (Yun *et al.*, 2001) and *Saccharomycess cerevisiae* (Ferraz *et al.*, 2004). Besides that, the ion exchanger resin in the cation form (Rengaraj *et al.*, 2001; Rengaraj *et al.*, 2003), zeolite (Barros *et al.*, 2004; Bosco *et al.*, 2005), bentonite (Chakir *et al.*, 2002) and activated carbon (Cordero *et al.*, 2002) have been used to remove trivalent chromium from water.

Numerous sorbents have been developed to remove arsenic from water. The sorbent used for the removal of arsenate and arsenite from water are natural zeolites-clinoptilolite (Elizalde-Gonzalez *et al.*, 2001b), cement (Kundu *et al.*, 2004), granular ferric hydroxide (Thirunavukkarasu *et al.*, 2003), zero-valent iron (Bang *et al.*, 2005), iron hydroxide-coated alumina (Hlavay and Polyák, 2005), iron oxide-loaded slag (Zhang and Itoh, 2005), ferruginous manganese ore (Chakravarty *et al.*, 2002), red mud (Altundogan *et al.*, 2000), iron(III) phosphate (Lenoble *et al.*, 2005), Zr-loaded lysine diacetic acid chelating resin (Balaji *et al.*, 2005), nanocrystalline titanium dioxide (Pena *et al.*, 2005) and mesoporous alumina (Kim *et al.*, 2004). Since the arsenate and arsenite exist in different forms in water, some sorbents cannot remove both species simultaneously. The commonly used sorbent for arsenate removal from water recently are synthetic zeolite (Shevade and Robert, 2004), natural zeolites (Xu *et al.*, 2002), natural iron ores (Zhang *et al.*, 2004), synthetic akaganeite (Deliyanni *et al.*, 2003), strong-base anion-exchange resins (Korngold *et al.*, 2001), metal-loaded clay (Lazaridis *et al.*, 2002), Ce(IV)-doped iron oxide (Zhang *et al.*, 2003) and biosorbents such as *P. chrysogenum* biomass (Loukidou *et al.*, 2003). Papers reported on the removal of arsenite from water is limited since arsenite (As(III)) is difficult to be removed from water using normal available treatment process. It is usually necessary to change the trivalent arsenic to the pentavalent form by adding an oxidant, generally chlorine (Kartinen and Martin, 1995). There is no paper found reporting the removal of arsenic from water by surfactant-modified zeolite, however, Sullivan *et al.* (2003) had reported the sorption of arsenic from water soil-washing leachate since the pentavalent arsenic resembles chromate that can undergo anion exchange by surfactant modified zeolite.

1.6.1 Adsorption Theory

The removal of toxic metals from sorbent is based on the adsorption at solid-liquid interfaces. Adsorption from dilute aqueous solution onto the particulate matter present in suspension may involve specific chemical interaction between adsorbate and adsorbent. The most common interactions of this type include an ion exchange process in which the counter ions of the substrate are replaced by ions of similar charge. The experimental determination of the extent of adsorption usually involves shaking a known mass of adsorbent with a solution of known concentration at a fixed temperature and fixed period of time. The concentration of the supernatant solution is then determined by chemical means, which equilibrium conditions have been established. An adsorption isotherm is a graphical representation showing the relationship between the amounts adsorbed by a unit weight of adsorbent and the amount of adsorbate remaining in test media at equilibrium and at a fixed of temperature. The major factors determining the shape of an isotherm are the number of compounds in the solution, their relative adsorb abilities, the initial concentration in the solution, the degree of competition among solute for adsorption sites and the characteristic of the adsorbent. Equilibrium studies on adsorption provide information about the capacity of the adsorbent or the amount required to remove a unit mass of pollutant. The most widely used isotherm equation for modelling the adsorption are the Langmuir and Freundlich models.

The simplest theoretical model that can be used to describe monolayer adsorption is the Langmuir equation. The Langmuir equation is based on a kinetic approach and assumes a uniform surface, a single layer adsorbed material at constant temperature. The Langmuir equation is:

$$\frac{x}{m} = \frac{bQ_o C_e}{1 + bC_e} \tag{11}$$

where:

x : mass of adsorbate adsorbed (mg or mmol)

m : mass of adsorbent (g or kg)

C_e : equilibrium concentration (mg/L or mmol/L)

b : langmuir constant related to the affinity of the binding site.

Q_o : maximum adsorption at monolayer coverage (mg/g or mmol/kg)

The equation (11) can be simplified, if:

$$\frac{x}{m} = q_e = \text{amount adsorbed at equilibrium (mg/g or mmol/kg)} \qquad (12)$$

Therefore:

$$q_e = \frac{bQ_oC_e}{1 + bC_e} \qquad (13)$$

The nonlinear form (equation 13) can be evaluated by transforming to the linear equation:

$$\frac{m}{x} = \frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{bQ_oC_e} \qquad (14)$$

When $\frac{m}{x}$ or $\frac{1}{q_e}$ against $\frac{1}{C_e}$, a straight line graph is obtained with slope is $\frac{1}{bQ_o}$ and intercept-Y is $\frac{1}{Q_o}$.

The Freundlich is an empirical equation based on the distribution of solute between solid phase and aqueous phase at equilibrium. The basic Freundlich equation is:

$$\frac{x}{m} = q_e = K_f C_e^{\frac{1}{n}} \qquad (15)$$

The abbreviation in equation 15 is similar to the Langmuir equation except for K_f and n is the empirical Freundlich constant. Equation 15 can be rearranged into a linear form:

$$\log\frac{x}{m} = \log q_e = \log K_f + \frac{1}{n}\log C_e \qquad (16)$$

When $\log\frac{x}{m}$ or $\log q_e$ against $\log C_e$, a straight line graph is obtained where the slope is $\frac{1}{n}$ and the intercept-Y is $\log K_f$.

1.7 Research Background and Objectives of the Study.

In order to remove the toxic metals, i.e. chromium and arsenic that can exists in the form of cation (Cr(III)), anions (Cr(VI) and As(V)) and neutral (As(III)) species as H_3AsO_3 in water depending on the oxidation states and the condition of water especially the pH of solution, the materials which have the properties of anion and cation exchanger simultaneously are essential and have to be developed. Therefore, the most important aim of this study is to develop such materials by attaching the zeolite with the cationic surfactant. Prior to modify the zeolite surface by cationic surfactant, the highly pure zeolite NaY must be produced and characterized by various characterizations techniques. The synthesis of the zeolite NaY requires a source of silica as a main raw material, hence, the rice husk ash which is known to have high content of silica can be used. In addition, the rice husk is produced in abundance in Malaysia as agro-waste and which needs to reprocess to value added product and thus to solve the environmental problem. The zeolite is well-known having permanent negative net charges allowed to cation exchanger and by attaching it to cationic surfactant, the external surface of zeolite may have positive charges resulting from the double layers provided by the hydrophobic bonding of surfactant at the external surface of zeolite enabling anion exchange. Thus, it can be used to sorb cation and anion species in aqueous solution.

The objectives of the study are as follows:

1) To prepare and characterize the rice husk ash as a raw material.
2) To synthesize zeolite NaY from rice husk ash as a source of silica.
3) To characterize the synthesized zeolite NaY by various methods.

4) To prepare the surfactant-modified zeolite Y by modifying the surface of zeolite NaY with cationic surfactant (HDTMA).
5) To characterize the surfactant-modified zeolite Y by a variety of methods.
6) To study the effectiveness of the modified and unmodified zeolite for the removal of Cr(III), Cr(VI), As(III) and As(V) from water.