Development of Magnetic Zeolites for Removal of Metallic Contaminants from Industrial Wastewater.

By
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CERTIFICATION OF APPROVAL

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Approved by,

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

SITI FATIHAH SALLEH

ABSTRACT

Since the discovery of multi- walled and single- walled carbon nanotubes (MWNTs and SWNTs, respectively), research on their application is being actively carried out. In this report, a series of magnetic Faujasite (FAU) zeolites are hydrothermally synthesized using traditional hydrothermal method by adding empty MWNTs and Fe_2O_3- filled MWNTs in the crystallization. The products were characterized with X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and fourier transform infrared spectroscopy (FTIR). The results show that all the synthesized products exhibit typical nature of FAU zeolites. Comparing the magnetic zeolites (FAU/ Fe_2O_3 MWNT) synthesized with pure FAU zeolites, their adsorption capabilities of Cr^{3+} are still high. When the magnetic zeolites are used to extract ion from solution disposed without molding, their powder products can be easily separated from solvent or solution by magnetic separation technology.

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TABLE OF CONTENT

CHAPTER 1: INTRODUCTION

CHAPTER 3: METHODOLOGY

CHAPTER 4: RESULT & DISCUSSION

LIST OF TABLE

LIST OF FIGURE

LIST ABBREVIATION AND NOMENCLATURE

V_r	final volume of retentate (l)
%T	transmittance percentage
1/cm	wavenumber
Lin	intensity(cps)
t	time(h)

CHAPTER 1
INTRODUCTION

1.0 INTRODUCTION

1.1 Background of Study

Zeolites are crystalline aluminosilicates containing pores and cavities of molecular dimension [1]. Their crystal structures are porous on a molecular scale, revealing regular arrays of channels and cavities. These structures create a nano-scale labyrinth which can be filled with water or other guest molecules resulting in molecular sieve ability. Typically, zeolites are able to accommodate a wide variety of cations, such as Na^+, Ca^{2+}, Mg^{2+} and others. These positive ions are rather loosely held and can readily be exchanged for others in a contact solution.

Many zeolites occur as natural mineral, where volcanic rocks and ash layers react with alkaline groundwater. Some of the more common mineral zeolites are analcime, chabazite, clinoptilolite, heulandite, natrolite, and phillipsite. Zeolites also crystallize in post-depositional environments over periods ranging from thousands to millions of years in shallow marine basins. However, naturally occurring zeolites are rarely pure and are contaminated to varying degrees by other minerals, metals, quartz, or other zeolites. Hence for this reason, naturally occurring zeolites are excluded from important commercial applications where uniformity and purity are needed or essential.

Although some natural zeolites occur in large amounts, they offer only a limited range of atomic structures and properties. Synthetic zeolites have a wider range of properties and larger cavities than their natural counterparts. The history of man-made zeolites can be traced back as early as 1862 by St Claire Deville and there are numerous discoveries and advances in thinking in the field of zeolite synthesis since then.

Today more than 100 different zeolites have been made, and the annual production of synthetic zeolites exceeds 12,000 tons. Zeolites are manufactured in a number of ways; one important technique involves mixing sodium, aluminum, and silica chemicals with steam to create a gel (an amorphous, noncrystalline, water-rich solid). The gel is aged, then heated to about 90°C (194°F). Another technique uses kaolin clay that has been heated in a furnace until it begins to melt, then chilled and ground to powder. This powder is mixed with sodium salts and water, aged, and heated. In all the synthesis methods, the zeolite produced depends on the compositions of the starting materials and the conditions of reaction, including acidity, temperature, and water pressure.

Industrial applications make use of synthetic zeolites of high purity, which have larger cavities than the natural zeolites. These larger cavities enable synthetic zeolites to absorb or hold molecules that the natural zeolites do not. On the other hand, some zeolites are used as molecular sieves to remove water and nitrogen impurities from natural gas. In addition, since they have the ability to interact with organic molecules, zeolites are important in refining and purifying natural gas and petroleum chemicals as catalyst. Zeolites are used to help break down large organic molecules found in petroleum into smaller molecules that make up gasoline in catalytic cracking process. Last but not least, zeolites are also used in hydrogenating vegetable oils and in many other industrial processes involving organic compounds.

1.2 Problem Statement

1.2.1 Problem Identification

The most fundamental consideration regarding the adsorption of chemical species by commercial zeolites is molecular sieving. In this process, species such as metal ions with a kinetic diameter which makes them too large to pass through a zeolite pore are effectively "sieved." This "sieve" effect can be utilized to produce sharp separations of molecules by size and shape.

The zeolites commonly used in the removal of heavy metal ions from industrial effluents are in the form of fine powders and should be recovered by solid-liquid separation subsequent to the purification process. Normally, adsorption based on molecular sieving is always reversible in theory and usually reversible in practice too. This allows the zeolites to be reused many times, cycling between adsorption and desorption, which accounts for the considerable economic value of zeolites in adsorptive applications.

However, although the separation is possible for single-phase liquid or gas detoxification process, the practical application of fine zeolite powders to complex multiphase system such as flue gas containing ash or industrial effluents containing finely divided particulates is rather limited.

1.2.2 Significance of Project

The development of magnetic zeolites is envisaged to extend the application of zeolites to a much wider range of systems. It opens the door for sorbent regeneration, safe disposal of waste and/or recovery of loaded valuable species without secondary contamination.

In the current practice, the composites of magnetic zeolites showed high adsorption capacities for the Cu^{2+}, Cr^{3+} and Zn^{2+} in aqueous solution and, more important, no reduction of the adsorption was produced by the formation of the composite. In addition, the magnetic composites showed good chemical resistance in a wide pH range 5–11.

The adsorption features of zeolites can be combined in a composite to produce magnetic adsorbents. The preparation is simple and does not require any special chemical or procedure. These magnetic adsorbents also show a good adsorption capacity for metal ions contaminants in water and can be used in a wide pH range.

1.3 Objectives and scope of study

First and foremost, the main objective of this project is to produce zeolites with magnetic properties so that it could be readily separated and recovered from complex multiphase systems by application of external magnetic field. Hence, a new approach is proposed to synthesis zeolites with filled multi-walled nanotubes(MWNTs).

The second objective is to conduct characterization analyses to ensure that the synthesized products are zeolites. The results obtained are then studied and discussed.

The third objective is to investigate and compare the adsorption capacity between pure zeolites and composite zeolites. Pure zeolite chosen for this project is of Faujasite(FAU) type while the composite zeolites are FAU/MWNTs and FAU/Fe_2O_3MWNTs.

1.3.1 Relevancy of Project

According to Toxic Release Inventory (TRI) National Analysis released by USA Environmental Protection Agency (EPA) [2], there are 21,695 facilities, including federal facilities, reported to the TRI Program in the year of 2008. They reported 3.86 billion pounds of on-site and off-site disposal or other releases of the TRI chemicals to the environment worldwide.

Over 87% of the total was disposed of or otherwise released on-site; 12% was sent off-site for disposal. Metal mining facilities accounted for 30% of the total in 2008, while electric utilities accounted for 23%. This gruesome statistics imply as if we are living in a virtual "sea of pollutants" and by consuming them, human beings carry many of these toxins and carcinogens within their bodies. That is why it is a great demand for ultra wise purification of water from hazardous contaminants for the benefits of the mankind.

Zeolite itself is often utilized as water purification material for its incomparable ion-exchange capacity and their primary use has been in water and wastewater treatment. The chemical and structural features of zeolites make them very effective for the removal of toxic metal ions (e.g. lead, nickel, zinc, cadmium, copper, chromium and/or cobalt), radionuclides as well as ammoniacal nitrogen (ammonia and ammonium) from municipal and industrial wastewaters, such as from electroplating effluents, agricultural wastewaters, and or coke-plant effluents.

Hence, this project is relevant to be conducted as it might help the industry by giving alternative to the traditional method of using pure zeolites. Also, this project gives a new idea on how to recover the zeolites and to regenerate them by using external magnetic separation technology.

1.3.2 Feasibility of Project

This project is aimed to be achieved in the time frame of one year. Therefore, it will not concern the fundamental point of view regarding the zeolites detailed morphologies. In order to run the experiments, this project utilized the all necessary equipments and facilities available in Universiti Teknologi PETRONAS (UTP). It is also low in cost for analysis and brings huge benefits for the future.

CHAPTER 2
LITERATURE REVIEW

2.0 LITERATURE REVIEW

In view of the industrial importance of zeolites and also because of the intrinsic scientific interest in their structural complexity and diverse chemistry, considerable effort has been directed into zeolite synthesis. Usually, aluminosilicate zeolites are synthesized under hydrothermal conditions from reactive gels in alkaline media. This section will briefly describe the hydrothermal zeolite synthesis pioneered by Barrer over 50 years ago, until the present day and beyond.

2.1 Historical view of hydrothermal synthesis of zeolite

Hydrothermal synthesis can be defined as a method of synthesis of single crystals which depends on the solubility of minerals in hot water under high pressure. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called autoclave, in which a nutrient is supplied along with water. A gradient of temperature is maintained at the opposite ends of the growth chamber so that the hotter end

The historical development of hydrothermal synthesis of zeolite has started since 1940s by two scientists honored as the Founding Fathers of the synthesis' science and practice [1]. Richard Barrer investigated the conversion of known mineral phases under the condition of strong salt solution at fairly high temperatures (170-270 °C) ref. In 1948, he synthesized the first zeolite and the discovery has initiated a lifetime contributions to all aspect of zeolite science [3-4] .Later in 1949, Robert Milton began his synthesis program in the laboratories of Linde cooperation and four years later, Milton and his colleagues had successfully synthesized 20 zeolites and many achievements were to follow [5].

In 1970s, the world has seen remarkable development of ideas on zeolite synthesis and more systematic studies on the synthesis kinetics and mechanism. There has been acceleration in interest after the discovery of ZSM-5. A new polymorph of silica (silicalite, refractive index 1.39, and density 1.76 g cm^{-3}) was then found in 1978 and was discovered to have a novel tetrahedral framework enclosing a three-dimensional system of intersecting channels. It was prepared by hydrothermal synthesis using alkylammonium cations. The concept of silicalite has lead to some important realizations which are; (i) High silica zeolites are essentially impure silica polymorphs and bear at least as much relationship to silicas as they do to Al-rich zeolites, feldspars and similar aluminosilicates, (ii) High-silica zeolites are intrinsically hydrophobic and organophilic, (iii) For a given structure, there is usually a smooth transition in properties.

Besides that, there were some other important discoveries in 1970's which are the use of F$^-$ as a mineralizer in zeolite synthesis, polymeric templates and Mazzite, the first synthetic phase found as a mineral. Thereafter, numerous advances in the study and understanding of zeolite synthesis have been seen in the following years including the building of mathematical models and studies on the genesis of zeolite crystal morphology (1980's), and also the use of advanced scattering and diffraction techniques to probe the earliest stage of zeolite formation (1990's).

The investigative works on the synthesis process have continued up to the present day, stimulated the discoveries of new materials and synthetic techniques. The recent studies on the synthesis mechanism are contributed in a very significant work by Chang and Bell [6]. The work was based upon studies of the formation of ZSM-5 from Al-free precursor gels at 90-95 °C using XRD, Si MAS NMR spectroscopy, and ion exchange. The work is then extended by Burkett and Davis that examine the role of TPA as structure-directing agent in silicalite synthesis. A team at Leuven later was responsible on expanding the ideas on a detailed characterization of the MFI precursor material originally described by Shoeman. The details of the main features of synthesis mechanism and their principle ideas by all the authors (1959-2004) are summarized in Appendix A [7].

2.2 Advances of hydrothermal synthesis of zeolite of present day

Moving forward to the year of 2000 and beyond, the practice of hydrothermal synthesis of zeolites has undergone continuous evolution of ideas specifically in the molecular modelling methods and experimental techniques. Recent years have seen many new zeolite-like materials (zeotypes) containing elements other than silicon and aluminium have been synthesized. In fact, more than hundred different kinds of zeolites have been synthesized by optimizing synthesis conditions such as choosing the suitable reactants, gel compositions, temperature, and adding suitable organic structure directing agents.

In order to keep this review within reasonable bounds, the subject matter has been restricted to the progress in the experimental techniques [1]. The first one is the application of microwave dielectric heating to zeolite synthesis. This technique offers convenient and often rapid sample products with high crystallinity. Also, there is a possibility of (genuine) selectivity. Other advantage of microwave synthesis including high heating rates that made it possible to distinguish between the crystal populations nucleated during the heating process and that arising from proto-nuclei generated during the room temperature aging of the precursor solutions in colloidal silicalite synthesis.

Second one is the increasing use of fluoride media as a useful alternative to the common hydroxide-based synthesis. Fluoride ion is considered as the structure-director as it always appears to be occluded in small cages within the zeolite framework. Next is a method called the high-pressure method. This method is referred as the mineralogist technique whereby the synthesis is carried at a very high (kilobar) pressure. The direct effect of pressure is observed for instance in the case of bikitaite synthesis which could not be synthesized under these conditions (170-270 °C, reaction time of 60 days) at 1 kbar pressure but was obtained at 2 kbar instead.

2.3 Zeolites: Linde Type A (LTA) and Faujasite (FAU)

A faujasite type zeolite has an oxide molar composition and can be represented by the formula below:

$$0.9 \pm 0.2 M_2O.Al_2O_3.xSiO_2.wH_2O$$

Wherein M stands for alkali metal cation, x is the number of from 2.5 to 6, and w is a number of 6 to 9.While LTA zeolite formula is $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]$: 27 H_2O. FTA and LTA are the two most extensively used zeolites in industrial processes such as ion exchange, adsorption and catalysis.

It is a great interest to synthesis high-quality zeolites nanocrytals [8]. This is because these nanocrytals are very important for a variety of studies such as to understand the fundamental and process of crystal growth at the zeolite external surface, especially the nucleation and growth process without any post-synthesis treatment by high-resolution electron microscopy (HREM).

2.4 Multi-walled carbon nanotube/zeolite nanocomposites

Research on the carbon-silicate nanocomposites has risen recently, causing significant interest in the laboratories working on the nanosized materials. The main reason is the potential production of novel matter with outlandish behavior. Several papers are published on the synthesis of various carbon nanotubes/polymer. However, there are very few papers in the literature dealing with the synthesis of carbon/silicate nanocomposites. According to a journal published in 2005 [9] , the studies of the hydrophobic /hydrophilic properties of carbon nanotubes and their modification by heat treatment at high temperature are important to be able to optimize the synthesize method from the carbon nano-tube side.

The journal studied the thermal characterization of multiwall carbon nanotubes containing zeolite based nanocomposites. Experiments to synthesize zeolites in the presence of carbon nanotubes are conducted on three different zeolites which are LTA, FAU, and MFI. The multiwall carbon nanotubes were prepared in the laboratory using Combustion Chemical Vapor Deposition (CCVD) synthesis technique. While for the zeolite composites of MWNT/LTA, MWNT/FAU and MWNT/MFI, the recipes are taken from Thompson, Kuhl, and Barrer respectively. Certain number of tests was carried out to investigate the morphologies and the thermal behaviour of the synthesized nanocomposites. They were X-Ray Diffracrion (XRD) analysis, Transmission Electron Microscope (TEM) test and also TG-DTG-DTA(TG: thermogravity, DTG: differentia thermogravity, DTA: differential thermal analysis) test to study the thermal behavior of the composites.

It was observed that the morphologies of the synthesized nanocomposites were significantly different. For FAU zeolite nanocrystals with a few nm in diameter were nucleated on the nanotubes covering their surface, however, for LTA and MFI zeolites bulky crystals with nanotubes crossing them were observed by transmission electron microscopy. TEM investigations also observed that the samples obtained by burning the MWNT's from zeolite crystal off, had holes of nanometer diameter. Thus, one of the most important discovery of the study was the generation of secondary mesoporosity in the zeolites after removing the carbon naotubes. Hence, because of their peculiar new properties, these materials might be considered to be used as adsorbents and/or catalysts.

2.5 Magnetic properties of aligned metal-filled carbon nanotubes

Carbon nanotubes are molecular-scale tubes of graphitic carbon with outstanding properties. They are among the stiffest and strongest fibres known, and have remarkable electronic properties and many other unique characteristics. For these reasons they have attracted huge academic and industrial interest, with thousands of papers on nanotubes being published every year. Commercial applications have been rather slow to develop, however, primarily because of the high production costs of the best quality nanotubes [10]. Nonetheless, the combination of magnetic materials and carbon nanotubes (CNT's) starts becoming a promising research direction. Particularly, to produce magnetically fuctionalized CNT's, the multi-walled nanocomposites are filled with ferromagnets. This system may be considered as magnetic nanowires encapsulated in thin carbon shells.

The synthesis of ferromagnetic (Fe, Co and Ni) filled MWNT's are performed by Chemical Vapor Deposition(CVD) processes in a quartz tube reactor inside a two-stage furnace. The materials are grown by simple pyrolysis of metallocenes [(biscyclopentadienyl) (Fe,Ni,or Co)] or by using the catalytic decomposition of hydrocarbon (methane, benzene) over Ni- particles. The metallocenes supply both, the carbon for the nanotube shell growth and the ferromagnetic metal for the nanowire inside the carbon tubes. The main parameters of the deposition process are the temperature of the first furnace for the sublimation of the metallocene, the total gas flow rate and the temperature of the hot zone (the second furnace) for the pyrolysis of the metallocene and for the deposition of the filled tubes.

During the synthesis process, particularly in the second furnace having a high temperature 900-1150 °C, the tubes grow on the inner wall of the reactor quartz tube as well as on the substrates placed within the reactor. Using TEM and Scanning Electron Microscope (SEM) studies, it is proven that the films deposited on the quartz tube wall consist mainly of a mixture of filled MWNTs and the metal particles encapsulated by carbon. The fraction of the tubes is up to 90% (refer to Figure 2.1). While XRD analysis as shown in Figure 2.2 indicates two main sets of diffraction peaks corresponding to the presence of α-iron (bbc) and γ-iron (fcc). The measured intensities of the respective peaks confirm the existence of clear textures for both phases: (110) for the α-Fe phase and (111) for the γ -Fe phase, respectively.

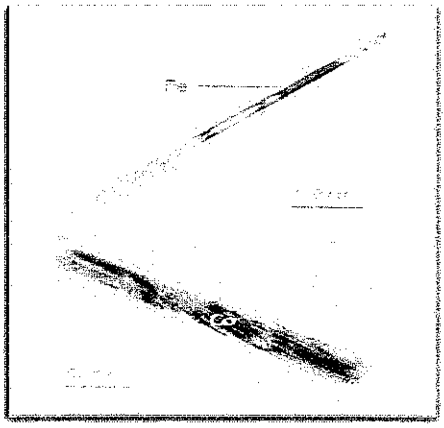


Figure 2.1: TEM image of homogeneously filled MWNT's[10].

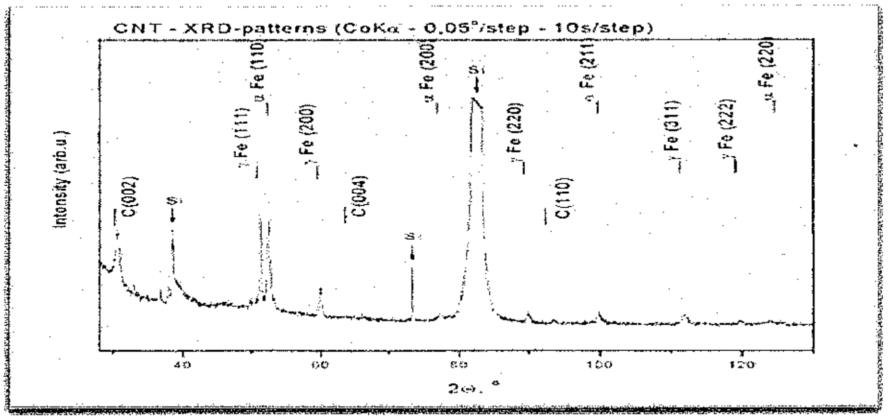


Figure 2.2: The XRD pattern reveals α-iron (bbc) as well as γ-iron (fcc)both having a pronounced texture[10].

Besides that, Alternating Gradient Magnetomery (AGM) is also used for a temperature-dependant integral magnetic characterization. The measurements show distinct magnetic anisotropy with the easy axis perpendicular to the substrate plane and parallel to the axis of the aligned MWNT's, respectively. Hence, it shows that the anisotropy shape is responsible for the magnetic behaviour differences. The low temperature behaviour suggests a negligible coupling between the two iron phases.

2.6 Fe_2O_3/Zeolite composites as the new adsorbent for removal of contaminants from water.

In recent years, considerable attention has been taken in the application area of magnetic particle technology. Generally, magnetic particles can be used to adsorb contaminants from aqueous or gaseous effluents and after the adsorption is carried out the adsorbent can be separated from the medium by a simple magnetic process.

Some examples of this technology are the use of magnetite particles to accelerate the coagulation of sewages (Booker et al., 1991), magnetite coated functionalized polymer such as resin to remove radio nuclides from milk (Sing, 1994), poly(oxy-2,6-dimethyl-1,4-phenylene) for the adsorption of organic dyes (Safarik et al., 1995) and polymer coated magnetic particles for oil spill remediation (Orbell et al., 1997).

However, these materials suffer from small surface area or small adsorption capacity, which limit their application. Moreover, the preparation of these magnetic materials demands several steps. Nevertheless, the magnetic adsorbent of iron oxide (Fe_2O_3)/zeolites composite is seen to overcome this problem. The adsorption features of zeolites with the magnetic properties of iron oxides have been combined in a composite to produce a novel magnetic adsorbent.

The composites were prepared by the precipitation of iron oxides or hydroxides onto the zeolite surface. After the preparation a test with a 0.3T magnet showed that the whole material was magnetic and completely attracted to the magnet. The chemical analyses and magnetization measurements are conducted to test and characterize the products obtained.

The pure Fe oxide prepared without the zeolite showed magnetization of 62 $JT^{-1}kg^{-1}$, which is similar to γ-Fe_2O_3 maghemite (Oliveira et al., 2000). Figure 2.3 shows a simple magnetic process to the attraction of the composite NaY:Fe oxide.

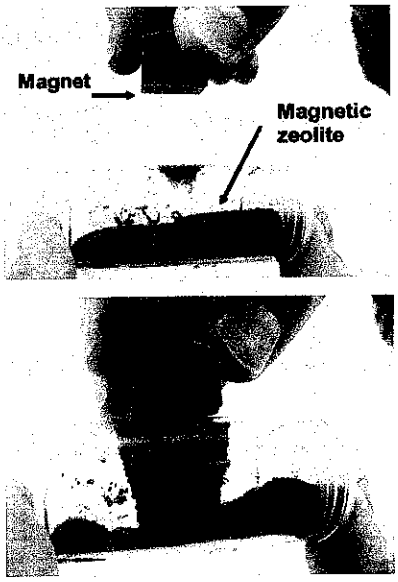


Figure 2.3: Photographs of the a NaY zeolite:Fe oxide composite[11].

Chemical analyses of the composites showed only the presence of Fe^{3+}, suggesting that the added Fe^{2+} is completely oxidized during the composite preparation. For the pure Fe oxide a Fe^{3+}/Fe^{2+} ratio of approximately 7 was observed by chemical analyses and Mossbauer spectroscopy. Other analysis includes X-Ray Diffraction (XRD) and N_2 adsorption isotherms. The results of N_2 adsorption isotherms analysis are shown in Table 2.1 and Figure 2.4 below [11].

Table 2.1: Magnetization, chemical analyses, and BET surface area measurements for the NaY Zeolite:iron oxide composites [11].

Sample	Fe oxide (wt%)	Bulky magnetization ($JT^{-1}kg^{-1}$)	BET surface area(m^2/g)
Fe oxide pure	ca.100	62	66
NaY pure	0	0	568
NaY:Fe oxide 3:1	8	18	361

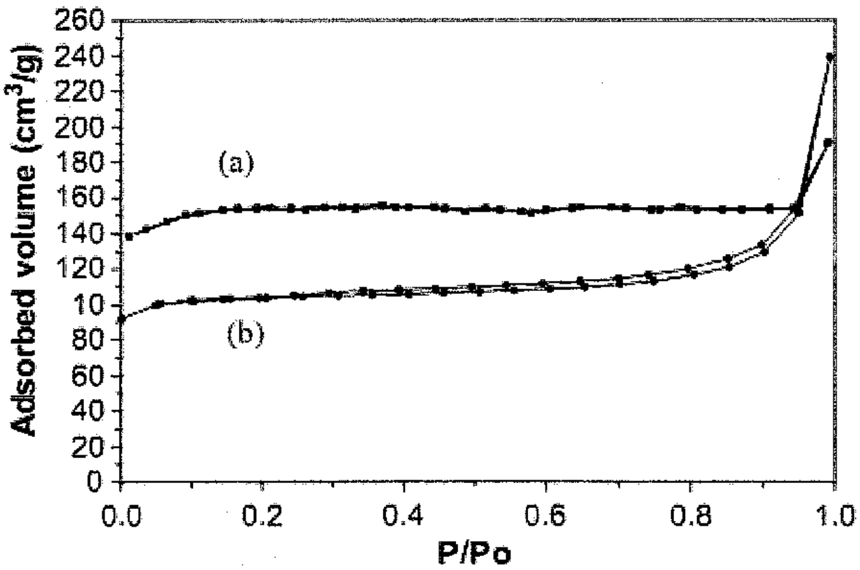


Figure 2.4: Nitrogen adsorption–desorption isotherms for (a) pure NaY zeolite and (b) NaY zeolite: Fe oxide 3:1 composite[11].

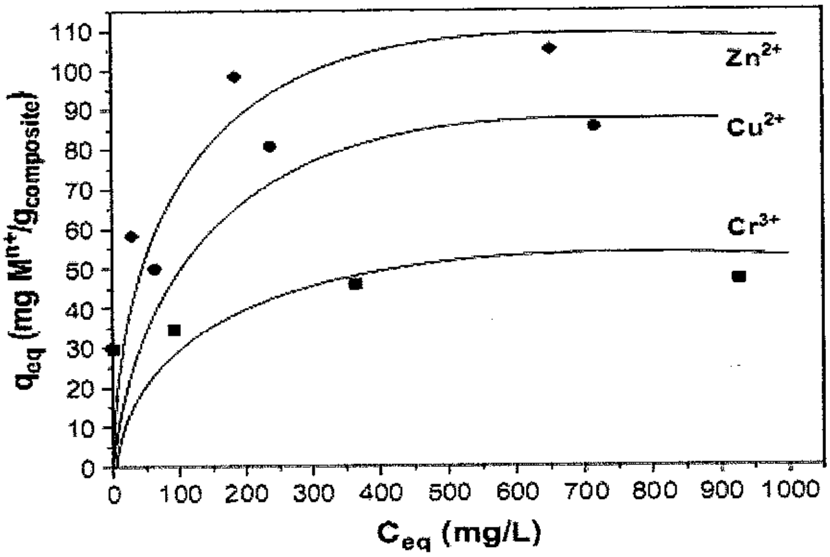


Figure 2.5: Adsorption isotherms for Cu^{2+}, Cr^{3+} and Zn^{2+} over NaY zeolite: Fe oxide 3:1 composite [11].

Nitrogen adsorption isotherms (Figure 2.5) shows for composite NaY/Fe oxide 3:1 and pure NaY zeolite surface areas of 381 (Vmicropores=0.148 cm^{3}g^{-1}) 68m2g 1(Vmicropores=0.267 cm^{3}g^{-1}), respectively. Interesting to note that, the composite showed a decrease of BET surface area and micropore volume compared to the pure NaY zeolite. The main reason for the surface area reduction in magnetic zeolite is due to the presence of 26% (w/w) of iron oxide, which has a smaller surface area compound to the pure zeolite.

While for the XRD analyses of the NaY:Fe oxide composite, Figure 2.6 showed a cubic iron oxide phase (d ¼ 2:50; 91; 1.60; 3.28A), which is likely related to the presence of maghemite with lattice parameter of ao=8.350A. For equation considering only the presence of the maghemit phase). Figure 2.6 shows the XRD analyses of the pure NaY zeolite.

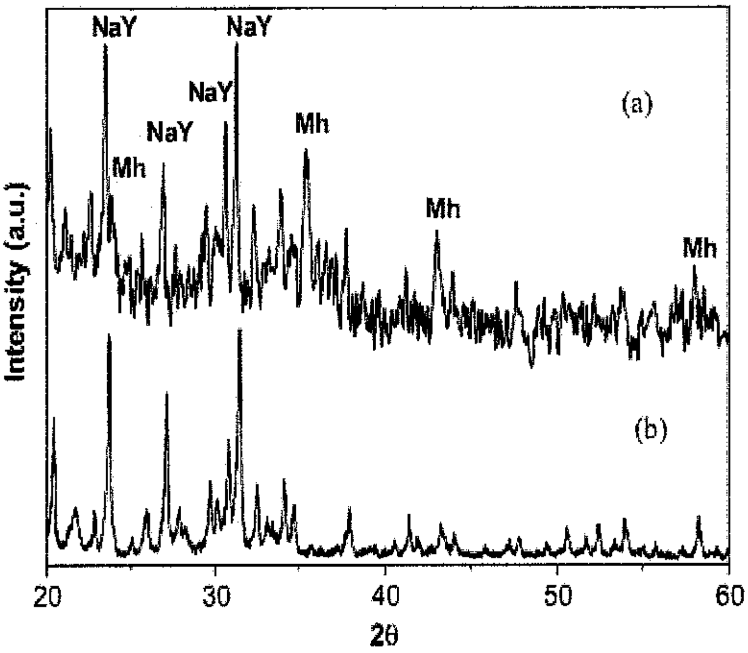


Figure 2.6: XRD for the (a) NaY Zeolite:Fe oxides 3:1 composite and (b) pure NaY. (NaY=zeolite and Mh=maghemite)[11].

2.7 Heavy metals presence in industrial wastewater.

Typically, industrial activities are the source of heavy metals penetrating the environment. The heavy metals are contained in many products and are a part of many waste substances. Utilisation of heavy metals and heavy metal compounds for various purposes in different industries results in accumulation of the heavy metals as hazardous and non-degradable wastes in the environment.

Moreover, the key sources producing the waste heavy metal are anthropogenic activities (mining and metallurgical plants), amortised products containing heavy metals, combustion of fossil fuel, traffic air pollutants, and excessive and/or incorrect application of pesticides and industrial fertilisers in agriculture.

The heavy metals that have appeared in the environment through various exposure paths and are dissolved there pose a major threat for the health of all living organisms, including people. They occur in the open nature as compounds. They are hardly present as separate elements.

Normally, these heavy contaminants get into waters through various exposure paths (for instance, by bedrock infusion or wash-away). The presence of heavy metals is always regarded as foreign and hazardous, since the heavy metals result in serious illnesses and damage to organisms. Table 2.2 shows the industrial processes that produce waste waters containing heavy metals and heavy metal compounds [12].

Table 2.2: Industrial processes and heavy metals compound in wastewater[12].

Industrial processes	**Heavy metals present**
Ore mining and ore processing	Fe, Zn, Hg, As, Se, Mn, Cu
Metallurgy	Al, Cr, Mo, Ni, Pb
Coal mining	Fe, Al, Mn, Ni, Cu, Zn
Mechanical engineering, metal surface treatment	Cr, Cu, Ni, Zn, Cd, Fe, Al
Chemical industry	Fe, Al, W, Mo, Zn, Pb, Cu, Hg
Painting, varnishing, pigmenting	Hg, Cr, Pb, Zn. Ti, Al, Ba, Sr, Mn. As, Se
Pulp and paper	Ti, Zn, Al, Ba, Sr, Cr, Se, Cu, Hg
Leather processing	Cr, Al, Fe
Textile industry	Cu, Zn, Cr, Pb, Fe
Polygraphy	Zn, Cr, Ni, Cd, Pb
Electrical engineering	Ag, Se, Ge, Mn, Ni, Pb, Cu, Hg

Absorption, adsorption and chemical sorption features of the sorbents make it possible to immobilise heavy metal cations. Efficient sorbents are substances with heavily disrupted porous surfaces. An adsorption activity of the surface is closely related to a flexure radius of local surface irregularities. The adsorption capacity is the highest in peaks and lowers in edges. It decreases on poles, reaching the lowest values in hollows.

Certain natural materials or industrial wastes with a high sorption capacity can be used to absorb heavy metal cations. All this considerably reduces heavy metal disposal costs. Cheap sorbents include: lignin, chitin, seaweed/algae, zeolites, xanates, clay, fly ash, torf, sand with sand grains covered with iron oxide, or modified cotton or wool.

2.8 Heavy metals adsorption by zeolite (FAU) from aqueous solutions.

Water—our most precious natural resource—is being threatened by a multitude of contaminants commonly the heavy metals arising mostly from industrial discharges. Waste streams containing low-to-medium level of heavy metals are often encountered in metal plating facilities, mining operations, fertilizer, chemical pharmaceutical, electronic device manufactures and many others [13]. Most of heavy metals are highly toxic and are not biodegradable; therefore they must be removed from the polluted streams in order to meet increasingly stringent environmental quality standards. Thus it is necessary to develop a technology which is not only reliable but at the same time is economical to remove all the contaminants from the industrial wastewater.

Adsorption is one of the few promising alternatives for this purpose, especially using low-cost natural sorbets such as zeolite. Generally, zeolite structure consists a three-dimensional framework of SiO_4 and AlO_4 tetrahedral [14]. The aluminum ion is small enough to occupy the position in the center of the tetrahedron of four oxygen atoms, a nd the isomorphous replacement of $Al^{3+}$for Si^{4+} raises a negative charge in the lattice. The net negative is balanced by the exchangeable cation (sodium, potassium and calcium). These cations are exchangeable with certain cations in solutions such as lead, cobalt, zinc and manganese. The fact that zeolite exchangeable ions are relatively innocuous (sodium, calcium and potassium ions) makes them particularly suitable for removing undesirable heavy metal ions from industrial effluent waters. The aim of the present investigation is to study the adsorption mechanism of Cr^{6+} ions onto synthesized FAU zeolites from wastewater.

CHAPTER 3
METHODOLOGY

3.0 METHODOLOGY

In order to produce the composite zeolites with magnetic properties, first, the zeolite gel of pure FAU need to be prepared in the laboratory. The recipe is as obtained from an article published in 1986 [16].

3.1 Pure Zeolite (FAU) Synthesis

While for FAU synthesis, an aqueous solution of Aluminum Sulfate (Al2O3= 9.89w/v %, H2SO4 = 28.52 w/v %) an aqueous solution of sodium silicate (SiO2= 15.00 w/v %, Na2O=6.06 w/v % , Al2O3 = 0.77w/v %) are simultaneously and continuously supplied at constant rate of 1 *l*/hr and 4 *l*/hr, respectively, to an overflow type reactor.

By using the laboratory stirrer, the temperature is set to 32 °C to allow the reaction to occur. The overflow slurry products from the reaction tank is subjected to solid-liquid separation using a centrifugal separator and wash with water until no SO_4^{-2} ion is detected in the washing liquid. Then, the reactor of the external heating type provided with an ordinary paddle agitator and reflux condenser at the top thereof is charged with 1926.8 g of an aqueous sodium hydroxide solution having a concentration of 33.2 % by weight, and 899 g of the homogeneous compound, corresponding to 14 % by weight of the total amount of the homogeneous compound to be used, is added and the mixture is stirred. Aging is conducted at the ambient temperature of 30 °C for 3 hours.

After completion of aging, the added homogeneous compound was completely dissolved and a transparent aqueous solution was formed. Subsequently, 2766 g of deionized water and 5521.2 g of the homogeneous compound, corresponding to 86% by weight of the total amount of the homogeneous compound, were added to transparent aqueous solution formed. The mixture is stirred and maintained at 30 °C for 1 hour. Then, the temperature of the slurry is elevated and the mixture is maintained at 95 °C by putting it into the oven for 20 hours with stirring to effect the crystallization. After crystallization complete, the product is separated from the mother liquor by filtration. Wash with water and dry at 110 °C. The expected dry product is 8 g.

Then, product characterization process will be conducted to verify the synthesized products are zeolites using TEM/SEM imaging, XRD and FTIR analyses.

3.2 MWNTs/ zeolite composites synthesises

As for the magnetic zeolite composites synthesises, mainly there are two types of zeolite composites to be produced which are the multi-walled carbon nanotubes (MWNT's)/zeolite composite and Fe_2O_3-filled multi-walled carbon nanotubes. The zeolite composites are synthesized by simply adding 1 percent of MWNTs (0.08 g) into the prepared gels of FAU prior to the synthesis.

3.3 Product Characterizations

Afterwards, samples of the synthesized zeolites will be analysed using several characterization techniques such as the Transmission Electron Microscope (TEM), Scanning Electron Microscope (SEM), X-Ray Diffraction (XRD), and Fourier Transform Infrared Spectroscopy (FTIR) to study the morphology, crystallinity, and chemical bonds respectively. The purpose of these tests is to ensure and verify that the synthesized products obtained are genuinely FAU zeolites. Consequently, Atomic Absorption Spectroscopy (AAS) test is conducted to determine and compare the absorption capacity of the zeolites.

3.4 Absorption Capacity Experiment

Zeolites are obtained from synthesized FAU zeolites produced by the previous experiment. Stock solutions of zinc and chromium are prepared in deionized water using the analytical reagent grade zinc chloride and chromium chloride. The exact concentration of metal ions is then verified by using atomic adsorption spectroscopy (AAS).

Absorption tests are conducted in 250 ml glass tubes. A zeolite sample of 1.0 g is mixed in 25 ml of chromium solutions of different initial concentrations which are 5, 1 0, and 25, 50, 75 and 100 mg/l by mechanical shaking at a speed of 250 rpm /min for a period of 24 hour. After shaking in a thermostatic system for an equilibrium period, the supernatant solution is filtered through 0.45mm micro porous membrane filter. This experiment is conducted at room temperature. The final concentrations of chromium ions at equilibrium were determined by the atomic adsorption spectroscopy (20±0.5°C) [17].

CHAPTER 4

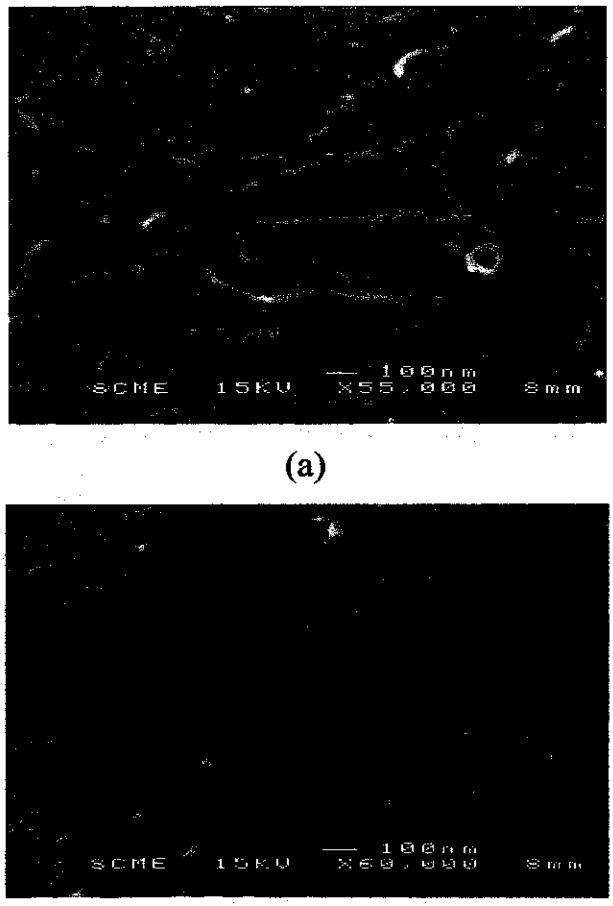
RESULT AND DISCUSSION

4.0 RESULT AND DISCUSSION

4.1 Characterization Analysis

Three samples of pure FAU zeolites, FAU/MWNT zeolites composites and FAU/ Fe_2O_3 MWNT zeolites composites have been analysed using several characterization techniques which are the TEM, SEM, XRD, and FTIR.

4.1.1 Scanning Electron Microscopy (SEM) Images.

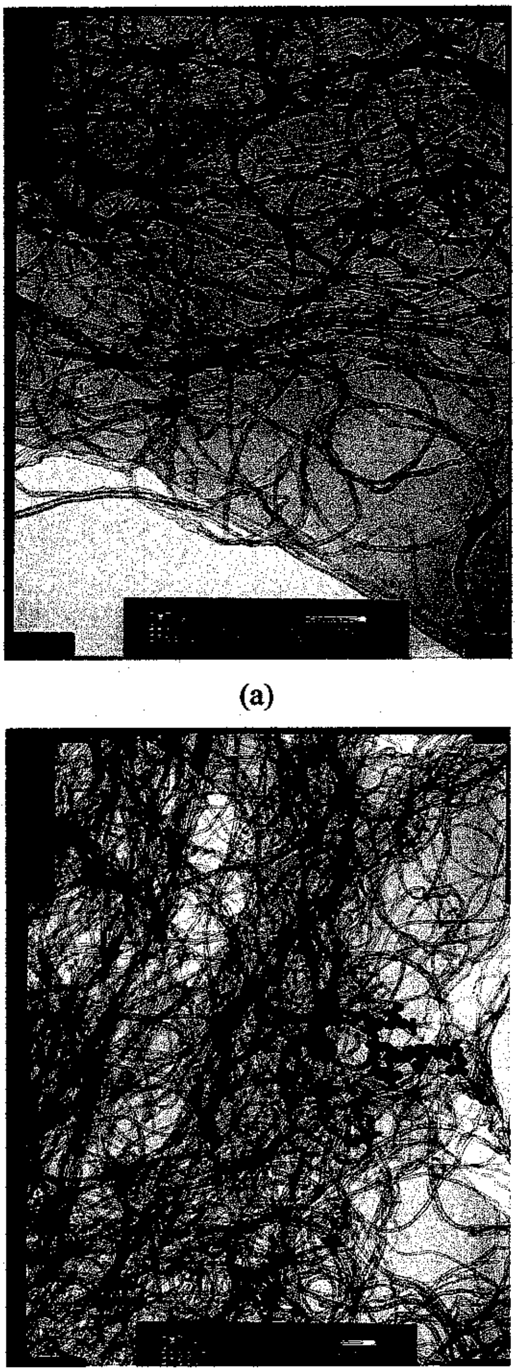


(a)

(b)

Figure 4.1 (a) and (b): SEM images of MWNTs

4.1.2 Transmission Electron Microscopy (TEM) Images.



(a)

(b)

Figure 4.2(a) and (b): TEM images of MWNTs.

The first characterization techniques were SEM and TEM analyses on MWNTs to study the morphology of these nanotubes. The results are shown in Figure 4.1(a),(b) and 4.2(a),(b) for SEM and TEM respectively. As shown in the results, the pristine p-MWNTs exhibit typical structure of nanotubes. Their diameter is ranged of 15nm to 30 nm and the clear images indicate that there are no amorphous carbon impurities inside the nanotubes.

4.1.3 XRD Patterns.

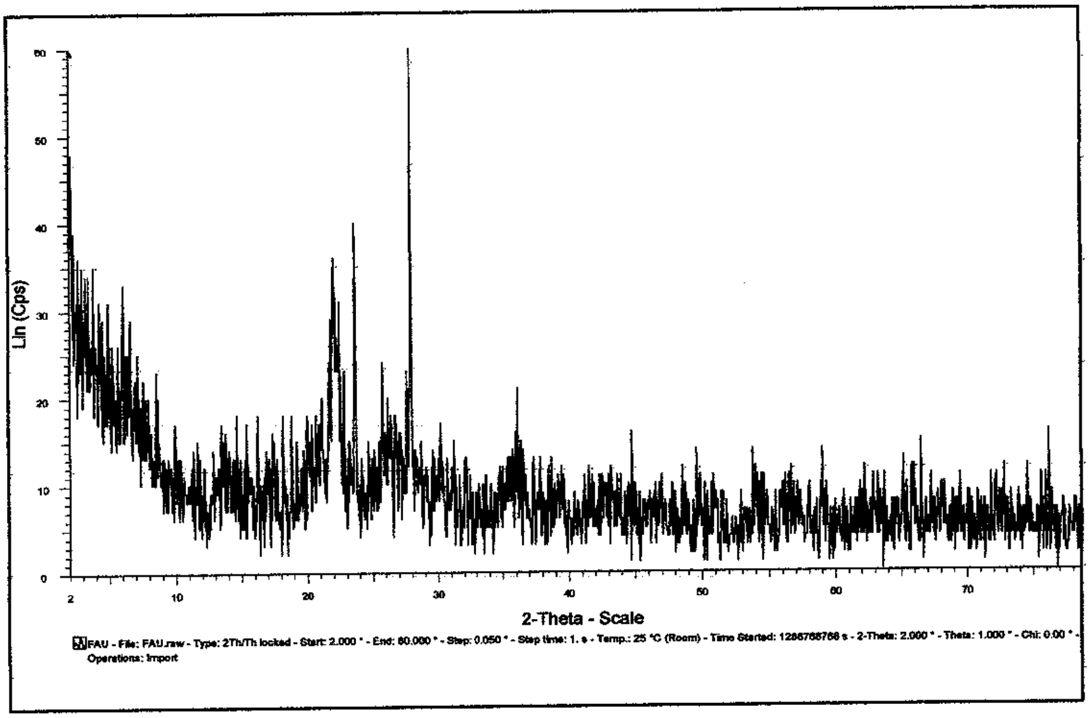


Figure 4.3 (a): XRD pattern of FAU zeolites

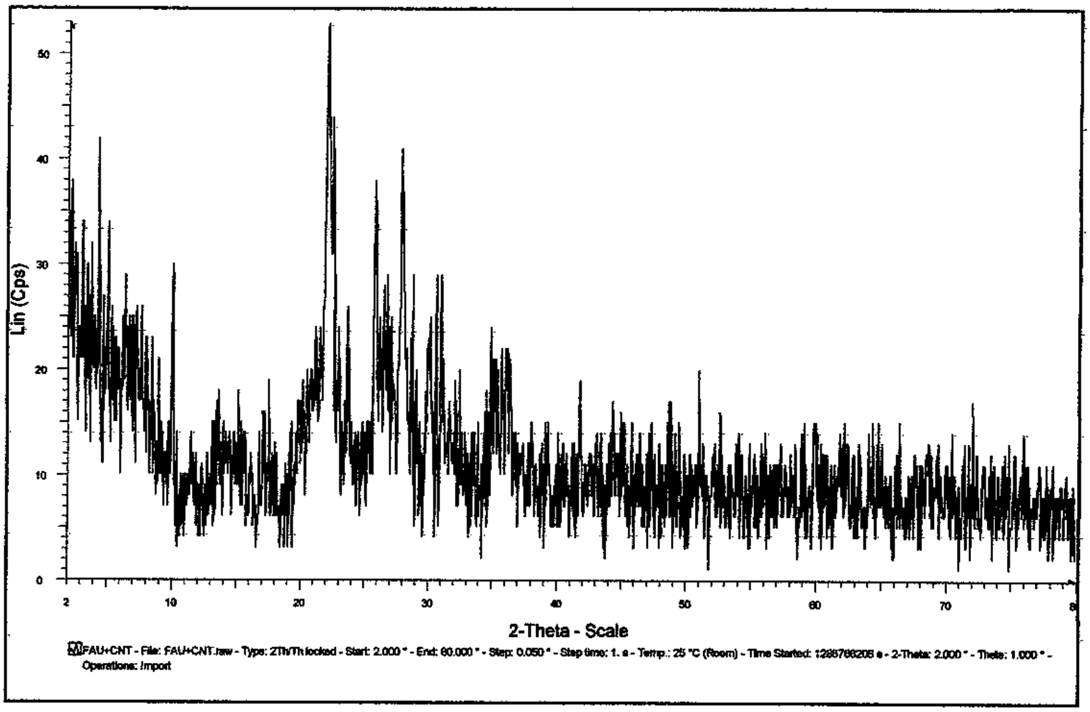


Figure 4.3 (b): XRD pattern of FAU/MWNT zeolites

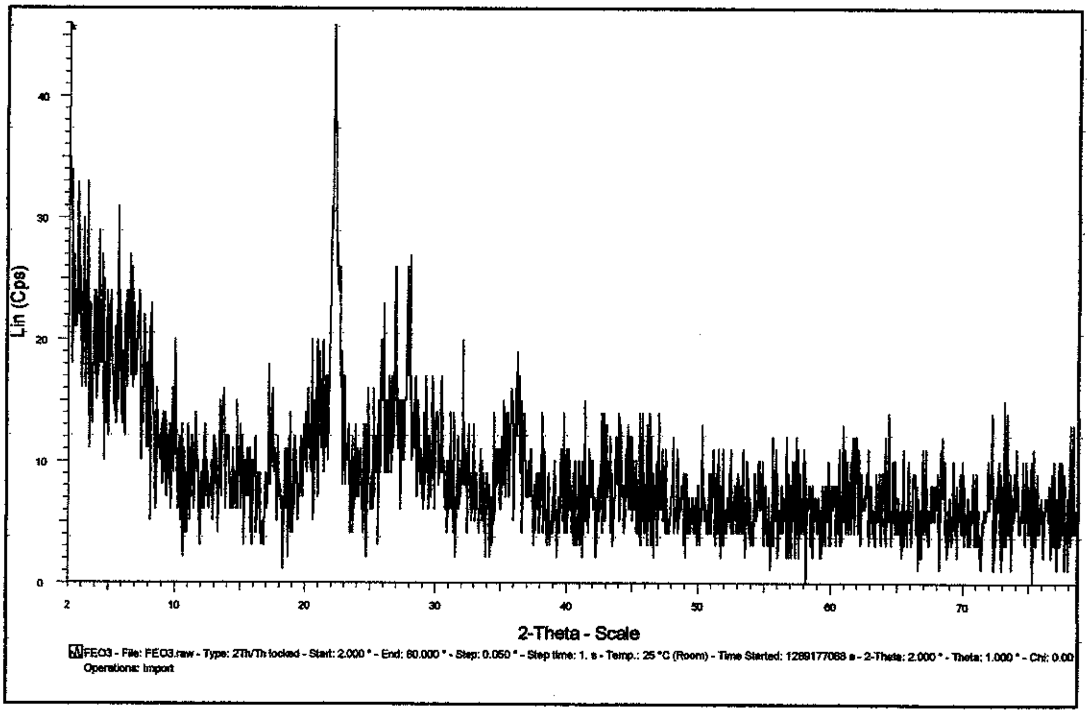


Figure 4.3 (c): XRD pattern of FAU/Fe_2O_3MWNT zeolites.

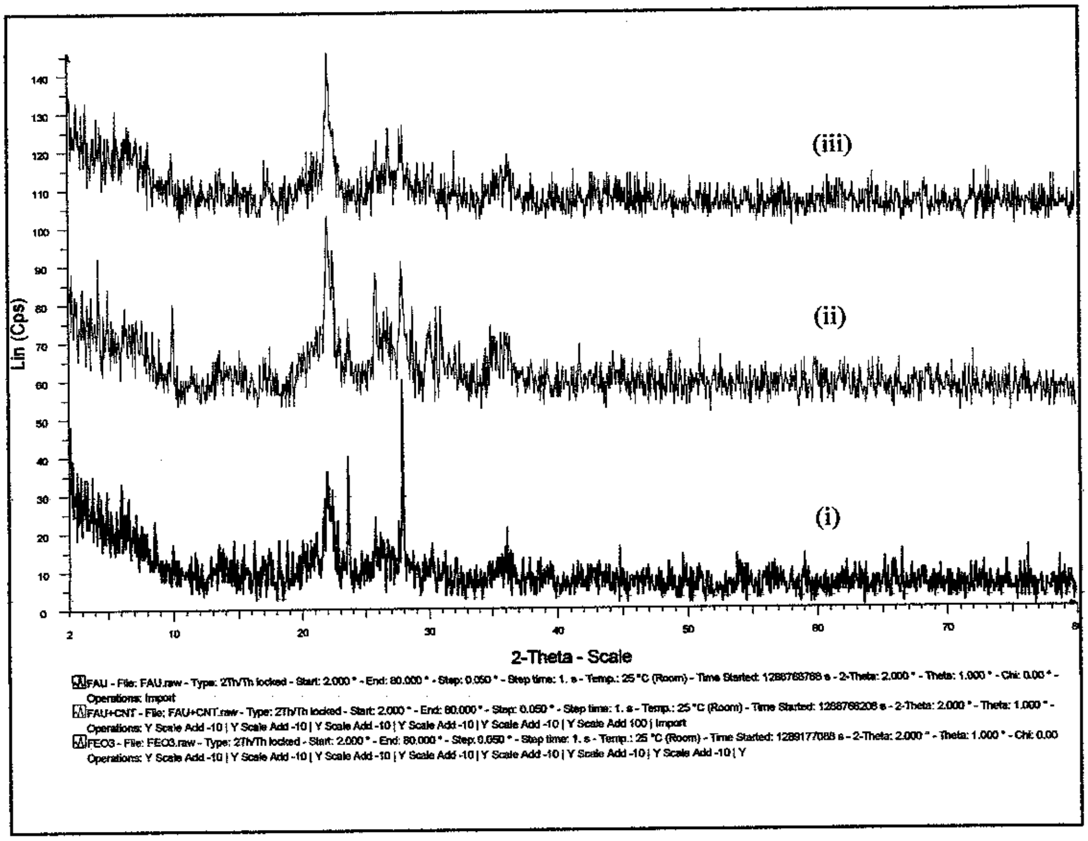


Figure 4.3 (d): Comparative XRD patterns of (i) FAU, (ii) FAU/MWNT and (iii) FAU/Fe_2O_3MWNT zeolites.

The second characterization technique was the XRD analysis. It is a technique that yields the atomic structure of materials and is based on the elastic scattering of X-rays from the electron clouds of the individual atoms in the system [18]. Powder samples of the synthesized zeolites were taken for X-ray diffraction (XRD) analysis in order to detect the presence or absence of crystalline phases. The XRD patterns of the synthesized zeolites are shown in Figure 4.3(a), (b), (c), and (d). The results show that these zeolites have perfectly character peaks. The sample has two significant characteristic peaks at 22.62° and 28.08°, which is entirely identical to the XRD pattern of typical FAU zeolites. Hence, the result indicates that the synthesized material is FAU zeolites.

4.1.4 Fourier Transform Infrared Spectroscopy (FTIR)

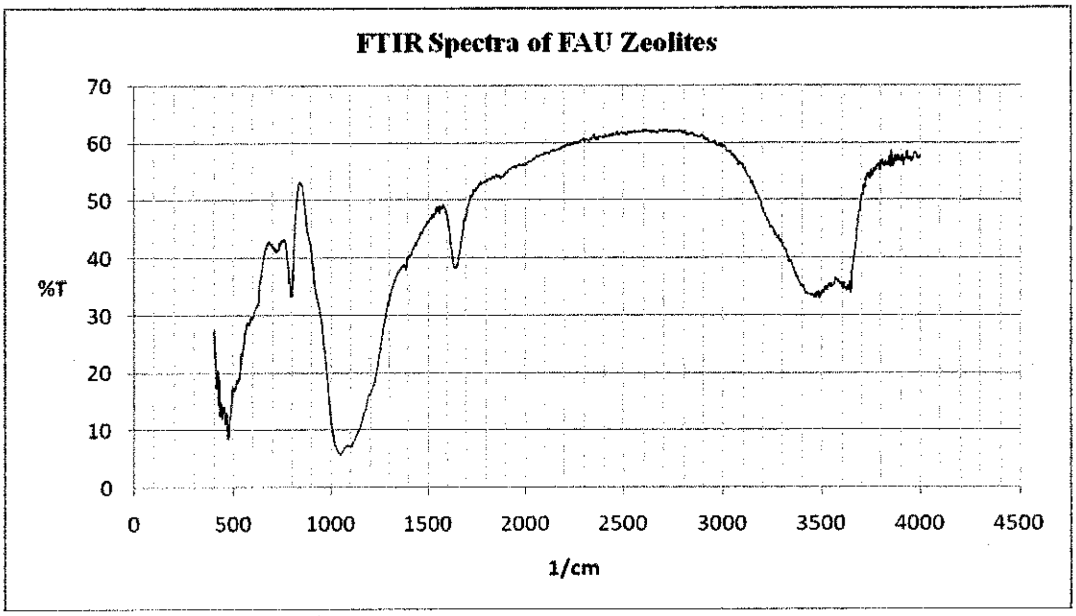


Figure 4.4(a): FTIR spectra of FAU zeolites

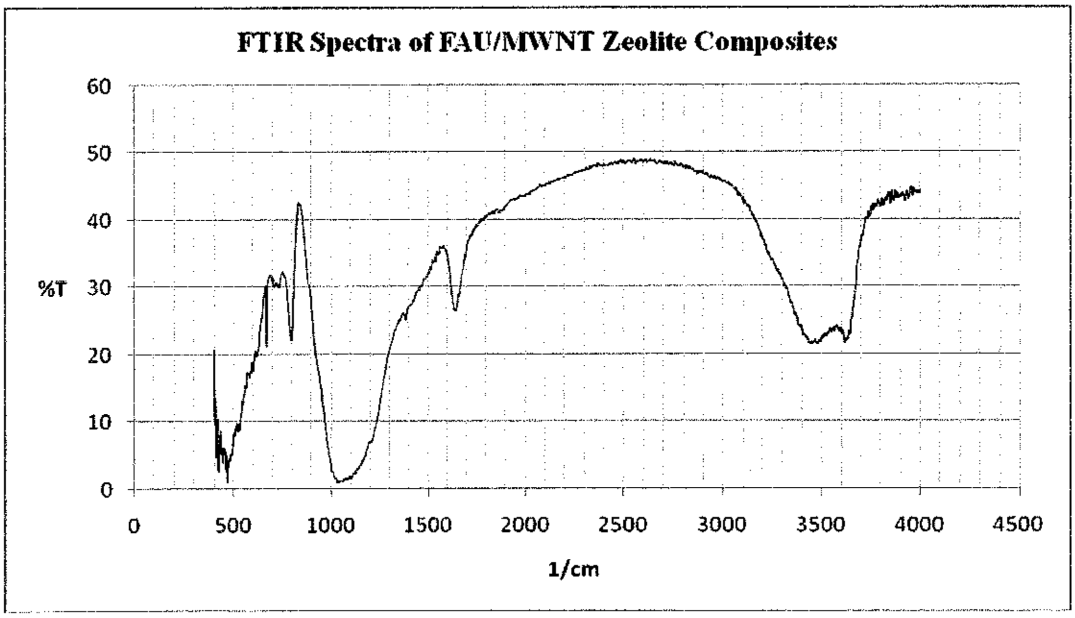


Figure 4.4(b): FTIR spectra of FAU/MWNT zeolites

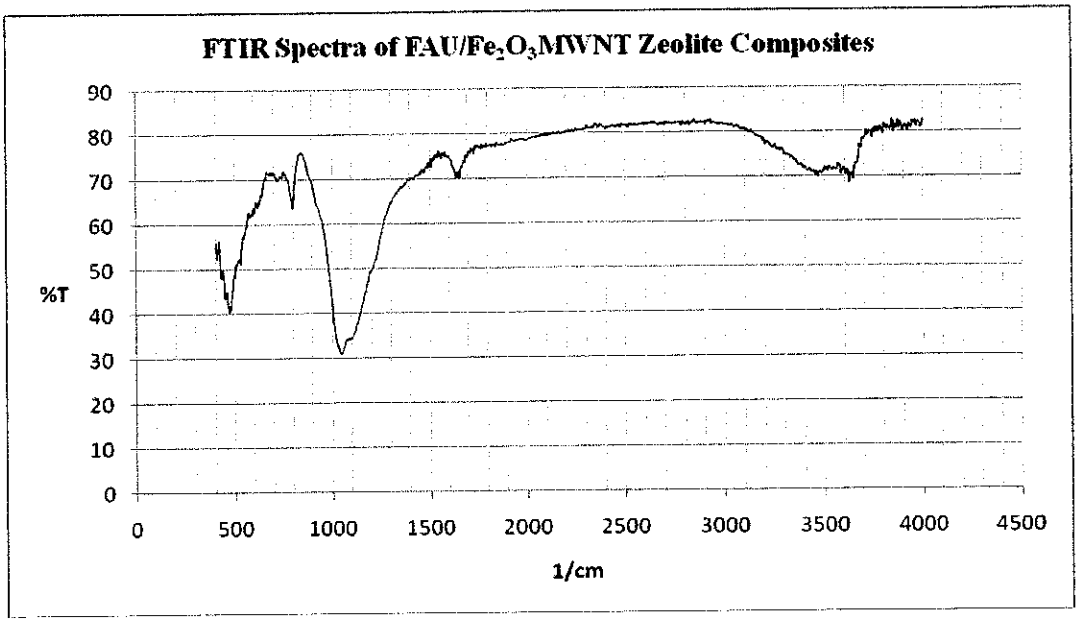


Figure 4.4(c): FTIR spectra of FAU/Fe$_2$O$_3$MWNT zeolites

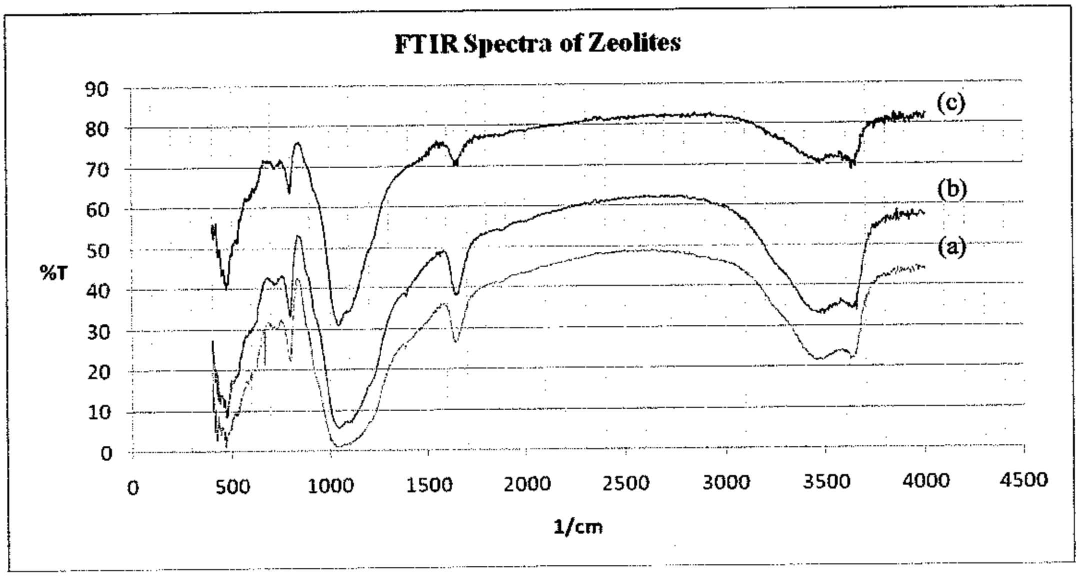


Figure 4.4(d): Comparative FTIR spectra of (a) FAU, (b) FAU/MWNT and (c) FAU/ Fe$_2$O$_3$MWNT zeolites

Finally, the samples were characterized by using FTIR. It is an invaluable tool in organic structure determination and verification involves the class of electromagnetic (EM) radiation with frequencies between 4000 and 400 cm^{-1} (wave numbers). The frequencies at which there are absorptions of IR radiation ("peaks" or "signals") can be correlated directly to bonds within the compound in question [19]. A summary of the most characteristic bands observed in the samples are presented in Table 4.1 [20], [21].

Table 4.1: Evaluation of the FT-IR spectrum

Absorption Frequency (cm^{-1})	Tentative assignments
1641	C=C stretching
1300-1100	C-C stretching
991,476	Si–O or Al–O
880	Si–O–Si tetrahedron
721	Al–O–Si octahedron
3441, 1637 and 470	O-H stretching

The FTIR spectra of FAU, FAU/MWNT and FAU/ Fe_2O_3MWNT zeolites can be seen in Figure 4.4 (a), (b), and (c). In overall, the characteristic absorption bands for both zeolites appear nearly at the same frequencies. At 991 and 476 cm^{-1} are the characteristics of vibration peak Si–O (or Al–O). While the absorption bands that appear at 880 and 721 cm^{-1} regions, belonging to characteristics of vibration peak Si–O–Si tetrahedron and Al–O–Si octahedron. Hence, all the samples exhibit the nature of FAU zeolites.

However, based on Figure 4.4(d), there are two criteria that help to distinguish these zeolites. First is, the intensity of all peaks of composite zeolites are weaker than that of pure FAU zeolite. While the second criteria is the vibration peak for composite zeolites expand at the absorption frequency range from 1050 to 1201 cm^{-1}, indicates the existence of C-C bonds of MWNT inside the composite zeolites. Also, in the region of 2250 to 3250 cm^{-1}, the intensity is the lowest for FAU/Fe_2O_3 MWNT. This suggests the existence of Fe^{3+} iron in the zeolites. Last but not least, the absorption bands at 3441, 1637 and 470 cm^{-1} appearing in the synthesis process is the character peaks of hydrate water in solid phase. Therefore in the crystallizing process, the sample firstly forms aluminosilicates gel and then transforms into zeolites.

4.2 Atomic Adsorption Spectroscopy (AAS) Analysis.

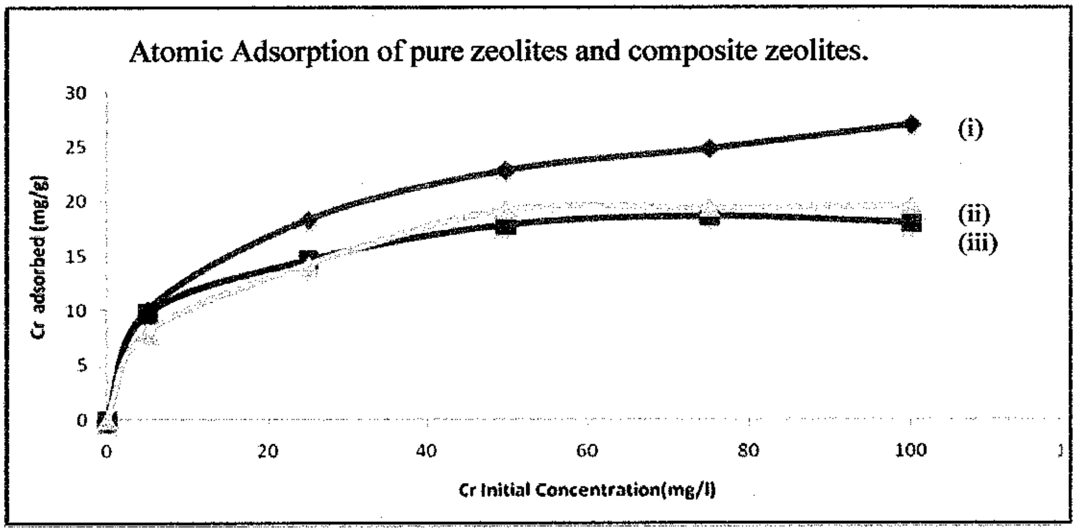


Figure 4.5: AAS of Cr $^{3+}$ over (i) pure zeolites (FAU) and composite zeolites; (ii) FAU/MWNTs and (iii) FAU/ Fe_2O_3MWNTs).

After the samples had been successfully characterized, adsorption experiment using AAS was conducted. The final concentration of metal ions was then verified by using atomic adsorption spectroscopy (AAS). Figure 4.5 shows the AAS result of Cr $^{3+}$ absorption over pure zeolites (FAU) and composite zeolites (FAU/MWNTs and FAU/ Fe_2O_3 MWNTs). The adsorption capacity of FAU shown has similar result as to previous work which is around 30 mgCr $^{3+}$ /g zeolite. On the other hand, the absorption capacity of both the composite are somewhat lower than that of FAU mainly because adding MWNT reduces slightly the surface area and micropore volume. The main reason for the surface area reduction in composite zeolite is due to the presence of 1% (w/w) of MWNT inside the crystal structure of zeolites.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

6.0 CONCLUSION

This project proposes a new approach to produce zeolites with magnetic properties of metal-filled multi-walled carbon nanotubes (MWNT's)/zeolite composites, so that it could be readily separated and recovered from complex multiphase systems by application of external magnetic field. Pure zeolites (FAU) and composite zeolites (FAU/MWNT and FAU/Fe_2O_3 MWNT) were synthesized and characterized using four characterization techniques which are TEM, SEM, XRD, and FTIR. All techniques conducted have successfully verified that the synthesized products are genuinely FAU zeolites and also managed to highlight some differences between the zeolites due to the existence of MWNTs and Fe_2O_3 in zeolite composites.

However, from atomic adsorption spectroscopy (AAS) analysis, the zeolite composites showed lower absorption capacities of Cr^{3+} in aqueous solution than that of pure zeolite, which are about 25 percent (%) reduction of the total absorption capacity. Nevertheless, in comparison to the magnetic zeolite made of iron oxide (Fe_2O_3) /zeolite in previous study, it shows larger absorption reduction due to the presence of 26% (w/w) of iron oxide in the composite crystalline structure. Hence, due to the advantages of neutral and micro-size attributes of the nanotubes, it can be concluded that the absorption features of zeolites can be combined in a composite of FAU/ Fe_2O_3 MWNT to produce better magnetic adsorbents in the future. The preparation is simple and does not require any special chemical or procedure. Recommendations for future include studying the effect of pH and ratio of pure zeolite/MWNTs to their adsorption characteristics, the effect of competing ions ,kinetic studies, and last but not least, the regeneration of the sorbents and disposal of the recovered metal salts.

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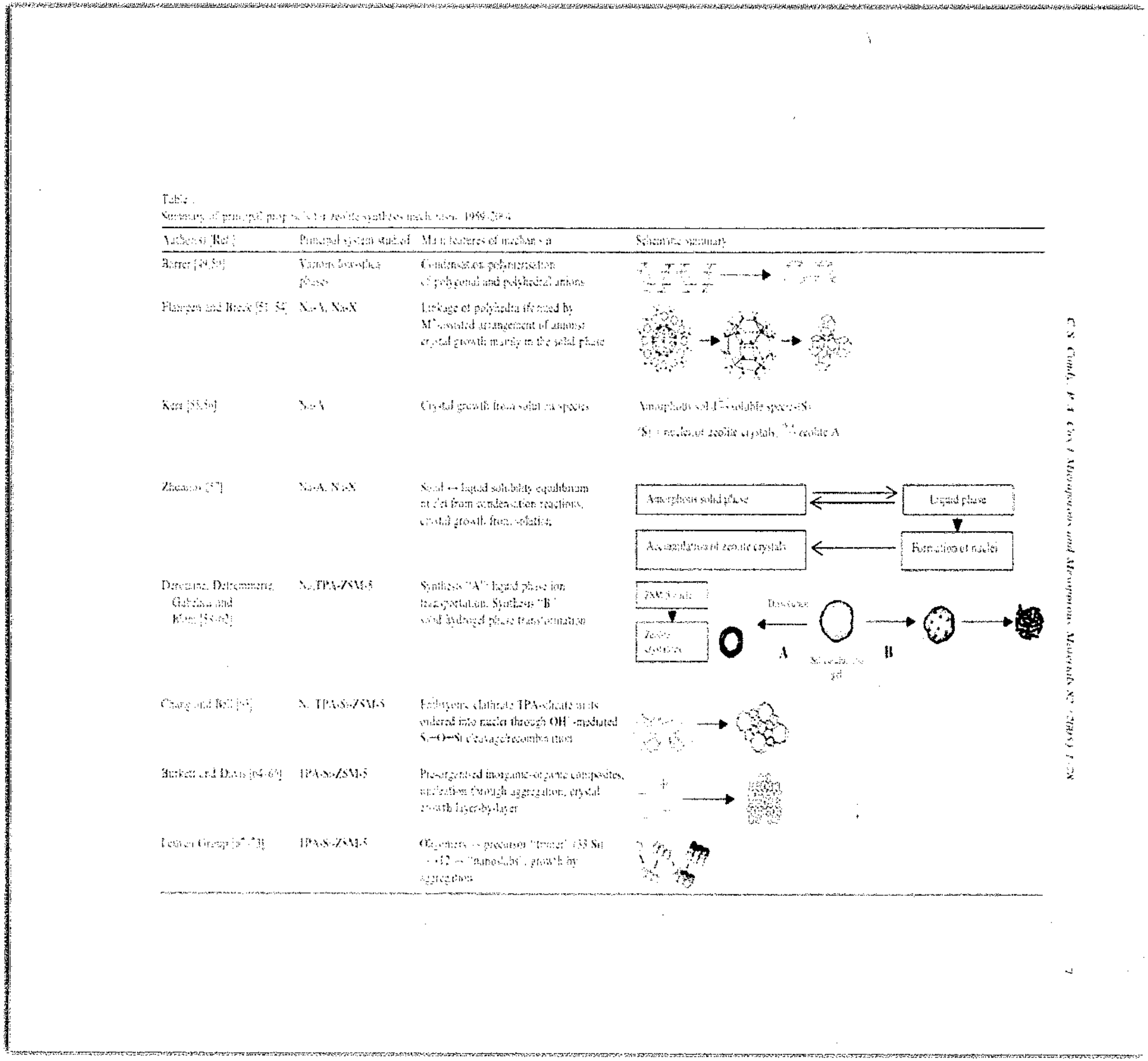
APPENDIX



C.S. Cundy, P.A. Cox / Microporous and Mesoporous Materials 82 (2005) 1–78

Table 1
Summary of principal proposals for zeolite synthesis mechanism, 1959–2004

Author(s) [Ref.]	Principal system studied	Main features of mechanism	Schematic summary
Barrer [49,50]	Various low-silica phases	Condensation polymerisation of polygonal and polyhedral anions	
Flanigen and Breck [51–54]	Na-A, Na-X	Linkage of polyhedra effected by M⁺-ordered arrangement of anions; crystal growth mainly in the solid phase	
Kerr [55,56]	Na-A	Crystal growth from solution species	Amorphous solid ⇌ soluble species (S) (S) + nuclei or zeolite crystals → zeolite A
Zhdanov [57]	Na-A, Na-X	Solid ↔ liquid solubility equilibrium set up from condensation reactions; crystal growth from solution	Amorphous solid phase Liquid phase Formation of nuclei Accumulation of zeolite crystals
Derouane, Detremmerie, Gabelica and Blom [58–62]	Na,TPA-ZSM-5	Synthesis "A": liquid phase ion transportation. Synthesis "B": solid hydrogel phase transformation	ZSM-5 nuclei Zeolite crystals Dissolution A B
Chang and Bell [63]	Na,TPA-Si-ZSM-5	Embryonic clathrate TPA-silicate units ordered into nuclei through OH⁻-mediated Si–O–Si cleavage/recombination	
Burkett and Davis [64–69]	TPA-Si-ZSM-5	Pre-organized inorganic–organic composites, nucleation through aggregation, crystal growth layer-by-layer	
Leuven Group [70–73]	TPA-Si-ZSM-5	Oligomers → precursor "trimer" (33 Si) → 12 → "nanoslabs", growth by aggregation	

7