TREATMENT OF WASTEWATER CONTAINING COBALT (Co-59) AND STRONTIUM (Sr-89) AS A MODEL TO REMOVE RADIOACTIVE Co-60 AND Sr-90 USING HIERARCHICAL STRUCTURES INCORPORATING ZEOLITES

A Thesis Submitted to the University of Manchester for the Degree of Doctor of Philosophy in the Faculty of Engineering and Physical Sciences

2013

(Environmental Engineering and Sustainable Technology)

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<th>Description</th>
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<tbody>
<tr>
<td>AC</td>
<td>Activated Carbon</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer, Emmett and Teller</td>
</tr>
<tr>
<td>CEC</td>
<td>Cation Exchange Capacity</td>
</tr>
<tr>
<td>Cel-ZA</td>
<td>Celatom-Zeolite A</td>
</tr>
<tr>
<td>Cel-ZY</td>
<td>Celatom-Zeolite Y</td>
</tr>
<tr>
<td>CRT</td>
<td>Cathode Ray Tube</td>
</tr>
<tr>
<td>DLS</td>
<td>Dynamic Lighting Scattering</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>EDAX</td>
<td>Energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>FAU</td>
<td>Faujasite - Zeolite Y</td>
</tr>
<tr>
<td>GOIC</td>
<td>Gulf Organization for Industrial Consulting</td>
</tr>
<tr>
<td>g</td>
<td>Gram</td>
</tr>
<tr>
<td>HLW</td>
<td>High Level Waste</td>
</tr>
<tr>
<td>I&lt;sub&gt;rel&lt;/sub&gt;</td>
<td>Relative intensity of the peaks</td>
</tr>
<tr>
<td>ICP</td>
<td>Inductive Couple Plasma</td>
</tr>
<tr>
<td>IPC</td>
<td>Iraqi Palm Tree Leafs Carbon</td>
</tr>
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<td>IPA</td>
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<td>IP</td>
<td>Iraqi Palm Tree Leafs</td>
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<td>IPClinp</td>
<td>Iraqi Palm Tree Leafs-Clinoptilolite composite</td>
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<tr>
<td>IUPAC</td>
<td>The International Union of Pure and Applied Chemistry</td>
</tr>
<tr>
<td>KeV</td>
<td>Kilo Electron Volt</td>
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<tr>
<td>L</td>
<td>Letter</td>
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<tr>
<td>mg.L&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>milligram of element per Letter</td>
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<tr>
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<td>Material Testing Reactor</td>
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<tr>
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<td>Magnification</td>
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<tr>
<td>MPa</td>
<td>Mega Pascal</td>
</tr>
<tr>
<td>NRC</td>
<td>Nuclear Regulatory Commission</td>
</tr>
<tr>
<td>NORMs</td>
<td>Naturally occurring radioactivity materials</td>
</tr>
<tr>
<td>PZA</td>
<td>Pure Zeolite A</td>
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<td>PClinp</td>
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<tr>
<td>PCS</td>
<td>Photon Correlation Spectroscopy</td>
</tr>
<tr>
<td>PCRE</td>
<td>Permissible Concentrations of Radioactivity in Effluent</td>
</tr>
<tr>
<td>RO</td>
<td>Reveres Osmoses</td>
</tr>
<tr>
<td>RWTS</td>
<td>Rad Waste Treatment Station</td>
</tr>
<tr>
<td>SBUs</td>
<td>Secondary Building Units</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SSA</td>
<td>A specific surface area</td>
</tr>
<tr>
<td>TS</td>
<td>Tamarind Stones</td>
</tr>
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<td>TSC</td>
<td>Tamarind Stones Carbon</td>
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<td>TSY</td>
<td>Tamarind Stones-Zeolite Y composite</td>
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<tr>
<td>TSClinp</td>
<td>Tamarind Stones-Clinoptilolite composite</td>
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<tr>
<td>TGA</td>
<td>Thermal Gravimetric Analyses</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TBq</td>
<td>Tera Becquerel</td>
</tr>
<tr>
<td>Who</td>
<td>World health organisation</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffractometer Powder</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>Å</td>
<td>Angstrom</td>
</tr>
<tr>
<td>$a_m$</td>
<td>The cross-sectional area occupied by each nitrogen molecule (0.162 nm$^2$)</td>
</tr>
<tr>
<td>$K_L$</td>
<td>The sorption equilibrium constant (L.mg$^{-1}$)</td>
</tr>
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<td>$q_e$</td>
<td>Adsorption Capacity (mg.g$^{-1}$)</td>
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<td>$W_p$</td>
<td>The weight of the product</td>
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<td>$X$</td>
<td>Displacement of a particle along a given axis</td>
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<tr>
<td>$\lambda$</td>
<td>Wavelength</td>
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ABSTRACT

The majority of this work in subject of reduces the pollution problems using zeolites. Zeolites were used in this study to remove two types of non-radioactive ions (Cobalt-59 and Strontium-89) from wastewater. This was designed to model the use of ion-exchange technique to remove radioactive Co-60 and Sr-90 from low level wastewater from Al-Tuwaitha site. Al-Tuwaitha site is a nuclear research in Iraq was used for radio-medical and radio-chemical purposes before 1990.

In this study, hierarchical microporous/macroporous structures were developed to overcome the diffusivity problem using zeolite. Diatomite and carbon were used to prepare the composite adsorbents by incorporating them with three types of zeolites (A, Y and clinoptilolite). From the XRD, SEM and EDAX measurement it was confirmed that successfully prepared of Iraqi palm tree leafs-Clinoptilolite (IPClinp) and Tamarind stones-Clinoptilolite (TSClinp) composites were obtained in this study as there is no evidence in literature of this being carried out before.

The carbons were prepared successfully through the Pyrolysis method for 2h at 900°C in an inert atmosphere from two types of raw waste plant materials of Iraqi Palm Tree leaves (IP) and Tamarind stones (TS). For both types of carbons, the SEM images show organised porosities in different shapes. A third material used as a zeolite scaffold was diatomite (Celatom FW-14) a readily available natural material (dead algae).

A hydrothermal treatment was used to build the hierarchical structure of zeolite onto carbon and diatomite materials, the scaffolds were seeded with nano-zeolite crystals prior to the treatment and thereafter mixed with the zeolite gel composition mixture in a stainless steel autoclave. Zeolite seeds were prepared using ball mill method to reduce the particle size of the commercial zeolite to sub-micron range for each type of zeolite. The surface area, morphology, element compositions and structure for each type of zeolite and composite material were characterised using BET method, SEM, EDAX and XRD. The amounts of each type of zeolite on the carbon composites were determined using TGA while that of the diatomite composite was determined by gravimetric analysis.

The results show that each type of zeolite was successfully deposited and uniformly organised onto the surface of all support materials. All pure zeolites and composite materials were successfully tested to remove Co²⁺ and Sr²⁺ ions from aqueous solutions. It was found that the composite materials had higher ability to remove both ions relative to the pure zeolites. This increase is attributed to the deposition of zeolite (microporous) onto the macroporous structure (carbon and diatomite) which increased the flow accessibility within zeolite in the hierarchical structured composites. Comparison of the removal between the two metal ions indicates that all of the materials had higher uptake for Sr²⁺ than Co²⁺ ions. The highest adsorption capacities were realised with Tamarind Stone–ZeoliteA (TSA) in the order 120mg.g⁻¹ and 290mg.g⁻¹ for Co²⁺ and Sr²⁺ ions, respectively. The effect of the experimental variables shows increasing uptake with increasing pH and initial ion concentrations while it decreased with increasing the solution temperature.

The Co²⁺ loaded composites was subjected to vitrification process at 1200°C for 2h. The encapsulated composites were leached for 90 and 120 days and no significant Co²⁺ was recorded in the leached solution.

The results show that the composite materials can be used effectively to remove the radioactive ion of Co-60 and Sr-90 as they display the same chemical behaviour as Co-59 and Sr-89 studied in this work.
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DECLARATION
No portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

Salam Khudhair Al-Nasri
Manchester, 2013

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DEDICATION AND ACKNOWLEDGMENTS

DEDICATION

I dedicate this work to my father who passed away during the period of completion of my studies. For as long as it encourages me and urging me to end this work in the best possible way. I hope to be a happy modest gift to his spirit in the eternal paradise.

As well as to dedicate this work to my compassionate mother that always supports me in her prayer. I specially dedicate this work to my wife Sabah Ali, whose has been with me in all circumstances as a companion and a source of encouragement. I also do not forget my lovely children Asal, Abdullah and Sama who were divine source of inspiration for me to accomplish this work. As well as, I dedicate this work to all my brothers, my family and friends who have communicated with me and been my source encouragement.

ACKNOWLEDGMENTS

Praise be to Allah, Lord of all Creations

I would like to express my sincere gratitude and appreciation to my supervisor, Dr. Stuart S.M for his guidance, advice, effort and cooperation throughout the stages of this study and to make the accomplishment of this study possible.

Great thanks are to my family for their support and prayers. Many thanks are due to the staff and colleagues of the school of chemical engineering and analytical science for their assistance in this study. Furthermore, I would like to thank my friends Dr. Andrew K. Campen, Edidiong, Sama Al-Jubouri, Fadil, Petrus, and John Riley (man city) for their contribution in making my research a success. Appreciation goes to Patrick I. Hill and Desmond J. Doocey for their invaluable help and for all the people whom supported, encouraged and helped me a great deal. Finally, I wish to thank Iraqi Ministry of Higher Education and Scientific Research for sponsored me to finish my PhD in Manchester University.

Salam K. Al-Nasri

2013
CHAPTER ONE

1. INTRODUCTION

The combination of rapid population growth and intensive industrial development all over the world has led to a range of environmental issues. Researchers are constantly looking for new ways to solve these environmental problems, and as a result, many operational processes, including effluent disposal, have been modified and implemented.

Heavy industrial activities and energy production generate a significant volume of waste. For example, some heavy metal waste from electro plating manufacture [1] and radioactive waste released from nuclear power plants[2], have been known to contaminate the surrounding environment and surface water.

Currently, there are several techniques employed to purify liquids that have been contaminated with heavy metals and/or radionuclides. These techniques include chemical precipitation, coagulation/flocculation, ion exchange/solvent extraction, cementation, complexation, electro-chemical operations, biological operations, adsorption, evaporation, filtration, and membrane processes. Moreover, these techniques aim to ensure that the liquids (wastewater) released into the environment are decontaminated and allow the conditioning of waste concentrates for disposal[3, 4].

Radioactive wastes originate from a variety of sources such as the nuclear industry, nuclear research centres, the generation of electricity by nuclear fission, accidents in nuclear power plants, and various uses of radioactive material for human requirements such as medicine. Radioactive waste may also result from the processing of raw materials that contain Naturally Occurring Radionuclides Materials (NORMs), such as in fertilizer manufacture [5].

In addition, in the petroleum industry radioactivity arises in the liquid and solid phases of sludge and scale. Production can involve elements such as uranium, thorium, radium and other natural radionuclides (NORMs). The presence of these radionuclides in the work environment can lead to an increase in the exposure of maintenance personnel.
1.2 TREATMENT OF INDUSTRIAL WASTEWATER

A variety of treatment options for the removal of heavy metals from aqueous solutions of wastewater can be implemented as stated in the previous section. Researchers have experimented with various treatment techniques for the removal of organic and inorganic pollutants from wastewater. Some of these techniques have been found to have limited viability due to the high costs involved and the tendency to produce secondary wastes [6].

The key methods that have been employed for the removal of inorganic matter from industrial, domestic and other wastewater, and their disadvantages, are described in the following section [7, 8].

1.2.1 Evaporation

This is the process of bringing wastewater to its boiling point until pure water vaporizes. Evaporation process has been used as an alternative technique in the process of wastewater treatment. This approach has the ability to concentrate and/or remove the heavy metals, salts and wide range of hazardous materials from aqueous solutions. Furthermore, as a treatment, this method can be used to concentrate liquid waste.

The advantage of this method is considered to be the high quality of the product. Reusable distillate is a very important factor where water conservation is a priority.

The disadvantages of this method are: [9]

- Relatively high capital costs
- Relatively high operational costs (particularly for vacuum systems)
- Energy intensive distillation processes
- Constraints on the size range of these systems imposed by the economics of distillation
- A requirement for highly trained personnel to operate and maintain complex systems

1.2.2 Dialysis

Dialysis is the separation of solutes via a process of diffusion through semi permeable membranes such as dialysis tubing, Figure 1.2. It is most useful in terms of improving the purity of solutions to be reused in manufacturing processes. It allows a micro-solute
from a given feed solution to permeate the membrane, while preventing macro-solutes in the same solution to pass through to the receiving solution. During the treatment process, the micro-solutes permeate the membrane more quickly than the macro-solutes. The pore size of the membranes is engaged to take into account the magnitude of the macro-solutes in order to block them (the typical range is between 2 to 6 nm). One of the most important applications of this technique is in the reduction of the toxic metabolism end products in the purification of blood for the treatment of kidney failure. Consequently the application of dialysis techniques has been confined to the pharmaceutical and medical sectors in which the intention is limited to the purification, rather than the recuperation of a product [10].

Figure 1.1 Dialysis tube shows that the small molecules in water can be separated by placing the mixture in a vessel of a semi-permeable membrane [10]

1.2.3 Electro-dialysis

Electro-dialysis is an electrochemical process in which, semi-permeable ion selective membranes are used to separate anions and cations (heavy metals). The ionic components migrate towards either cathode or anode electrodes due to the introduction of an electrical potential between the two electrodes. The ions move from the low concentration solutions (dilute) to the high concentration solution (permeated). Figure 1.3 shows that, under the influence of an electric field, the negative charge carriers in the salt solution move towards the positively charged anode side, while the positive charge carriers move in the direction of cathode side.
This process is used widely in the production of table salt from seawater, the production of drinking water from brackish water, and in the treatment of boiler-feed water. The ability to remove nitrogen (nitrate, ammonium) from drinking water, the desalination of organic substances, and the concentration of salts, acids and bases, are considered the principal advantages of this technique. The creation of metal hydroxide leading to the blocking of the membrane is considered its main disadvantage [9].

**Figure 1. 2 Shows the electro-dialyses process [11]**

### 1.2.4 Ion Exchange

Ion exchange is an effective method for the removal of undesirable cations and anions, such as heavy metals, from wastewaters. It works by exchanging them through a reversible reaction with ions already contained in the exchange media (resin, zeolites and other) such as sodium and hydrogen. These ions are held by electrostatic forces in the exchange media.

Due to its efficiency, ion exchange is widely employed in the process of removing dissolved solids from wastewater. It is suitable for use in the field of water purification. For example, many chemical materials (acidic and bases types) are ionized in solutions during metal finishing processes, these ions can then be removed effectively via ion exchange.
The principal benefits of the ion exchange technique are: [9]

- It can economically separate dilute concentrations of ionic species from solutions.
- The process can consistently provide high purity water under a broad range of conditions.
- The resins used for separation are durable in severe chemical environments.

The disadvantages of this method are:

- Metallic fouling (from Fe, Mn, Cu, etc) of the ion exchange media
- Fouling due to oil, grease, silt, clay, colloidal silica, organic materials, and microbes. (Although the selection of an appropriate cleaning regime can restore much of the lost efficiency) [12]
- The reduction of operational efficiency due to the presence of free acid
- Relatively high operational costs
- Diffusion

1.2.5 Algae

In order to grow, algae need to absorb a number of different types of elements. Nine minor elements (iron, manganese, silicon, zinc, copper, cobalt, molybdenum, boron and vanadium) and seven major elements (carbon, nitrogen, phosphorus, sulphur, potassium, magnesium and calcium) are considered essential for optimum growth. This quality makes algae useful for removing minerals from wastewaters and means that it is also able to serve as an indicator of water pollution. Brown algae are a good biosorbent of heavy metals [13].

The main advantages of bio-sorption are [14]:

- Low cost
- High efficiency
- Minimisation of chemical and/or biological sludge
- No requirement for additional nutrients
- Regeneration of biosorbent
- Potential for metal recovery
While, the major disadvantages of biosorption techniques are [7]:

- The long duration of the process
- The necessity to create an optimal favourable environment
- The maintenance.

1.2.6 Reverse Osmosis

Reverse osmosis (RO) is a technique for the removal of heavy metals via a semi-permeable membrane. Sufficient pressure is required to force a concentrated fluid through a semi-permeable membrane. In conventional osmosis solution moves from a low concentration solution into high concentration solution through a semi-permeable membrane until equilibrium is reached. Reverse osmosis can be achieved through the application of an external pressure that is greater than the osmotic differential pressure of both solutions. This pressure separates the dissolved salt in the solution from the water, Figure 1.4. This phenomenon is called “reverse osmosis”[15].

RO membranes are similar to dialyzer membranes, but the pores are smaller. Due to its small pores, solutes containing ions such as Na\(^+\) or organic matters are unable to pass through the RO membrane. As with the dialyzers, there are three different types of RO membrane: cellulosic, synthetic, and thin composite. Chlorine, chloramines, pH, disinfectants, and bacteria are all capable of destroying the membrane. Chemicals are more harmful to synthetic membranes and bacteria more detrimental to cellulosic membranes, while composite membranes are generally more resistant. By using this technique, the salinity of brackish water is reduced by more than 92% and seawater by more than 98.5%. The main drawback of this technique is its high cost [16].
1.3 ZEOLITE AND ADSORBENTS FOR ION EXCHANGE

Activated carbon is considered to be the most effective of media for the adsorption of undesirable ions because of its large surface area; with typical ranges between 500 and up to 2000 m$^2$.g$^{-1}$ [18]. It is used as a powder or granular due to its possession of certain properties such as a meso and/or micro porous structure, which gives it an extensive surface area and thus the capacity for the adsorption of undesirable ions and molecules.

The global agricultural industry produces vast quantities of organic waste matter. For example, date production in Iraq and the Kingdom of Saudi Arabia (KSA) generates large amounts of palm tree stones and branches. Current statistics show that there are at least 15 million palm trees in Saudi Arabia [19, 20] and more than 30 million date palms in Iraq [21]. Similarly, olive production in Jordan [22] and Spain [23] produces huge amounts of olive stones. Although organic plant waste is considered to be a problem, in theory this type of waste could be converted into significant volumes of carbon.

Current scientific literature highlights numerous instances of activated carbon production from a variety of different organic waste sources. Examples include almond shells, beech wood shells, rice husk [24], coconuts shells [25], and palm tree branches [20]. For example one of the investment opportunities supported by the Gulf Organization for Industrial Consulting (GOIC) is the manufacture of activated carbon from local waste materials such as olive and date stones [26].
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INTRODUCTION

Adsorbent types can be evaluated as adsorption materials in terms of the quality of pore structure, particle size, total surface area, and the void space between particles. The high cost of the production and regeneration processes is considered to be the main drawback from industries seeking more efficient and economic adsorbent materials[27, 28]. The cost and efficiency of purification techniques have become increasingly important in implementing industrial waste disposal [3, 29].

Zeolites are one of the few microporous materials that have proved effective in environmental remediation due to their ion exchange properties [30]. Ebenezer reported that the use of zeolites for the decontamination of low and intermediate level radioactive liquid waste and as carriers for the removal of undesirable radionuclides in nuclear reactors, has attracted widespread attention[31].

Moreover, zeolites are considered one of the most important ion exchange media due to the existence of abundant mineral deposits (large quantities of zeolites have been discovered in over 50 countries worldwide) [32, 33].

Zeolites are a family of alumino-silicate frameworks with very open three dimensional structures, Figure 1.1. They are primarily comprised of [SiO$_4$]$^{-4}$ and [AlO$_4$]$^{-5}$. They have pores of uniform size from 0.3 to 0.13 nm [33]. Zeolites have cavities and channels within their structures which form about 50% of their total volume. Cations such as Na$^+$, K$^+$, Ca$^{2+}$ and Mg$^{2+}$ and water molecules can be held within zeolite frameworks through these cavities and channels. These cations have a high degree of mobility and the ability to exchange with each other [30, 34]. However, due to the intra-crystalline diffusivity problems of zeolite powder, zeolites are of limited efficacy for high volume processes[35].
The ability to produce a hierarchical structure of composite micro/macro porosity, in which a layer of zeolite crystals is deposited on the surface of a macroporous support, maximises the exposed crystallite surface area and allows the use of zeolite powders without problems of diffusion and/or back pressure during the process. The ideal macroporous backbone is one that is abundant, inexpensive and chemically robust.

Microscopic algae called diatomite which are found in every aquatic environment and two specific types of carbons (more details about diatomite and carbons in the next Chapter) were examined in this study to provide a hierarchical structure and a surface capable of holding and attaching the particle seeds of three different types of zeolite (A,Y and clinoptilolite) in an efficient and economical way [37].

Two plant waste samples, Tamarind Stones (TS) and Iraqi Palm Tree leaf’s (IP), were prepared through carbonisation and separately combined with the three types of zeolites. The organic waste samples were chosen due to their surface areas and their availability. The creation of these new composite materials (diatomite /zeolite and carbon/zeolite) structures has been suggested as a method to overcome the diffusivity problem of the fine particle size zeolite [38].
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1.4 RATIONALE

The Al-Twaiitha nuclear research centre site in Iraq, Figure 1.5, has a number of generators of low and intermediate level radioactive waste. These originate from radiochemical, and radiomedical activities as well as the reactors. Since 1991, all of these activities have ceased and most of the facilities have been completely destroyed. The Rad Waste Treatment Station (RWTS) has large storage tanks which are used to store the radioactive liquid wastes generated from these activities. In addition, three big reactors: the 14-Tammuze reactor, the Material testing reactor (MTR), and the MTR (swimming pool reactor type) have also been destroyed [39]. The buildings which housed those reactors are contaminated. Specialist emergency and health physics teams removed the radioactive wastewaters which were found inside the reactor pools. The reactors were filled with freshwater to minimise the exposure rate to the environment. As a result of the previous operation of the reactors, number of radionuclides, such as Co-60, Sr-90 and Cs-137, were released to the ground water [40, 41]. In this study, hierarchical structures materials (diatoms and carbon) were used, with three types of zeolites (A, Y and clinoptilolite), and applied to remove two types of non-radioactive ions (Co-59 and Sr-89) from aqueous water, using the ion-exchange technique to model extract ion of Co-60 and Sr-90.

Zeolites will be the main media for this research because they possess unique properties. They are thermally stable, can survive both acidic and basic conditions, can be used with membranes, and have the capacity to exchange with other cations.

The economical production of these materials is enhanced by the use of ‘ground’ zeolite seeds as precursors for the zeolite films. The use of colloidal nano-seeds is the accepted methodology for the growth of hierarchical structures. However, these are complex and costly to synthesise. In this study we have taken ready-made, commercially available zeolites and ball-milled them to produce the seeds to synthesise the hierarchical structures.

A variety of A, Y and clinoptilolite type zeolites will be prepared. These will be employed to remove Sr$^{2+}$ and Co$^{2+}$ from wastewater by studying several variables in batch mode. Some of the variables to be investigated include temperature, pH, and materials, in order to identify the optimum ion exchange conditions and structure.
1.5 PROJECT OBJECTIVES
The objectives of this study are as follows:

1- Reduce the pollution problem in case of wastewater using zeolites.

2- Develop and characterize a hierarchical zeolite structure to overcome the diffusivity problems of using zeolites as an ion exchanger media for the removal of metals from synthesis wastewater.

3- The project will model the behaviour of the low and intermediate waste of the radio-nuclides of Sr-90 and Co-60 by removing the non-radioactive Co-59 and Sr-89 from aqueous solution which displays the same chemical behaviour (they occupy the same position in the periodic table and have the same number of proton but different number of neutrons).

4- Moreover, the project will aim to selectively and optimally remove the metal ions using the composite materials under different conditions (different pH, Temperature and initial ion concentrations).

5- An overview of the most important properties of synthesis pure zeolite and synthesised composite materials, to give information that can assist in choice of materials for practical purposes especially radionuclides.
The structure of this thesis is organised onto seven chapters as follows,

Chapter 1 described the pollution problem in case of wastewater and the objective of this study.

Chapter 2 described a review of the zeolite structures and the relevance literature to this study, especially on synthetic zeolites and its applications. This chapter also covered different topics including the support materials which can be used to zeolite particles to build the hierarchical structure materials, radioactive wastewater pollution and its sources and water treatment by adsorption method.

Chapter 3 discusses the characterization techniques which were used to investigate the product of the synthesised zeolite and its composites with carbon and diatomite materials.

Chapter 4 described the incorporated two types of zeolites (zeolite A and zeolite Y) onto diatomite surface. Two methods were used to prepare zeolite seeds, first the hydrothermal treatment method and second the ball mill method.

Chapter 5 discussed the preparation of carbon from two raw plant waste materials (Iraqi Palm Tree leaves and Tamarind stones) and them incorporated with three types of zeolites (zeolite A and zeolite Y and clinoptilolite). This chapter described the novelty of this study by incorporated clinoptilolite onto the carbon of Iraqi Palm Tree leaves and Tamarind stones surface.

Chapter 6 discussed the application of zeolites in wastewater treatment using batch method to investigate the ion exchange ability of the synthesised zeolites and the composite materials to remove $\text{Co}^{2+}$ and $\text{Sr}^{2+}$ from aqueous solutions.

Chapter 7 conclusions that can be drawn from this work, suggestions and recommendations for further works were covered in this chapter.
CHAPTER TWO

POROUS MATERIAL

2.1 ZEOLITES BACKGROUND

Zeolites as shown in Figure 2.1 are microporous minerals commonly used as commercial adsorbents. Zeolites were first discovered as a new group of minerals in 1756 by Swedish mineralogist, Axel Fredrik Cronstedt, when he noticed that natural minerals lost water when heated. He named the new group of materials “Zeolite” (from the Greek ξεω(zeo (boil)) and λιθος (litha (stone)), because they formed a frothy mass when heated in a blowpipe [34, 43].

Natural zeolites have been formed through the reaction between volcanic glass and saline water at temperatures between 27°C and 550 °C over periods varying from 55 years to 50,000 years. Natural zeolites contain other minerals such as quartz (SiO₂), SO₄⁻ and amorphous glass, as well as other types of zeolite. There are over 50 types of natural zeolite possessing a variety of physical and chemical properties. There is variation within, as well between, the different categories of zeolite. The source of the zeolite and the environmental conditions in place during its formation have a significant bearing on these variations [44].

In 1777 the phenomenon of adsorption on charcoal was reported by Fontana. In 1840 Damour found that zeolite crystals could be reversibly dehydrated without damage or alteration to their transparency or morphology.
The first use of X-ray diffraction for identification in mineral synthesis was documented by Leonard in 1927. In 1930, Taylor and Pauling identified the first zeolite structures. In 1932 the term "molecular sieve" was coined by Mc Bain to describe porous solid materials that act as sieves on a molecular scale [43]. The first synthesis process for zeolites was carried out in 1948 by Barrer. This was followed between 1949 and 1954 by the discovery of zeolite A, X and Y by R.M. Milton and D.W. Breck. In 1954 synthetic zeolites were commercialized for the first time as a class of materials for industrial separation and purification processes, after which their sphere of application expanded rapidly [45]. Zeolites (Hydroaluminosilicates) have been shown to have valuable properties as ion exchange media. They are present in large deposits across a wide geographical area including over 50 countries [46, 47].

2.2 STRUCTURE OF ZEOLITE

Zeolites are tetrahedral aluminosilicate frameworks with very open three dimensional structures [34]. They have pores of uniform size ranging from 0.3 to 0.13nm in diameter, compared to approximately 5.0nm for those of a typical silica and 10.5nm for activated carbon [34, 48]. Zeolites are primarily composed from [SiO$_4$]$^4$ and [AlO$_4$]$^5$. As shown in Figure 2.2a, the tetrahedral structures consist of a central core silicon or aluminium atom which is linked together by oxygen atoms Figure 2.2b. These linked structures are composed of infinite lattices made of crystalline materials. Cavities and channels within the zeolite structures form approximately 50% of their total volume, while water represents 10 to 12% of their weight.

These cavities and channels allow cations and water molecules to be held within the zeolite frameworks. Cations such as Na$^+$, K$^+$, Ca$^{2+}$ and Mg$^{2+}$ are also contained within the zeolites structure. These cations have a high degree of mobility and ability to exchange with other cations [34, 44, 48].
Figure 2.2 Shows (a-) Tetrahedral units (SiO₄ or AlO₄) are the basic structural component of zeolite networks and (b-) TO₄ tetrahedral where α is the O-T-O bond angle and β is the T-O-T bond angle (T=Si or Al) [49].

Breck [50] proposes a typology which classifies zeolites according to their structure. Based on their Secondary Building Unit (SBU), zeolites can be divided into seven categories which encompass all the known zeolite frameworks. Merier posited the conceptual framework of the Secondary Building Units [34], which are shown in Figure 2.3. The seven groups are listed in Table 2.1.

In the conceptual SBUs, Al or Si is located at each intersection. Oxygen atoms are not shown. The oxygen atoms are located close to the mid-points of the lines connecting each pair of T (T=Al or Si) atoms, Figure 2.4. As a result of electrostatic forces, it is not possible to create an Al-O-Al bond [51].

Due to this process of linking, zeolite natrolite and scolecite have tectosilicate frameworks that can only be composed from 4-1 SBUs. The 5-1 SBUs form the basis of the ferieite, epistilllite and morganite zeolite frameworks. Likewise 4-4-1 SBUs are the building blocks for stilbite and heulandite. Occasionally more than one SBU can be joined together. In this way the analacime topology can be completed from 4- and 6-ring units, linde zeolite A from 4-, 6- and 8- rings and cubic units; faujasite from 4- 6- and 8- rings together with the 6-6 hexagonal prisms, and paulingsite and phillipsite from 4- and 8- rings.
The general chemical formula for a zeolite chemical structure is:

\[ \text{M}_{2n}\text{O}: \text{Al}_2\text{O}_3: x\text{SiO}_2: y\text{H}_2\text{O} \]

\( M \) represents any alkali or alkaline earth cation, \( n \) the valence of the cation, \( x \geq 2 \) and \( y \) is the water in the zeolites with structural cations \( \text{Si}, \text{Al} \) and \( \text{Fe}^{3+} \) and exchangeable cations \( \text{K}^+, \text{Na}^+ \) and \( \text{Ca}^{2+} \)[52].

The important properties of zeolite structures are [53]:

1- The crystal structure of many types of zeolites maintains stability when dehydrated. Dehydration generally occurs at temperatures under 400°C.

2- The capacity for the adsorption of gases, vapour and other molecules and the possession of a large void volume, low density and uniform sized molecular channels.

3- Cation exchange and catalytic properties.

Table 2.1 Zeolite Structure classified by their Secondary Building Unit (SBU)[54].

<table>
<thead>
<tr>
<th>Group</th>
<th>Secondary Building Units</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>S4R</td>
<td>Analcime, Harmotome</td>
</tr>
<tr>
<td>2</td>
<td>S6R</td>
<td>Levynite, Sodalite Hydrate</td>
</tr>
<tr>
<td>3</td>
<td>D4R</td>
<td>Zeolite A, ZK-4</td>
</tr>
<tr>
<td>4</td>
<td>D6R</td>
<td>Faujasite, Zeolite X</td>
</tr>
<tr>
<td>5</td>
<td>4-1</td>
<td>Natrolite, Mesolite</td>
</tr>
<tr>
<td>6</td>
<td>5-1</td>
<td>Mordenite, Bikitaite</td>
</tr>
<tr>
<td>7</td>
<td>4-4-1</td>
<td>Heulandite, Clinoptilolite</td>
</tr>
</tbody>
</table>
Figure 2.3 The Secondary Building Units (SBUs) of zeolite structures [34].

Figure 2.4 Sodalite cages can form different frame work structure of zeolites by linking the secondary building block [55].
Figure 2.5 shows the distribution of pore size in the particles. The International Union of Pure and Applied Chemistry (IUPAC), classifies pores according to the size of their diameters (dp) [56]

1- Micropores: dp ≤ 2nm, such as zeolite.
2- Mesopores: 2nm < dp ≤ 50 nm, such as SiO₂.
3- Macropores: dp > 50 nm, such as activated carbon and clays.

Activated carbon in powder and granular form is widely used as an effective adsorbent medium for the removal of heavy metals from contaminated effluent waters. However, it is less economic than zeolite due to the high cost of its production and of the regeneration of spent carbon [57].

![Figure 2.5 Schematic representation pore size distributions.](image-url)
2.3 NATURAL AND SYNTHETIC ZEOLITES

Natural zeolites are less expensive than their synthetic counterparts, so are increasingly used in various fields such as agriculture, agronomy and wastewater treatment and pollution control. However, although natural zeolites are available in large quantities, they offer an imperfect range of atomic structures and properties in terms of the shape and size of the cavities and channels. Synthetic zeolites possess enhanced properties such as a greater uniformity in the shape and size of cavities and channels.

Zeolites can be manufactured via a number of different methods, one of which is through mixing sodium, aluminium and silicate chemicals with water to prepare an aluminosilicate gel. The type and structure of zeolite product can be affected by any modifications made during the synthesis process. For example, altering the Si source or Si concentration in the gel composition will generate a different type of zeolite. Therefore, it is essential to have a comprehensive understanding about this process as it ultimately determines the application appropriate to each type of zeolite.

The composition of the starting materials or precursors and other factors such as the reaction conditions (temperature, acidity (pH) and pressure) play a crucial role in determining the resulting zeolite products. The precursors affect the properties of resulting material in terms of structure, particle size, size distribution and morphology [34].

Typical precursor materials (starting materials) are (see Table 2.2) [34]:

1- Oxide source: SiO₂, Al₂O₃.
2- Template (organic cations): Ammonia, alkyl ammonium salt, alcohol and others.
3- Mineralising base: Like NaOH, NH₄OH.
4- Solvent.

The template ions are usually an organic cation (an organic template) and are added to the reaction mixture during the synthesis. They play a vital role in the formation of a large number of zeolite materials by creating voids after calcinations. Hydroxide concentration [OH⁻] serves as a robust mineralizing agent which functions to transport
reactants from the solid phase into the solution. Generally, an increase of the hydroxide concentration \([\text{OH}^-]\) in the reaction mixture causes the formation of zeolites with a lower Si/Al ratio, due to the retention of the Si-species in the solution [58].

Table 2. Shows the chemical sources and their functions in zeolite synthesis [43, 59].

<table>
<thead>
<tr>
<th>No.</th>
<th>Chemical sources</th>
<th>Functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SiO$_2$</td>
<td>Primary building unit(s) of the framework.</td>
</tr>
<tr>
<td>2</td>
<td>AlO$_2$</td>
<td>Origin of framework</td>
</tr>
<tr>
<td>3</td>
<td>OH</td>
<td>Mineralisers, guest molecule</td>
</tr>
<tr>
<td>4</td>
<td>Alkali Cation, template</td>
<td>Counter-ion of AlO$_2^-$, guest molecule.</td>
</tr>
<tr>
<td>5</td>
<td>Water</td>
<td>Solvent, guest molecule</td>
</tr>
</tbody>
</table>

Non-homogeneity and the presence of impurities are considered the principal arguments against the use of natural zeolites for many advanced applications. Synthesized zeolites with properties such high levels of purity and larger cavities have been developed to meet industry requirements. These unique properties have led to synthesis zeolites being widely employed as ion exchange media in industrial applications [57].

Usually reaction mixtures are prepared from suitable sources to obtain the requisite Si/Al ratio for zeolite framework composition. There are a number of parameters for the formation of a synthetic structure such as gel composition, chemicals used, reaction time, temperature, seeding and order of mixing [34].

Each type of zeolite is abbreviated according to its original chemical composition and/or according to the name of the zeolite or the material type e.g., FAU from the mineral faujasite, LTA from Linde Type A and MFI (Mordenite Framework Inverted) for ZSM-5 (Zeolite Socony Mobil five) [54]. The expense in the zeolite synthesis process is incurred from the cost of the commercial chemical materials such as sodium silicate, colloidal silica, sodium aluminate. To prepare zeolites, researchers have investigated cheap and readily available sources of silica and alumina. Fly ash [60-65], rice husk [66-68], and kaolin [69-77] have been used in experiments as cheap and available silica sources. Kaolinite has been discovered to be a suitable source of silica and alumina for
the production of low silica zeolites such as zeolite A, Y and X. Contamination from trace amounts of Fe, Ti, Ca, Mg, quartz and others is considered the main drawback of this product. These traces derive from ancillary minerals in the naturally occurring kaolinite [60, 78].

Synthetic zeolites can be characterized by techniques such as optical and electron microscopy, X-ray powder Diffraction (XRD) and particle size analysis. X-ray analysis is undertaken during the synthesis to confirm the correct formation of the product. Characterisation techniques are outlined in the next chapter.

The types of zeolites that are used extensively in industry were discovered between 1950 and 1970. The Si/Al ratio in their framework structures was used to place these types into three categories [79].

1- Low-silica" zeolites A and X, hydrophilic (ratio Si/Al ≤ 2)

Zeolite A and X are the most common commercial adsorbents due to their characteristics in terms of composition, pore volume and channel structure. Their surface is highly selective for water, polar and polarisable molecules which makes them useful for many applications, particularly drying and purification processes.

2- Intermediate silica" zeolites: zeolite Y, mordenite (ratio 2 < Si/Al ≤ 5).

These types of zeolites contain higher silica content than zeolite A and X. The Si/Al ratio of this type of zeolite ranges from 2.0 to ~5.0 and its morphology is similar to zeolite-X. Zeolite-Y has a greater stability in the face of acid and water vapour from steam than zeolite A and X. In addition, the composition and structure of zeolite-Y and mordenite mean that they are much sought after for catalyst applications including hydrocarbon conversion and as adsorbent medium [80].

3- High silica" zeolites: zeolite beta, ZSM-5, hydrophobic (Si/Al ratio > 5).

This type of high content silica was discovered between the late 1960's and early 1970's at the Mobil Research and Development Laboratories. Zeolite beta and ZSM-5 are two types of high silica group with Si/Al ratios from 10 to 100+. These high silica content
zeolites have more homogenous surfaces and exhibit an organophilic-hydrophobic discrimination [80].

2.4 SYNTHESIS OF ZEOLITES

Zeolite production in the laboratory began as a result of the need to replicate the qualities of the naturally formed zeolites. However, it is not possible to apply exactly the same parameters of time and the corresponding conditions required to achieve analogous zeolite products. Attempts were made by Barrer and a group under the leadership of Breck working at the Linde Corporation, to produce these types of zeolite under laboratory conditions. These attempts led to the discovery of the potential for the formation of zeolite in alkaline conditions at temperatures ranging between 100-200°C using autogenous pressures [44].

Currently, synthetic zeolites rather than natural zeolites are used for most commercial purposes due to issues of crystal purity and uniformity of particle size. Moreover, synthetic zeolites can be prepared using cheap starting materials. Batch modes are employed in their preparation using a caustic aluminate solution mixed with a caustic silicate solution. The required temperature range is between 60°C and 180°C under which crystals grow through nucleation at autogenous pressures over periods of time ranging from hours to days. An additional advantage of synthetic zeolites is their ability to be synthesised with a wide range of chemical properties, thermal stability and pore size. Zeolites produced in laboratory correspond to the majority of naturally occurring zeolites. Researchers have not simulated all the types of naturally occurring zeolite, as the complex relationship between all the parameters in zeolite synthesis and the effect of the variation of these parameters on the characteristics of the final product, are not yet fully understood [54,60]. Nevertheless, synthetic zeolites such as zeolite A, X and Y have been fabricated with characteristics that are not present in nature. Nucleation and crystallisation are considered the two principal processes during zeolite synthesis. In nucleation, a nuclei is formed from the small aggregates of the precursor materials and becomes larger with increased synthesis time, it follows the typical ‘S’ shape of zeolite crystallization curve with an induction time until the crystallinity reached a summit after sufficient time as can be seen in Figure 2.6.
Crystallisation may be described as the stage in which product crystals are formed [81]. These three steps of gel formation, nucleation and crystallisation are set out below in Eq. 1:

\[
\text{NaOH (aq) + NaAl(OH)}_4\text{(aq) + Na}_2\text{SiO}_3\text{(aq)} \\
\downarrow \text{gel formation} \\
\text{Na}_a\text{(AlO}_2)_b\text{(SiO}_2)_c\cdot\text{NaOH.H}_2\text{O} \\
\downarrow \text{crystallisation} \\
\text{Na}_x\text{([AlO}_2]_x\text{[SiO}_2]_y\text{).mH}_2\text{O + solution} \quad \text{Eq. 1}
\]

In general, the major reagents required for the synthesis of zeolites through hydrothermal treatment can be summarised as: a silica source, an alumina source, a mineralizing agent (alkali hydroxide) and sometimes organic molecules as structure-directing agents and solvent (water).

![Figure 2.6](image.png)

**Figure 2.6** The effect of temperature on the crystallization of zeolite ZSM-5 [82, 83].
2.5 EFFECT OF SOME SYNTHESIS PARAMETERS ON ZEOLITE CRYSTALLISATION

The main factors that can effect zeolite formation are:

1- Composition of the reaction mixture

All zeolite types have a specific range of molar composition that can be expressed as the trio of elements that are used in its composition: Na$_2$O, Al$_2$O$_3$ and SiO$_2$. Some types of zeolite can be manufactured within the narrow Si/Al ratio range such as zeolite A, X and Y. Other types of zeolite, which contain a high silicon content, such as ZSM-5, can be produced in a wide range of Si/Al ratios from 7 to infinity. Increasing the Si/Al ratio in the synthesis of zeolites strongly influences the physical characteristics of the product [84].

2- Temperature and time

In the process of zeolite synthesis, temperature plays an important role in the configuration of the nucleation. Crystallisation rate of zeolites working under Ostwald law of successive phase transformation i.e. the crystallization start by the thermodynamically least favourable phase then swap with time to more stable phases[85]. It has been observed that crystal growth rates correlate directly with an increase in temperature.

Parameters employed in the crystallization process must be modified to ensure the production of desired phase of zeolite, and to reduce the time in order to ensure the achievement of the highest purity of zeolite [58].

3- Nature of reactants and their pre-treatment

Synthesis of zeolites can be carried out using organic and inorganic precursors. It has been shown that the inorganic materials are more hydroxylated, while organic precursors can be integrated more easily with the metals within the structure [86].

4- pH of the medium

The process of zeolitization is conducted in the presence of an amorphous gel phase in an alkaline medium (pH>10). OH$^-$ modifies the nucleation time through the transport of silicates from the solid phase to solution [86].
5- Seeding

This common technique is employed to decrease the induction time and to encourage the growth of zeolite crystals to get certain zeolite phases by promoting the crystallisation. It is also used to drive the reaction to generate the required product. This process can be managed by adding certain amounts of zeolite to the synthesis mixture [87].

6- Other Factors

There are several other factors which may affect the process of zeolite synthesis. For example, small amounts of salt may affect the final products. In addition, impurities can also encourage heterogeneous nucleation. The material of the vessels employed can also have an impact. For example, the tiny seeds tend to stick to glass vessels which make them hard to remove. All the equipment which is used to synthesize zeolite must be cleaned thoroughly before the process commences. The method of stirring, the order in which the reactants are added, and the nature of the reaction vessel can also affect the product [34, 88].
2.6 OVERVIEW OF SOME IMPORTANT ZEOLITE STRUCTURES

2.6.1 Zeolite A (LTA)

Zeolite-A (Linde Type A), first synthesized by Miydn in 1959 [35], is commonly used as a molecular sieve and as an ion exchange material. Figure 2.7, shows the structure of zeolite-A [89] as an arrangement of β-cage [4^6] pseudo-cornershare via 4-4 structure units showing α-cage [4^{12}_6^{8}_8] at the centre of the unit cell. It has a Si/Al ratio equal to 1 [32]. Zeolite-A has a three-dimensional pore system and molecules can diffuse in all three directions in space by moving across the 8-ring windows that connect the cavities. The windows have a free diameter and it has specific pore size ranging between 0.35-0.45 nm [86]. Zeolite-A has a void volume fraction of 0.47 and thermally decomposes at 700°C [90]. Zeolite-A is one of the most important industrial zeolites because its ability to use in detergent to remove Ca^{2+} and Mg^{2+} from the hardness water. Hundreds of thousands of tons of it are produced every year[43].

![Figure 2.7](image)

Figure 2.7 The structure of zeolite type A as a network of β-cages, (teal) which interconnect via 4-4 units (maroon). The centre of each β-cage resides on the corner of the crystallographic cell) [91, 92].
2.6.2 Zeolites X and Y (Faujasite)

Zeolites X and Y, Figure 2.8 have the same type of framework structure (FAU) with large pores and a double 6-ring. However, they differ in terms of their framework properties and composition. Zeolite-X has a Si/Al ratio≈1.25 and zeolite Y ≈1.5-2.3. Zeolite-Y presents a lower amount of aluminium and as a consequence is less hydrophilic than zeolite X and A[93].

The main use of zeolite-X is as an adsorbent and in gas drying. In addition, zeolite-X has become an important adsorbent in the separation of oxygen from air using pressure-swing adsorption. On the other hand, zeolite-Y is primarily used as a solid-acid catalyst or for ion exchange applications [59]. The pore size for both types of zeolite ranges from 0.6 to 0.8nm.

The arrangements of sodalite cages within the zeolite-Y framework are similar to that of carbon atoms in diamonds and are linked to one another by double 6-rings. This creates a supercage with four tetrahedrally-orientated 12-ring pore openings and a 3-D channel system. The void volume fraction of zeolite-Y is 0.48 and thermally decomposes at 793°C [48, 90].

![Figure 2.8 From right to left zeolite Y and X, faujasite (FAU) [59].](image-url)
2.6.3 ZSM-5 (Zeolite Socony Mobil – 5)

ZSM-5 (Zeolite Socony Mobil–5) is one of the most complex zeolite framework types known. ZSM-5 is a synthetic zeolite with 5-1 SBUs joined to another identical ring by oxygen bridges to form pentasil chains, Figure 2.9. ZSM-5 has a three-dimensional pore structure enclosed by 10 oxygen windows. It has two distinct pore systems: one consisting of zigzag channels with near-circular cross-sections and another of straight channels of elliptical shape, Figure 2.10 [94]. It has a Si/Al ratio from 7 to infinity [86]. ZSM-5 has a tetragonal crystal shape and a low aluminium content and therefore contains a relatively small number of cations. Furthermore, it has a low water content and, unlike most other zeolites, its framework exhibits hydrophobic tendencies. It has a void volume of $0.10\text{cm}^3$ per gram and pore size of $(0.54 \times 0.56)$ nm and $(0.55 \times 0.51)$ nm [40].

Due to its low water content, ZSM-5 is generally synthesised at high temperatures (up to $350^\circ\text{C}$). ZSM-5 has been used widely in different commercial processes such as a heterogeneous catalyst for hydrocarbon isomerization reactions in the petroleum industry [95].

![Figure 2.9 The ZSM-5 framework [94].](image-url)
2.6.4 Clinoptilolite

Clinoptilolite is the most widely distributed naturally occurring type of zeolite in the world. It is part of the heulandite family of zeolites which have a Si/Al ratio above 4. This type of zeolite is commonly found within sedimentary rocks enriched with potassium and sodium. The formula for its chemical composition is (Na, K)\(_6\) (Al\(_6\)Si\(_{30}\)O\(_{72}\)) 20H\(_2\)O [96]. The \([\text{SiO}_4]\)\(^4\) and \([\text{AlO}_4]\)\(^5\) are joined together via oxygen atoms in layers within the framework of the zeolite structure. Clinoptilolite, Figure 2.11 a-b, has a two dimensional channel system having a ten-membered (0.79x0.35nm) channel A and eight membered (0.44 x0.3nm) tetrahedral rings channel B. In addition, it has an eight-membered channel C that runs parallel to the a-axis [97].

In general, studies that have been undertaken have demonstrated the difficulty in the synthesis of clinoptilolite. In 1983, Chi and Sand[98] succeeded in synthesising a single phase of clinoptilolite. However, Williams in 1997 was unable to successfully reproduce Chi and Sand’s product. Clearly, difficulties in the preparation clinoptilolite for synthesis under laboratory conditions have been reported in the studies that have been conducted. Therefore, any information which can be obtained regarding the factors impacting on the capacity to replicate the process of clinoptilolite synthesis is of considerable importance for science [99].
Due to the variation in the diameter of clinoptilolite pores, which range from 0.45 to 0.6 nm, cations are able to pass through and thus effect ion exchange. The change in pore diameter may result from altering the exchanging cation. In Figure 2.12, pictures of natural clinoptilolite are presented according to cation type [100]. Figure 2.13a shows that the images of natural clinoptilolite (tuff) containing mordenite using scanning electron microscopy (SEM) can be presented in different shape, while Figure 2.13b shows the synthesis type of clinoptlolite using hydrothermal solution treatment [101]. The distinctive properties of natural clinoptilolite such as chemical stability in various caustic media, thermostability, and high rate of sorption equilibrium, favour its use in the environmental protection industry [100].

Figure 2.11 (a) shows two dimensional channel system of clinoptilolite [97] (b) shows ten and eight membered channels of Clinoptilolite with their size [51].

Figure 2.12 Some kinds of natural clinoptilolite: (a). Clinoptilolite – K; (b). Clinoptilolite-Na; (c). Clinoptilolite – Ca[100].
Due to its natural availability as well as its chemical properties, clinoptilolite has been employed in an extensive range of applications such as adsorption, catalysis and ion-exchange, petrochemical cracking and gas and solvent separation and removal, radioprotection, soil disinfection (clinoptilolite was used successfully to treat and neutralise the soil around the power plant after the Chernobyl accident in 1986) and biomedical applications. Extensive deposits of clinoptilolite are found in the Western United States, Russia, Bulgaria, Hungary, Yugoslavia and Japan[100].

Figure 2.13 SEM images of the (A) tuff sample of natural clinoptilolite collected from Miicica area (Cluj county) Romania (including fibre-like of mordenite including mordenite phase [101] and (B) synthesis products obtained via hydrothermal treatment of clinoptilolite-rich tuff in solutions at 100° [102].
CHAPTER TWO
POROUS MATERIALS

2.7 APPLICATIONS OF ZEOLITES

Zeolites have unique chemical and physical properties which make them applicable for a wide range of industrial processes. For example, they can be used as ion exchange media because of their capacity for replacing or absorbing ions dissolved in water. Their structural architecture enables them to be used as water softeners to remove calcium and magnesium ions from hard water. The zeolites absorb these elements and release Na\(^+\) ions to the water. Zeolites can also be employed to treat radioactive waste such as Sr-90, Co-60 and Cs-137 in aqueous solutions and to treat ammonium from sewage water. The applications of zeolites A, X, Y, ZSM-5 and clinoptilolite are set out in section 2.6 in this chapter [103, 104].

2.7.1 Zeolites as Ion Exchange Material

The aluminium atom has a 3+ (Al\(^{3+}\)/4O\(^2-\)) charge, whilst silica atom has a +4 (Si\(^{4+}\)/4O\(^2-\)) charge. In isomorphous substitution within the zeolite structure this leads to a negative charge in the aluminium atom [105]. This is balanced by cations; ion exchange arises from the presence of framework cations, Figure 2.14. The cations within the zeolite framework have a high degree of mobility and the ability to exchange with other undesirable cations such as Pb, Cu, Cr and others. In this way the zeolites serve as ion exchange media, for example in water softening processes, for the removal of Ca\(^{2+}\) (Figure 2.15) and Mg\(^{2+}\) from hard water by replacing them with sodium ions [60]. The number of cations present with a zeolite framework structure depends on the numbers of [AlO\(_4\)]\(^5-\) present within the framework. When the Si/Al ratio decreases, the number of cations in the pore structure of the zeolite increases, due to the presence of [AlO\(_4\)]\(^5-\) in the framework. This is called increased Cation Exchange Capacity (CEC). Conversely, increasing the Si/Al ratio results in a decrease in the framework charge and a drop in the numbers of cations[34].
Figure 2.14 Cation sites of a faujasite framework showing the large and sodalite cages, site I is located in the centre of double 6-ring, sites I’ and II’ are located inside the sodalite cage. Sites II and III are located inside the supercage [106].

Figure 2.15 Shows the exchange $\text{Ca}^{2+}$ ions with two $\text{Na}^+$ ions inside a zeolite structure [107].

Several factors can affect the equilibrium process (degree of cation exchange).

These factors can be summarized as [34, 108]:

1. The type of cation being exchanged: its diameter and density charge
2. Temperature
3. Morphology characteristics of the species (zeolite) and its Si:Al ratio
4. The position of cations in the species (zeolite)
5. The concentration of cation species in the solution and
6. Any prior treatment of the zeolite.

Equation 2 shows the formula which underpins this process of exchange [108].

\[
Z_B A^Z_A (S) + Z_A B^Z_B (Z) \rightleftharpoons Z_B A^Z_A (Z) + Z_A B^Z_B (S) \tag{Eq. 2}
\]

\(Z_A\) and \(Z_B\) are the charges of the exchange cations A and B. \(A^Z\) and \(B^Z\) refer to the cations within the zeolite structure. These cations are called the in-going cations. S and Z refer to solution and zeolite[34, 50]. Equations 3 and 4 depict the proportions of the exchanging cation in the solution and zeolite phases.

\[
\bar{A}_s = \frac{Z_A m_A}{(Z_A m_A + Z_B m_B)} \tag{Eq. 3}
\]

\[
\bar{A}_Z = \frac{Z_A M_A}{(Z_A M_A + Z_B M_B)} \tag{Eq. 4}
\]

\(\bar{A}_s\) and \(\bar{A}_Z\) = the proportion of ionic species in the solution phase and in the zeolite. \(m_A\) and \(m_B\) represent the concentrations of the ions in the solution phase [109, 110]. \(M_A\) and \(M_B\) refer to the concentration of ions in the exchange phase. Figure 2.16 shows the structure of ion exchange. Cations with the capacity to exchange with other cations are located near the AlO\(_4\)– tetrahedral, due to the dominance of negative charges in this position. Figure 2.17 shows the ion exchange capacity of zeolites for both a univalent and divalent reaction.

![Figure 2.16 Schematic of zeolite in the Na\(^{+}\) form.](image)
Figure 2.17 Schematic of zeolite ion exchange with a divalent ion (Ca$^{2+}$) Na$^+$ is exchanged for Ca$^{2+}$.

A single Ca$^{2+}$ ion is required to balance the charge of two AlO$_4^-$ tetrahedra. In the authentic zeolite, the negative charge is not contained on one or two tetrahedra, but rather is dispersed across the structure of oxygen ions [111]. Due to the Lowenstein rule, it is forbidden to form any Al-O-Al bonds because of the electrostatic effects resulted from the negative charges. Mainly zeolites are synthesized in the alkali cation form (mostly Na$^+$) [112]. In this case the positively charged cations will balance the negatively charged framework system.

Researchers have compared the characterization of natural zeolites with that for their synthesized counterparts (A, X and Y), to identify the differences between them, during ion exchange in aqueous solutions, in terms of their structure, cation sites, cation population and distribution [109]. Table 2.3 shows the difference in ion exchange capacity for a selection of natural zeolites and selection of synthesized zeolites (A, X and Y) [113].

There is an industry preference for synthetic over natural zeolites due to their greater purity and more extensive cavities. These properties mean that the capacity of synthetic zeolites to absorb or hold molecules is superior to that of natural zeolites.
Table 2.3 CEC of some natural and synthetic zeolites[113]

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Typical Formula</th>
<th>Ion exchange capacity CEC (meq. g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM-5 (MFI)</td>
<td>Na₉Al₉Si₉₆−nO₁₉₂.₁₆H₂O, 0&lt;n&lt;27</td>
<td>2.07</td>
</tr>
<tr>
<td>Natural Clinoptilolite (HEU)</td>
<td>(Na₃K₃)(Al₆Si₃₀O₇₂).₂₄H₂O</td>
<td>2.16</td>
</tr>
<tr>
<td>Zeolite A (LTA)</td>
<td>Na₁₂Al₁₂Si₁₂O₄₈.₂₅H₂O</td>
<td>5.48</td>
</tr>
<tr>
<td>Zeolite X (FUG)</td>
<td>Na₈₆Al₈₆Si₁₈₆O₃₈₄.₉₄H₂O</td>
<td>4.73</td>
</tr>
<tr>
<td>Zeolite Y (FUG)</td>
<td>Na₂₀Al₂₀.₄₈Si₄₈O₁₃₆.₈₉H₂O</td>
<td>3.26</td>
</tr>
</tbody>
</table>

2.7.2 Zeolites as Molecular Sieves

The structures of zeolites are composed of a series of cavities and channels. The grouping of single and double rings SBU's are regular in terms of pore size and shape. This allows zeolites to retain water molecules within their structure. Molecular sieves are porous solids containing pores with a diameter of 0.3 to 1.3 nm. Evicting the water molecules from these voids within the zeolite frameworks, primarily through the application of thermal heat, allows other molecules to be sorbed. This method is called ‘sorption’. The shape and size of channels and cavities vary according to the type of zeolite. This variation enables zeolites to function as molecular sieves by separating mixtures of gaseous or liquid phase molecules. Zeolites have pores within a 0.3 to 0.13nm size range. The pores are able prevent molecules which exceed this diameter range from passing through them. Zeolites pores have smaller diameters than those of activated carbon, activated alumina and silica gel. This makes them more effective at separating out molecules with smaller diameters. Undesirable cations and water molecules can be trapped within the pores of the zeolites, Figure 2.18. Cations can be exchanged to adjust the adsorption characteristics and the pore size.
Figure 2.18 Shows that the open, porous structure of zeolite enables it to act as a molecular sieve straining the air of contaminated particles [114].

A 4Å Molecular sieve is commercially produced form Zeolite-A. Other types of zeolite A are also available and vary according to the diameter of their pores. When sodium ions exchange with potassium ions the pore size decreases to 3Å. These are called 3A molecular sieves. If the exchange occurs with calcium ions, the pore size increases to 5Å and the zeolites are defined as 5A molecular sieves [22].

Zeolites in dehydrated forms have a high internal surface area. This characteristic makes them highly sought after for adsorption processes. Nevertheless, it is important to understand that not all zeolites dehydrate without difficulty and not all contain easily accessible voids [34, 48].

2.7.3 Catalysis Using Zeolites

Zeolites have become important materials for catalytic processing. For example, the catalytic cracking of crude oil distillate for fuel manufacture in petroleum refining units and the conversion of crude oil fraction to gasoline in the presence of hydrogen through the hydrocracking process [52]. The lattices within structure of zeolites make them suitable catalysts for a variety of industrial processes as they are endowed with high selectivity and the capacity to maintain stability during reactions [19]. The modification of zeolite frameworks can lead to enhance the active sites accessibility and thermal stability. This can be affected by isomorphous substitution between Si and Al sites within
Every type of zeolite has distinct catalytic properties. For example, only a few types of zeolites have the necessary physical and chemical characteristics to act as catalysts for catalytic cracking or hydrocracking. This is because the catalysts are required to have pores that are sufficiently large to allow reactant molecules access to their surface.\[43\]

There are several reasons why zeolites function as effective catalysts. These are described below [34, 43]:

1- Shape Selective Catalysis: This is a result of the geometry of zeolite structures, their pore size, and the shape and orientation of reactants, Figure 2.19. Shape selectivity is a quality which is unique to zeolites.

2- Internal Surface Area: The presence of voidage and channels which contain the active sites within the crystal structure promotes catalysis. Zeolites X and Y are considered good examples of this quality.

Figure 2.19  Catalysis mechanisms in zeolites: (a) Reactant selectivity, (b) Transition state selectivity and (c) Product selectivity. Based upon diagrams by Dyer [34].
2.7.4 Adsorption using Zeolites

Zeolites are used to adsorb different types of materials. They have the ability to remove water to very low partial pressures and are very effective desiccants, with over 25% of their weight consisting of water. They can separate isomers and mixtures of gases and remove volatile organic chemicals from air streams.

Species with a kinetic diameter which makes them too large to pass through a zeolite pore are effectively "sieved." By virtue of its shape and configuration, this sieve can be used to separate molecules. The extent of the attraction of a particular species to a zeolite cavity is related to the presence of electric fields. The strength of the electrostatic field within the cavity is correlated with the strength of the interaction with polar molecules such as water. As a consequence of the polarizing force of this electric field, non-polar molecules are also strongly adsorbed. Thus, even in the absence of steric hindrance, exceptional separations can be realised by zeolites. Adsorption based on molecular sieving, electrostatic fields and polarizability are reversible. This means that the zeolite can be utilised again and again, alternating between adsorption and desorption. This explains the cost-effectiveness of zeolite as an adsorption medium [34].

2.8 SYNTHESIS OF ZEOLITES ON SUPPORT MATERIALS

Ordered porous solids that enable ions, atoms or molecules to engage with each other, via their surfaces, as well as through the mass of the material, are of significant scientific interest and are attractive to a variety of industries [115]. For example, in the last two decades, there has been increased interest in the development of highly effective membranes which have the capacity to function under the most difficult conditions.

Due to the properties such as the possession of a three-dimensional framework, zeolites are widely used in a variety of applications such as the molecular separation of mixtures, Figure 2.20. In addition, the advantageous properties of zeolite made it useful in molecular sieve processes, as an adsorbent, and in ion exchange. Despite these advantages, there are some flaws that inhibit its use in some industries.
The size of the crystal that is synthesized hydrothermally is generally small and ranges between 1 and 10μm, and sometimes even below that [116]. It has been observed that the direct use of these materials leads to a number of problems in the process such as high pressure drops, difficulties in separation, and handling. To prevent these problems zeolite products are pelletized. This method is employed in a wide range of industries. However, it requires the use of a binder, which may mean that significant parts of the pores become blocked, which is crucial because a large part of the zeolite is in the interior, and therefore unavailable for reactions [117].

Alternative methods to enable these problems to be eradicated from zeolite and resolve this issue have been proposed, such as the use of different materials in different forms and modifications to the thickness of the zeolite layers [118]. Research has been undertaken to identify different support structures which result in fewer problem within the layers of zeolite [118,119].

![Image](image_url)

Figure 2.20 The separation by zeolite membrane process (a) Molecule pass through the porous alumina and the mesoporous layer; only the zeolite layer effects separation and (b) Pore structure of ZSM-5. All other areas are solid [120].

Ceramics and polymers are the most common support materials. However, they have some practical flaws. For example, the polymers have low chemical and thermal stability. This leads to the problem of decomposition during the regeneration process, which is conducted under high temperatures, leading to a shorter product lifetime.
Ceramics are considered more stable than the polymers. However, they are expensive and fragile with the potential for the shape of the zeolite product to be modified due to the dissolution of support materials within the synthesis solution.

Several researchers have used carbon as a support material for zeolites because of characteristics such as chemical stability, a low thermal expansion coefficient, a capacity to take different structural forms and for the modification of its surface chemistry [120].

In this study, two different types of support materials, carbon and diatomite, have been selected due to their properties which are Iraqi palm tree Leafs and tamarind stones as carbon sources and celatom FW-14 (trade name of Diatomite).

2.9 POROUS CARBON

Carbon is considered to have brought about a revolution in the science of materials. Its properties have made it an attractive material for a wide range of industrial applications. For example, graphite is considered one of the best materials for the process of lubrication and as a conductor of electricity, and activated carbon is endowed with the capacity to adsorb gases [121, 122]. The use of carbon in water treatment and purification can be traced back to 2000 BC.

It has been discovered that the ancient Egyptians used charcoal in water purification for medical purposes. In the thirteenth century, the Japanese used coal to purify water wells by placing it at the bottom of the well. Thereafter, Europeans used coal products from wood char and later bone char in the beet sugar refining processes. The use of porous carbons was initiated during World War I because of the imperative to develop gas masks [123-125]. Since then the application of sophisticated technologies and processes have evolved in the formation and treatment of this versatile material [124]. Investigations undertaken into carbonisation processes have demonstrated that the pore size and structure of activated carbons is highly influenced by the nature of the starting materials [126].

A number of criteria are pertinent in the selection of raw materials for the process of carbon manufacturing, including cost, a low ash (high carbon) and a low organic matter
content. Preferred materials have a high carbon content, possess a high-density structure which enhances the strength of carbon to withstand different treatment processes, and a volatile content, which leads, during the process of pyrolysis, to the formation of pores [127]. The characteristics and applications of different raw materials used in the preparation of carbon are set out in Table 2.4 [128-130].

Table 2.4 Characteristics of various conventional raw materials used for making activated carbon [128].

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>Carbon (%)</th>
<th>Volatile (%)</th>
<th>Density (Kg/m³)</th>
<th>Ash (%)</th>
<th>Texture of activated carbon</th>
<th>Application of activated carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softwood</td>
<td>40–45</td>
<td>55–60</td>
<td>0.4–0.5</td>
<td>0.3-1.1</td>
<td>Soft, large pore volume</td>
<td>Aq. Phase adsorption</td>
</tr>
<tr>
<td>Hardwood</td>
<td>40–42</td>
<td>55–60</td>
<td>0.55-0.8</td>
<td>0.3-1.2</td>
<td>Soft, large pore volume</td>
<td>Aq. Phase adsorption</td>
</tr>
<tr>
<td>Lignin</td>
<td>30–45</td>
<td>58–60</td>
<td>0.3-0.4</td>
<td>-----</td>
<td>Soft, large pore volume</td>
<td>Aq. Phase adsorption</td>
</tr>
<tr>
<td>Nut shells</td>
<td>40–45</td>
<td>55–60</td>
<td>1.4</td>
<td>0.5-0.6</td>
<td>Hard, large multi pore volume</td>
<td>Aq. Phase adsorption</td>
</tr>
<tr>
<td>Lignite</td>
<td>55-70</td>
<td>25–40</td>
<td>1.0-1.35</td>
<td>5-6</td>
<td>Hard, large multi pore volume</td>
<td>Waste water treatment</td>
</tr>
<tr>
<td>Soft coal</td>
<td>65–80</td>
<td>25–30</td>
<td>1.25-1.5</td>
<td>2.12</td>
<td>Medium hard, medium micropore volume</td>
<td>Liquid &amp; vapour, adsorption</td>
</tr>
<tr>
<td>Petroleum</td>
<td>70–85</td>
<td>15–20</td>
<td>1-35</td>
<td>0.5-0.7</td>
<td>Medium hard, medium micropore volume</td>
<td>Gas–vapour adsorption</td>
</tr>
</tbody>
</table>

2.9.1 Pyrolysis of Carbon

Pyrolysis is used to prepare activated carbon from different carbonaceous materials of natural or synthetic origin such as coal, shells, wood, fruit stones, and polymers such as viscose rayon. This process is conducted in an inert atmosphere and involves the decomposition of organic materials that are ultimately converted into a hard porous carbon mass. After pyrolysis, the products are predominantly macroporous but contain residual materials which block these pores. However, the surface area, measured in
square metres per gram, can be developed through the physical or chemical activation of carbonised material. There are three stages to the development of activated carbon: the selection of raw material, carbonisation and activation [127, 128].

Under this process non-carbon species are eliminated, producing a fixed carbon mass and rudimentary pore structure [131]. The process is usually conducted at a temperature below 800°C and in an inert atmosphere. The yield of carbonisation product and its quality are determined by the parameters of (1) the heating rate, (2) the final heat, and (3) the heating time [118].

The basic microstructure of the char is formed at 500°C. However, during the Pyrolysis process tarry products block some of the pores. Further heating to around 800°C is an option. However, because of the partial alignment of graphitic planes within the carbon structure, an increase in temperature to 1000°C may solidify the carbon structure and diminish its porosity, thereby slowing down activation [128].

In this study two different types of raw material are used to prepare carbon materials: Iraqi palm tree Leaves (IP) and tamarind stones (TS). These act as support materials to hold the fine particles of zeolite on their surface in order to build hierarchical structures.

2.9.2 Structure of Carbons from Agriculture Waste

Porous carbons are produced from a wide range of materials using pyrolysis and one major source of raw materials for this is from agricultural activities. Figure 2.21 depicts micrographs of carbon materials which have organised pores. This quality is common to all plants, with variations in the shape, size and surface area. For example, after activation, for the carbon sources of coconut shell, Pecan shell and fibre the BET surface area was found to be 1565, 900 and 652 (m².g⁻¹) respectively [38]. Pore size for activated carbons is classified as being macropore, mesopore or micropore (Figure 2.21). Furthermore, it was found that some of the pores of carbon plants such as
bagasse, babool wood, castor oil wood and pine are equally distributed, have a similar shape and size and are organised in a roughly circular fashion [128].

In this study carbons are utilized to support the zeolite particles because of their structural strength, porosity, pore size and high thermal stability [117].

![Figure 2. 21 SEM micrographs of porous carbons: (a) castor oil plant wood, (b) bagasse and (c) babool wood [128].](image)

### 2.10 ZEOLITE ONTO CARBONS

An active reaction centre can be provided by microporous structures, while quick mass transportation and molecule diffusion can be obtained via macroporous structures [132]. A number of studies have researched the ability to graft different types of zeolite on a range of naturally occurring organised structures such as carbons to combine multiple levels of porosity. For catalysis and ion exchange, this problem can be minimized if zeolites are combined with a macroporous material with a large surface area. Researchers have investigated different materials including synthetic carbon fibres, alumina fibres, mullite, cellulose fibres [117], multicellular filaments of bacteria [133] and polymer spheres [134].

A more active surface can be prepared by coating the surfaces of the macroporous material with a thin layer of zeolite. In 1996 Svetlana Mintova and Valentin Valtchev successfully deposited zeolite A on various vegetal fibres using in situ zeolite crystallization. They found that the degree of coverage was affected by the chemical composition and structure of the support material. However, they also reported that the
pre-treatment of the support material may affect the amount of the zeolite deposited [117]. Hiroaki Katsuki et al[135], 2005 successfully supported ZSM-5 on a carbonised rice husk using microwave and conventional hydrothermal reactions to prepare a zeolite/porous carbon composite. They found that a microwave hydrothermal (M-H) reaction at 150°C increased the rate of ZSM-5 formation 3 to 4 times in comparison with conventional hydrothermal (C-H) reactions. In addition, the M-H reaction yielded small particles of zeolite ranging from 0.3 to 5 μm, with a micro- and mesoporous composite. Figure 2.22 shows that the XRD patterns of zeolite under a C-H reaction appeared between 8 to 16h, while Figure 2.23 reveals the XRD patterns of zeolite under a M-H reaction presented between 3 to 4h. Figures 2.24 a and b show the SEM of ZSM-5 zeolite crystals on the surface of carbonized rice husk synthesized at 150°C for the C-H and M-H reactions respectively [136].

![XRD patterns of ZSM-5/carbonized rice husk composite synthesized at 150 °C using conventional hydrothermal (C-H) reactions[136].](image)

Figure 2.22 XRD patterns of ZSM-5/carbonized rice husk composite synthesized at 150 °C using conventional hydrothermal (C-H) reactions[136].
Figure 2.23 XRD patterns of ZSM-5/carbonized rice husk composite synthesized at 150 °C using microwave hydrothermal (M-H) reactions [136].

Figure 2.24 SEM images of ZSM-5 crystals on the carbonized rice husk synthesized at 150 °C for (a) 1 day using conventional hydrothermal (C-H) reaction and (b) 4 h using microwave hydrothermal (M-H) reactions (scale bar=1µm) [136].

S.P.J Smith et al investigated the possibility of employing a hollow-fibre carbon membrane produced from polyacrylonitrile (PAN) to prepare composite zeolite-carbon membranes utilizing thermo-oxidative stabilisation. The carbon membrane was used as a porous support for three different types of zeolites: ZSM-5, mordenite and silicate-1. The surfaces of the carbon membrane were modified to create nucleation sites to assist zeolite growth. Two methods were used to modify the carbon membrane surfaces:
firstly, oxidation of the surface involving a hot air treatment for 2h at 150-160°C. The second method was conducted via ozone treatment for 30 min at 25°C using a Fisher 503 ozone generator to impregnate the membrane outer surface with silicon atoms. The oxygenated membrane was flushed with tetraethoxysilane during this process, followed by a heat treatment in air. Then PAN precursors were dipped for 2h in a 1.17% silicon rubber solution prior to carbonisation. It was reported that the deposition processes of the zeolites were considerably enhanced by the generation of the silicon-containing sites on the surfaces of the membrane [137]. Electrical depositions have been investigated as alternative method [138].

The use of macroporous materials as scaffold, by coating them with a thin layer of zeolite, makes the seeding process in the synthesis technique very important. However, current techniques are complex and costly mainly due to the use of the synthesis template. In addition, these templates must be removed later to enable the creation of voids inside the structure of the products [38,139].

2.11 DIATOMS

Diatoms are microscopic algae which are found in every aquatic environment. They are formed by fragments of the skeletons of diatom algae. Diatomite rock belongs to the silica-bearing group of materials [139]. Diatoms , Figure 2.25, have special properties, such as a low density, a high porosity, a low thermal conductivity [140], a high melting point (1400°C to 1750°C depending on impurities), solubility only in strong alkaline solutions and hydrofluoric acid, the quality of being chemically inert, [141] high permeability, and a high surface area (12 m².mg) [142, 143]. These properties make them useful for a wide range of applications both as a fossil and living organism.

Diatoms are used as environmental indicators for oil exploration [144,145]. Furthermore, diatomite is used in the reinforcing, stiffening and hardening of organic solids and catalysts[146, 147]. Diatomite is a loosely cemented porous, soft and light weight sedimentary rock. It is produced from an accumulation of diatoms, which grew and were deposited in seas or lakes. It is composed principally of the silica microfossils of aquatic unicellular algae. Diatoms most distinctive characteristic is the external wall they secrete, called a frustules, Figure 2.26.
Diatoms possess many useful characterizations owing to these delicate frustules, which are composed of amorphous opaline silica (SiO$_2$. nH$_2$O) and produced from the uptake of silica from the environment (usually in the form of silicic acid). Diatoms then use transporter proteins to build the frustules. In general the size of diatoms ranges between 10 to 100 µm. Some of the diatoms are large ≈1mm in a structure composed of up to 80-90% voids [149].

It is estimated that 1 in $^3$ of diatomite may include 40 -70 million diatoms [150]. Diatom frustules have a density (specific gravity) nearly that of double water, but the open structure and the perforations of the frustules gives diatomite a lower effective density of between 0.12 to 0.25g/cm$^3$ and a high porosity 75 to 85%, that enable it able to absorb and hold up to 3.5 times its actual weight in liquid. The complex shapes of diatoms endow them with an extremely large surface area and properties of absorption [151].

The proportions of both clastic particles (clay and slit) and of organic material determine the character and type of diatomite and the nature and scope of its industrial applications. Some high commercial-grade diatomite consists of volcanic glass with up
to 90% SiO₂, with minor levels of calcium carbonate and terrigenous particles [152, 153].

Figure 2.26 Frustules of the diatom Stephanodiscus niagarae Ehrenb, viewed in a SEM (Micrograph by M. B. Edmund, Science Museum of Minnesota) [146].

Preservation of the opaline silica in diatom frustules depends on:

(i) Local levels of alkalinity (pH 9 is favourable)
(ii) The presence of dissolved silica in pure water
(iii) An association with volcanic ash.

The amorphous, opaline silica (SiO₄•nH₂O, commonly called opal-A) of diatom frustules is progressively converted to anhydrous silica or porcellanite and finally to quartz (SiO) in the hard dark rocks [154, 155].

2.11.1 Zeolitization of Diatoms

The last decade witnessed the first attempt to use diatoms as a silica source in zeolite synthesis. Many types of zeolite have been made successfully using diatoms as a cheaper silica source, such as zeolite A, mordenite, silicate, phillipsite, cancrinite, analcime and hydroxysodalite [156].
Porous materials are important for a variety of functions and processes such as catalysis, separation technology, ion exchange and filtration. Thus, pore engineering to control the pore size and connectivity over a wide scale was investigated. Anderson, M.W, Holmes, S.M and others, 2000 [157, 158] successfully coated zeolite on the surfaces of diatomaceous earth and succeeded in developing a low cost hierarchical porous material to be used in ion-exchange and catalysis processes for dealing with fluid waste in industry. This process of “zeolitization” onto diatom surface was conducted using a simple method which involved the construction of a micro-porous/macroporous material through the seeding of nano-zeolites onto the surface of the diatoms with the subsequent application of hydrothermal treatment for the growth of more crystals [159].

In this project different techniques will be used for the crystallisation of diatomite for the purposes of zeolite Y and A composition. Oscar H. and S.M. Holmes [139] successfully supported zeolite Y on the Celatom FW-14, Figure 2.27, using the synthesis (using template) and ball mill method to prepare zeolite Y seeds. In this study this technique will reused to prepare zeolite-Y, zeolite-A and clinoptilolite.

Figure 2.27 SEM images showing faujasite crystals growing on the surface of a diatomite frustules (scale bar = 10 µm) [139].
2.12 RADIOACTIVITY AND ITS SOURCES IN WATER

Radioactivity in water originally comes from rocks which naturally contain radioactive minerals and from the fallout of cosmic-ray produced nuclides such as H$_3$ and C-14. Artificial radioactivity is produced by the activity of the nuclear power industry, nuclear weapons testing, and peaceful applications of nuclear materials and industries [160]. Uranium, thorium and actinium are Naturally Occurring Radioactive Materials (NORM) and the decay series of these elements results in radioactive daughters. Both the radioactive elements and their radioactive daughters are known principally for reasons of health and as potential energy sources. The quantitative measurement of radiation is shown in Table 2.5.

Table 2.6 and Figure 2.6 show the three natural decay series which are headed $U - 238$ ($t_{1/2} = 4.51E9$ yr), $Th - 232$ ($t_{1/2} = 1.41E10$ yr), $U - 235$, ($t_{1/2} = 7.13E8$ yr) & $K - 40$ ($t_{1/2} = 1.28E9$ yr) [160-161].

The three chains of natural radionuclides are presented in Figure 2.28. Radionuclide emission gamma rays with no series are presented in Table 2.6.

Table 2.5 The units of quantitative measurement of radiation [162].

<table>
<thead>
<tr>
<th>Quantity</th>
<th>New name of unit and symbol</th>
<th>SI unit</th>
<th>Old unit and symbol</th>
<th>Relationship of new to old unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activity</td>
<td>Becquerel ($Bq$)</td>
<td>$s^{-1}$</td>
<td>Curi ($Ci$)</td>
<td>$1 Bq \approx 2.7 \times 10^{-11} Ci$</td>
</tr>
<tr>
<td>Exposure</td>
<td>Roentgen ($R$)</td>
<td>$Coul/kg$</td>
<td>Roentgen ($R$)</td>
<td>$1 C/kg \approx 3876 R$</td>
</tr>
<tr>
<td>Absorbed dose</td>
<td>Gray ($Gy$)</td>
<td>$J/kg$</td>
<td>Rad ($Rad$)</td>
<td>$1 Gy \approx 100 Rad$</td>
</tr>
<tr>
<td>Equivalent dose</td>
<td>Sievert ($Sv$)</td>
<td>$J/kg$</td>
<td>Rem ($Rad$)</td>
<td>$1 Sv \approx 100 Rem$</td>
</tr>
<tr>
<td>Collective dose</td>
<td>Man-sievert</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 2.6 Radionuclide emission gamma rays with no series[161].

<table>
<thead>
<tr>
<th>No.</th>
<th>Decay Mode</th>
<th>Half-life</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>$Be - 7 \Rightarrow Li - 7$</td>
<td>53.6 d</td>
</tr>
<tr>
<td>2.</td>
<td>$K - 40 \Rightarrow Cu^{40}$</td>
<td>$1.3 \times 10^9$ yr</td>
</tr>
<tr>
<td>3.</td>
<td>$La - 138 \Rightarrow Ce - 138$</td>
<td>$1 \times 10^9$ yr</td>
</tr>
</tbody>
</table>

Figure 2.28 Uranium-238, Thorium-232, Uranium-235 decay series [162].

2.12.1 Overview Some Important Radionuclides Introduced Into Surface Water

The principal radionuclides introduced naturally and artificially into surface water are:

1. **Strontium-90 (Sr-90)**: is the result of a nuclear fission process in combination with Sr-89 (half-life =50.8 d). The long half-life of Sr-90 (half-life =38.9 yr.) makes its impact more significant in terms of environmental pollution worldwide. It is found in soil, water, food and biological materials and is widely distributed. The “Water Quality Criteria, 1972” recommends that the total limit of Sr-90 in drinking water should be $5\text{pCi/d}[163]$.

2. **Caesium-137(Cs-137)**: is a radioactive isotope, mainly generated from nuclear fission products in combination with eleven other isotopes. It has a long half-life
(30.07 yr.) and beta decay makes it a strong radiation hazard. It is also very slow to reach stability. 1 g of Cs-137 has an activity of 3.4 Terabecquerel (TBq). Most of Cs-134 and Cs-137 has been released from nuclear weapon tests and nuclear power plant accidents such as the Chernobyl accident in 1986. The majority of the radiation from this accident was from Cs-137 together with Cs-134, I-131 and Sr-90. The concentration of Cs-137 found in Germany after the Chernobyl accident was (2000-4000) Bq/m². The hazardous nature of Cs-137 also comes from its solubility in water and its toxicity in small quantities. Biologically, Cs-137 exhibits same behaviour as Potassium. After entering the body most Cs-137 accumulates in muscle tissue [164, 165].

3. Cobalt-60 (Co-60): is a radioactive isotope of cobalt. The half-life of this radionuclide is 5.27 years. It is produced artificially (not found in nature), the radionuclide Co-60 decay by emitting gamma-rays at two energies 1.17 and 1.33 MeV. 1 g of Co-60 has an activity 44 TBq (about 1100 curies) [166]. Co-59 which is used in this experiment is a carcinogenic ion and displays the same chemical behaviour as Co-60. External exposure to Co-60 is considered a significant threat to humans. Liver, kidney and bones are considered the main receptors of Co-60 and people may ingest Co-60 with food and water that has been contaminated, or may inhale it in contaminated dust. Long term exposure to any ionizing radiation including that of Co-60 is known to cause cancer[167].

2.12.3 Application of Zeolites in Wastewater Treatment and Nuclear-Waste

Although the use of natural zeolites is problematic due to the inherent complexity of wastewater, this does not prevent their use for the abatement of heavy metals such as Pb²⁺ released from storage batteries and generated by ceramics industries [168]. Natural zeolites, in the form of clinoptilolite, were used in the treatment of wastewater (mixed metals contaminated effluents) in 1997 by Kesraoui-Ouki and Kavanagh. The results revealed that 90% of heavy metals could be removed within 15 minutes of mixing. The selectivity sequence for clinoptilolite was demonstrated to be Pb > Cu > Cd > Zn > Cr > Co > Ni [169].
Natural zeolite, such as clinoptilolite, mordenite, erionite and chabazite are used widely in the field of radioactive waste applications. The key characteristics that make zeolites particularly effective “buffers” are sorption capacity relative to the radionuclides, thermal conductivity, as well as their chemical stability and mechanical strength. When the zeolites are exhausted the resultant mix of zeolite and radionuclides is compressed and sent for disposal. There is no treatment or regeneration of the natural zeolite after it has been exhausted or becomes saturated [170]. Amis, considered the pioneering researcher in this field, started in the late 1950’s [168]. Amis found that the zeolites clinoptilolite and mordenite have high selectivity for Cs\(^+\), Ba\(^{2+}\) and Sr\(^{2+}\) with the selectivity sequence Cs\(^+\)>K\(^+\)>Na\(^+\)>Li\(^+\) and Ba\(^{2+}\)>Sr\(^{2+}\)>Ca\(^{2+}\)>Mg\(^{2+}\). Due to high selectivity these types of zeolites can take up Cs\(^+\), Ba\(^{2+}\) and Sr\(^{2+}\) from solution, even in large amounts of mixed cationic species including small amounts of radionuclides. Due to high Cation Exchange Capacity (CEC) of both types of zeolites (clinoptilolite and mordenite) and high selectivity for Cs\(^+\) and Sr\(^{2+}\), they are used in radioactive wastewater applications. Additionally, the use of zeolites for the removal of radionuclides from nuclear power plant water shows further advantages for zeolites in use [168]:

1) Good radiation and heat resistance, which prevents contaminant leakage.
2) Compatibility with cement in capsulation and vitrification (more details in the next sections).
3) Radionuclide recovery to be used as source of heat and radiation.

2.13 ADSORPTION
Adsorption is a mass transfer process that plays an important part among other types of wastewater treatment due to its efficient and economical process [171]. The adsorption process can be pictured as follows: Substances which are present in the fluid phase (liquid or gas) are extracted via the adsorption process and concentrated or accumulated at the surface of the adsorbents (solid phase) due to the attractive force existing between the solid surface and the adsorbate substances or molecules thus removing them from the fluid, see Figure 2.29 [172]. Consequently, the removal process occurs by adsorbing the particles on the surface of adsorbent through chemical or physical bonding. It is applied in a wide range of fields such as the purification of drinking water and removal
of harmful pollutants from wastewater as well as in controlling air pollution and many processes in chemical engineering [173].

![Adsorption process of gas molecules onto an activated charcoal surface.]

**Figure 2.29** Shows the adsorption process of gas molecules onto an activated charcoal surface.

A porous solid material of large surface area per unit mass in which adsorption of liquids or gases occurs on its surface is known as an "adsorbent". The material to be adsorbed on the adsorbent is known as "adsorbate" [174, 175].

The adsorption process involves the following consecutive steps [176]:
1. Substances adsorb to the exterior of the adsorbent.
2. Substances move into the adsorbent pores.
3. Substances adsorb to the interior walls of the adsorbent.

Several advantages of the adsorption process over other traditional advanced treatment methods can be illustrated, these are [176]:

- It can remove a wide spectrum of constituents (organic and non-organic) even at very low concentration.
- It is a safe and easy operational technique.
- It can be used in batch wise or continuous operations.
- There are no chemical additives; therefore there will be no sludge formation.
- The adsorbent can be regenerated and reused again.
2.13.1 Types of Adsorption

Physical (physisorption) and chemical (chemisorption) adsorption are the two general types of adsorption. The adsorption phenomena can be classified into these two types due to the nature of the bonding between the adsorbate (fluids) and the adsorbent (solids)[177]. Almost all solid surfaces have a capacity to adsorb; however their effectiveness in the treatment of wastewater is a function of their structure, degree of polarity, porosity and specific area [178]. Table 2.7 gives examples for the major types of adsorbent materials.

Physical adsorption is the most important technique used for removing organic contaminants. The weak bonding process occurs as a result of energy difference and/or electrical attractive forces (weak Van der Waals forces) caused by the attractions of intermolecular forces. The adsorbate molecules become firmly physically fixed to the adsorbent surface [179].

Table 2.7 Shows different types of adsorbent [180, 181]

<table>
<thead>
<tr>
<th>Adsorbent Type</th>
<th>Characteristics</th>
<th>Use</th>
<th>Disadvantage</th>
<th>Typical specific surface area (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon</td>
<td>Hydrophobic, favours organics over water</td>
<td>Removal of organic pollutants</td>
<td>Difficult to regenerate</td>
<td>600-2000</td>
</tr>
<tr>
<td>Silica Gel</td>
<td>Hydrophilic, high Capacity</td>
<td>Drying gas streams</td>
<td>Trace removal not effective</td>
<td>500-750</td>
</tr>
<tr>
<td>Zeolites</td>
<td>Hydrophilic, polar, regular channels</td>
<td>Air separation, dehydration</td>
<td>Low total capacity</td>
<td>400-500</td>
</tr>
<tr>
<td>Activated alumina</td>
<td>Hydrophilic, high Capacity</td>
<td>Drying gas streams</td>
<td>Trace removal not effective</td>
<td>50-300</td>
</tr>
</tbody>
</table>
2.13.1.1 Physisorption

Physical adsorption can be described as the electrostatic attraction between the adsorbate and the adsorbent surface. Usually the more highly charged of cations (generally heavy metals such as Co$^{2+}$) or anions such as phenol (Ph) have more ability to be attracted toward a site of opposite charge than others with less charge such as Na$^+$. Electrostatic attraction is the most important mechanisms for heavy metals. Physical adsorption, a reversible equilibrium process, needs enough energy to be supplied in order to overcome the attractive forces and generally occur at low temperatures [182]. Physisorption can form a single or multiple layers of adsorbate on the adsorbent surface and requires relatively low activation energy (enthalpy) of adsorption, usually less than 40 KJ/mole. This means the adsorbate is not held strongly to the adsorbent [183, 184]. Also, due to the nature of the surface charge, particles near the adsorbent surface can be faced with either electrical attraction or repulsion caused by Van der Waal's forces; they are also subjected to hydraulic forces resulting from the movement of the fluid.

2.13.1.2 Chemisorption

The chemical adsorption (also called Langmuir adsorption) occurs only at the surface and involves actual chemical bonding. In this case of adsorption the adsorbate will undergo a chemical interaction with the adsorbent. Chemisorption creates a single layer of adsorbate attached to the adsorbent surface by chemical bonds. The chemical adsorption is the result of much stronger forces, comparable with those leading to the formation of chemical compounds [185]. The chemisorption is irreversible because the adsorbate is chemically bonded to the surface and on adsorption the original substance will often be found to have undergone a chemical change. The heat of adsorption is typically characterised by a high enthalpy, above 200 (KJ/mole). Table 2.8 compares physical and chemical adsorption properties for different parameters [186].
Table 2.8 Comparison between the physical and chemical adsorption properties for different parameters[186].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Physisorption</th>
<th>Chemisorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wastewater treatment</td>
<td>most common type of adsorption mechanism</td>
<td>rare in wastewater treatment</td>
</tr>
<tr>
<td>Type of bonding</td>
<td>Van der Waal’s forces</td>
<td>specific exchange of electron, chemical bond at surface</td>
</tr>
<tr>
<td>Type of reaction</td>
<td>exothermic, reversible</td>
<td>exothermic, irreversible</td>
</tr>
<tr>
<td>Heat of adsorption</td>
<td>4-40 KJ/mole</td>
<td>&gt; 200 KJ/mole</td>
</tr>
<tr>
<td>Process speed</td>
<td>Limited by mass transfer</td>
<td>Variable</td>
</tr>
</tbody>
</table>

2.13.2 Factors Affecting Physical Adsorption

The quantity of adsorption of a sorbate on the adsorbent surface can be affected by several factors such as surface area of adsorbent, nature of solute, nature of solvent, temperature, pH and inorganic salts [187].

2.13.2.1 Surface area of adsorbent

There is a direct relationship between the amount of adsorption and the surface area of the adsorbent. Generally, surface area depends on the size of the particle diameter; small particle sizes give high surface areas which means high adsorption.

2.13.2.2 Nature of adsorbate

The degree of ionization of the solute is considered one of the most important factors affecting the adsorption of inorganic ions which are the interest and focus of this study. These ions may vary in dissociation and this will affect the adsorption process, for example NaCl has strong dissociation and does not adsorb at all, while HgCl is weakly dissociated and can adsorb well.

For an organic sorbent, the low aqueous solubility and large molecule are preferred in the adsorption process. However, in some cases the molecules become so large that leads to the blocking of most of the pores in porous solid adsorbents [187].
2.13.2.3 The nature of the solvent

Solvent nature can play as significant a role as the solid adsorbent in attracting the adsorbate. In the appearance of solvent, the degree of ionisation can play a vital role in the adsorption process [187].

2.13.2.4 Temperature

Generally, the adsorption decreases with a rise in temperature (inverse relationship) because of the adsorbed molecules being more excited and breaking away from the adsorbent surface due to their greater energy [187].

2.13.2.5 pH of the solution

A significant relationship is found between the pH of the solution and the degree of ionization, this can directly affected the degree of adsorption. The adsorption process can be increased by increasing the pH values due to the species adsorbed on the surface of the adsorbent all holding similar electrical charge. However, they cannot be piled up very densely on the surface due to mutual electrical repulsion. On the other hand, when no charge is carried by adsorbate molecules (neutral), they have ability to pack together on the adsorbent surface and adsorption is maximised. Hence, it is clear that acidic species adsorb at low pH and basic species at high pH [187]. The extent of this phenomenon differs for different pH values and for different metals, but the usual sequence of hydrolysis is the formation of hydroxylated monomeric species, followed by the formation of polymeric species and then the formation of crystalline oxide precipitates after aging [188]. For example, in the case of nickel solution, [189]. It is indicated that within the pH range from 1 to 7, nickel existed in solution as Ni\(^{2+}\) ions (90%); whereas at pH 9, Ni\(^{2+}\) (68%), Ni\(_6\)OH\(_4^{4+}\) (10%) and Ni (OH)\(^+\) (8.6%) co-existed. The same thing can happen with Co\(^{2+}\) in the present study. The different chemical species of a metal occurring with pH changes will have variable charges and adsorbability at solid–liquid interfaces.
2.13.2.6 Effect of inorganic salts

Adsorption can be enhanced by the presence inorganic salts such as NaCl in the system. This is due to the ability of inorganic salts to hold an opposite charge to the adsorbent, as well as fitting in between adsorbed molecules and thus screening the repulsive forces on the surface [187].

2.14 ADSORPTION ISOTHERMS

An isotherm is usually used to describe adsorption/biosorption and represents the equilibrium state between the concentration (loading) of adsorbate in the solid phase (\(q_e, \text{mg. g}^{-1}\)) and the adsorbate concentration in the fluid phase (\(C_e, \text{mg. L}^{-1}\)) at a given temperature. The quantity of adsorbate ions per unit weight of adsorbent (\(q_e\)) and the equilibrium concentration of the adsorbate remaining in solution (\(C_e\)) can be obtained over a wide range by changing the amount of adsorbent (W, g), the initial concentration of solute (element, \(\text{mg. L}^{-1}\)) and the volume of liquid [187]. One or more equilibrium isotherm models can be fitted by plotting \(q_e, (\text{mg. g}^{-1})\) against \(C_e, (\text{mg. L}^{-1})\), Figure 2.30. Commonly, the increasing concentration leads to an increase of adsorbate (solute) in the solid phase (adsorbent/biosorbent), but not in direct proportion, the figure also shows some typical isotherm shapes as arithmetic graphs [190, 191]. These curves in the figure show that adsorption of specific possessions can be affected by the nature of the solid-liquid system (adsorbate-adsorbent or sorbate-biosorbent system).

In this study, two isotherm models (Langmuir and Freundlich models) will be used to fit the theoretical data with the experimental data.
2.14.1 Langmuir model

The first mathematical fit to an isotherm was given by the Langmuir model isotherm. It was first published by Irving Langmuir in 1918 for fluid adsorbed on adsorbent to describe and quantify sorption on localised adsorption sites. It is an empirical isotherm derived from a proposed kinetic mechanism. It can be used to describe both physical and chemical adsorption, but is only valid for single-layer adsorption [192-194]. In addition, it depends on the supposition that the highest adsorption corresponds to a saturated monolayer of adsorbate molecules on the solid surface, that the energy of adsorption is constant and there is no transmigration of adjacent adsorbed molecules [178].

The hypotheses of Langmuir model based on [195]:

1- It is supposed that all sites are equal on the uniform surface of adsorbent.
2- There is no interaction between the adsorbed molecules.
3- All adsorption is formed via the same system.
4- Maximum adsorption occurs on a monolayer only at the defined sites of the adsorbent and no others.
The non-Linearised form of the Langmuir model can be described as follows in Eq. 5[196].

\[ q_e = \frac{K_L b C_e}{1 + K_L C_e} \]  \hspace{1cm} \text{Eq. 5}

Where: \( q_e \) is the equilibrium ion uptake (mg.g\(^{-1}\)), \( C_e \) represents the equilibrium concentration (mg.L\(^{-1}\)), \( b \) is the sorption equilibrium constant (L.mg\(^{-1}\)) and \( K_L \) is the maximum adsorption capacity (mg.g\(^{-1}\)).

The dimensionless constant separation factor \( R_L \) was calculated by Weber and Chakravorti (1974) to express the essential characteristics of the Langmuir isotherm terms equilibrium parameter using Eq.6 [197, 198].

\[ R_L = \frac{1}{1 + K_L C_o} \]  \hspace{1cm} \text{Eq. 6}

Where: \( C_o \) is the highest initial concentration of element (mg.L\(^{-1}\)), the value of \( R_L \) indicates the type of isotherm as shown in Table 2. 9.

<table>
<thead>
<tr>
<th>Values of RL</th>
<th>Type of isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>RL &gt; 1</td>
<td>Unfavourable</td>
</tr>
<tr>
<td>RL = 0</td>
<td>Linear</td>
</tr>
<tr>
<td>0 &lt; RL &lt; 1</td>
<td>Favourable</td>
</tr>
<tr>
<td>RL &lt; 0</td>
<td>Irreversible</td>
</tr>
</tbody>
</table>

Table 2. 9 Values of separation factor and type of isotherm [197, 198].
2.14.2 Freundlich model

The second mathematical fit to an isotherm was published by Freundlich and Küster in 1907 [199]. The empirical Equation 7 describes the form of the Freundlich sorption isotherm in terms of sorbate concentration [200, 201].

\[ q_e = K_F (C_e)^{1/n} \quad \text{Eq. 7} \]

Where: \( K_F \) (mg.g\(^{-1}\) (L.mg\(^{-1}\))\(^{1/n}\)) and \( n \) are the constants of the Freundlich isotherm related to adsorption capacity and adsorption intensity respectively.

The Freundlich model has capable of being used with non-ideal sorption on heterogeneous surfaces as well as for multilayer sorption [202].
CHAPTER THREE

CHARACTERISATION TECHNIQUES
CHAPTER THREE
CHARACTERISATION TECHNIQUES

3. CHARACTERIZATION TECHNIQUES

All samples of zeolites were investigated to check their properties using a range of characterization techniques. In this chapter all the instruments which were used in this study will be explained. The dried samples were analysed by powder X-ray Diffraction (XRD) [a Rigaku Miniflex instrument] using CuKα radiation to study the structure of each pattern. A Scanning Electron Microscope (SEM) [FEI Quanta 200ESEM] was used to monitor the distribution of the zeolite particles and their morphology. Transmission Electron Microscopy (TEM) was used for high resolution images. Energy Dispersive X-ray Spectroscopy (EDAX) was employed to identify the element types and compositions on the bulk of the products. A Dynamic Light Scattering (DLS) (Zetasizer 1000 HS by Malvern instruments) was used to measure the fine particles of ground zeolite.

The specific surface areas of products were measured by the nitrogen adsorption isotherm, measured at -196°C using an automatic Micrometrics ASAP 2010 volumetric sorption analyser using a BET method (Brunauer, Emmett and Teller). The samples were degassed at 350°C under vacuum conditions for 24 h. While, the amount of zeolite on the carbon surfaces for each sample was determined and the changing weights with temperature were studied for all composite samples using Thermo-gravimetric Analysis (TGA) at 600°C by increasing the temperature 10°C/min. Finally, Inductive Coupled Plasma spectroscopy (ICP-OES model Vista-MPX by Varian) was used to measure cobalt and strontium ions with a 228.3 nm wavelength for Co²⁺ and 238.9 nm for Sr²⁺.

3.1 X-Ray Diffraction Analysis (XRD)

In this study X-ray diffraction [Rigaku Miniflex instrument utilizing Cu Kα radiation (λ 1.5406 Å)] was used to investigate the degree of crystallinity of zeolite samples. In general, it can also be used to determine the electronic distribution of atoms in a zeolite structure. The powder diffraction technique dates back to 1938 [203]. The X-ray diffraction machine has been used to identify an unknown specimen and to measure the crystallinity degree of samples (crystal structures such as the long range ordering, grain size preferred orientation, defects etc. and lattice constant) of zeolite and composite samples. It is considered to identify the crystalline solid materials as fingerprint
characterization. A powdered sample of zeolite is supported on a table that is free to rotate about its perpendicular axis, located at the origin. The electronics are used to amplify and filter signal pulses from the detector, Figure 3. 1. An x-ray source is used to supply x-rays that are scattered from the sample and focused at the slit before reaching the detector [203]. Wave length selection is done by using a monochromator beam which includes background Kβ radiation that is released from the sample and radiation of florescent. Filters for removing Kβ may be located in the beam path on the generator or detector end of the path. A monochromator is normally positioned on the detector side between the receiving slit and the detector.

A detector, electronics and specialized software are used to record the angles and intensities of diffractions electronically resulting in a plot of 2θ (horizontal axis) versus intensity (vertical axis) for the specimen [203]. Strong peaks are expected when the Bragg condition is satisfied as described in Eq.8, Figure 3. 2 [204]

\[ n \cdot \lambda = 2d \cdot \sin \theta \]  
\text{Eq. 8}

where \( n \) is an integer, \( \lambda \) is the wavelength of the X-rays and \( d \) is the interplanar spacing generating the diffraction (\( \lambda \) and \( d \) are measured in Angstroms (Å)) and \( \theta \) is the diffraction angle.

The specimen preparation is very important as it is considered a critical factor influencing the quality of any analytical data.

Samples were prepared by putting the solid powder into the holder, the powder was then slightly pressed so that the powder is stuck onto the holder. Then the solid phase sample was analysed by using an x-ray diffractometer to determine the per cent crystallinity of zeolite in each sample. The crystallinity of zeolite is defined as the ratio of peak area of the intense peaks to the peak area of the intense peaks of reference zeolite (commercial type).
Figure 3.1 Detector and table rotate about origin. Also shown: the X-Ray Diffractometer[203]. A: aperture slit, B: scattered radiation slit, C: Kβ filter, D: detector slit[205].

Figure 3.2 (a-) Reflection from a lattice plan (b-) Schematic representation of Bragg’s law [203].

In this work the x-ray equipment used was a Rigaku Miniflex instrument. Counts were used for zeolite patterns found in the angles between $2\theta = 5^\circ$ - $50^\circ$ with scan speed 1.5 $\theta^\circ$. min$^{-1}$ with a 0.03$^\circ$ step, 30 kV voltage, and 15 mA current longing about 30 min to get a trace.
The most important factors which should be taken into account are described in the following points[204, 206]:

1- The positions of peaks are usually measured in 2θ whose range is from 5° to 50°. This range was enough to cover the most important part of the XRD pattern for all samples to identify the structure. The peaks in the sample should correspond with the peaks in the standard sample.

2- The level of sample crystallization is presented by the relative intensity of the peaks (Irel), it is sometimes not easy to compare the degree of crystallinity of the sample with the reference sample (standard). The most popular relation used to express the calculation of crystallinity is described below in Eq.9 [48, 207].

\[
\text{Crystallinity \% (I=I_o)} = \frac{\sum \text{intensity of XRD peaks of product}}{\sum \text{intensity of XRD peaks of standard zeolite}} \quad \text{Eq. 9}
\]

The widths of peak can give an indication of the size of the crystallite and the quality of the sample.

3- Normally a high level of crystallization in a zeolite sample displays a sharp profile of steep peaks set against a low baseline.

### 2.18.2 Scanning Electron Microscope (SEM)

The first SEM image was generated by Max Knoll in 1935 using an SEM to show electron channels contrast. Further work was performed by Manfred Von Ardenne who produced a British patent in 1937. Later, this apparatus underwent a further modification by Professor Charles Oatley and his postgraduate student Gary Stewart and was first marketed in 1965 by the Cambridge Instrument Company as the "Stereoscan" [62].

A Scanning Electron Microscopic (SEM) can be defined as a microscope which uses a high energy electron beam to produce magnified real images of solid specimens. A range of different types of signals can be generated by a SEM. These signals can be caused by secondary electrons, back-scattered electrons (BSE), characteristic X-rays,
light (cathodoluminescence), specimen current and transmitted electrons. Very high resolution images of a specimen’s surface can be produced by a SEM. The micrographs produced from SEMs have a large depth of field which produces a three-dimensional image that can be used to study the structure of a sample. The order of magnification using a SEM is from 10 to 500,000 times [208]. A series of condensed and objective lenses are used with conventional light microscopes to bend light waves and create a magnified image Figure 3. 3. A SEM uses electrons which are small enough to achieve an extremely high level of resolution.

The microscope has three chambers:

1- The electron gun chamber, which includes the tungsten filament at the top of column. The electron beam is produced from the electron gun by heating the tungsten loop. Thus increasing the kinetic energy of the electrons until they have sufficient energy to escape from the surface. This process is undertaken within a vacuum in order to prevent the formation of unstable electrons and to avoid the ionization of gas molecules. The positive electrode (anode) is used to accelerate the emitted electrons.

2- The electron beam condenser, which occupies the middle of the column, uses a number of a condenser lens to condense the monochromatic electron stream. Additional sets of lenses are used to focus the electrons into an extremely thin, tight and coherent beam. In fact, both the condenser and objective lens are electromagnetic, so the electron beam is controlled in the chamber by a magnetic field produced by the scan coils which also concentrate the electron beam.

3- Finally, in the bottom of the sample chamber, the incident electron beam interacts with the specimen to create a signal. As described before this process produces different reactions. The types of signal can be backscattered electrons, Auger electron, x-ray fluorescence, or secondary electrons. Because the secondary electrons are generated near to the surface of the sample they are able to exit and are then collected by the detector which located close to the sample so as to collect all possible electrons. The detector is used to convert the secondary electron beam into an image with the assistance of a Cathode Ray Tube (CRT). There is an inverse relationship between the magnification (Mag) and the width of the electron beam. An increase in magnification (Mag) has been found to correlate with a decrease in the width of the electron beam,
while the width of the CRT is fixed. The relationship of magnification to electron beam width is described as follows in Eq.10 [209].

\[
\text{Magnification (Mag)} = \frac{\text{Width of the CRT (W)}}{\text{Width of the electron (w)}} \quad \text{Eq. 10}
\]

The surface of the specimen must be conductive to prevent the accumulation of electrostatic charge. Zeolites surfaces are nonconductive, so it is important to coat them with a thin layer of conductive material, such as gold or platinum with a thickness of 1 nanometre. This coating is applied using a sputter counter before putting the samples into the SEM instrument [210].

![Diagram of a Scanning Electron Microscope (SEM)](image)

**Figure 3.3** Main components of a Scanning Electron Microscope (SEM) [57].
2.18.3 Energy Dispersive X-Ray Spectrometer (EDAX)

An SEM instrument can be used to apply EDAX using FEI Quanta 200 ESEM to obtain more specific information by focussing on small portions of the sample to determine the composition of zeolite samples. The results appear as a graph and a table presenting the relative amounts of elements. In addition, regarding zeolite samples, the Si/Al ratio can be calculated from the result aiding characterisation. In fact, the results of both the SEM and EDAX give only results characteristic to the focused part of the sample. The images or relative amounts may vary from place to place on the same sample [211].

EDAX is used in a wide range of applications in fields such as in the chemical, electronic and food industries as well as in refineries with different forms of samples such as solids, powders and frozen liquids. Characterisation of the structure, topography and compositional descriptions of a sample can be collected through the images which result from the back scattered electron and secondary electron signals, as can be seen in Figure 3.4. In the process an energy beam (using a low acceleration voltage) of 20 kV was used on the samples to restrict beam damage and the spectra collected during 60 s. This generated x-ray energy which was measured by the EDAX. X-ray is produced when an electron collides with an atom. This displaces an electron from the innermost shell (K) and generates a vacuum which is, in turn, occupied by an electron from an outer high energy shell (L or M). The differential in the energy between the higher and lower energy shell is released as an x-ray. Thus each element has a distinctive and identifiable wavelength which is measured by EDAX and therefore allows the chemical composition of the sample to be determined. In this study five spots were chosen at random to obtain the average data for the chemical composition of each sample. The elements which were detected in the area of examination appeared in the spectrum as peaks. Table 3.1 shows the interference of some elements due to them very close wavelengths which is considered one of the overlap problems of this technique [212].
Figure 3.4 Electron signals produced from specimen interaction with incident beam.

Table 3.1: Show the interference of some elements using the EDAX technique

<table>
<thead>
<tr>
<th>Element</th>
<th>Interference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti $K_\beta$</td>
<td>V $K_\alpha$</td>
</tr>
<tr>
<td>V $K_\beta$</td>
<td>Cn $K_\alpha$</td>
</tr>
<tr>
<td>Cr $K_\beta$</td>
<td>Mn $K_\alpha$</td>
</tr>
<tr>
<td>Mn $K_\beta$</td>
<td>Fe $K_\alpha$</td>
</tr>
<tr>
<td>Fe $K_\beta$</td>
<td>Co $K_\alpha$</td>
</tr>
<tr>
<td>Co $K_\beta$</td>
<td>Ni $K_\alpha$</td>
</tr>
<tr>
<td>S $K_\alpha$ &amp; $K_\beta$</td>
<td>Mo $K_\alpha$ &amp; Pb $M_\alpha$</td>
</tr>
<tr>
<td>W $M_\alpha$ &amp; $M_\beta$</td>
<td>Si $K_\alpha$ &amp; K$_\beta$</td>
</tr>
<tr>
<td>Ta $K_\alpha$ &amp; $M_\beta$</td>
<td>Si $K_\alpha$ &amp; K$_\beta$</td>
</tr>
<tr>
<td>Ti $K_\alpha$</td>
<td>Ba $L_\alpha$</td>
</tr>
<tr>
<td>As $K_\alpha$</td>
<td>Pb $L_\alpha$</td>
</tr>
<tr>
<td>Sr $L_\alpha$</td>
<td>Si $L_\alpha$</td>
</tr>
<tr>
<td>Y $L_\alpha$</td>
<td>P $K_\alpha$</td>
</tr>
</tbody>
</table>
2.18.4 Dynamic Light Scattering (DLS)

A laser particle instrument (Malvern instrument, Zetasizer 1000 HS) was used in this study to determine the particle size distribution of the fine zeolite particles suspended in solution. Zeolite particle-size distributions were measured using the wet method by mixing with deionised water to disperse them. DLS, also known as PCS - Photon Correlation Spectroscopy, is used to measure the Brownian motion which results from the differential in size and weight between the particles. Brownian motion can be defined as the continuous motion of particles resulting from the random collision of molecules in a liquid or gas. This was first discovered in 1827 by the Scottish botanist Robert Brown when he noticed the movement of pollen grains in water was irregular [213]. The DLS technique involves passing a laser beam (light) through the solution containing fine particles, and measuring the intensity of the scattered light, as shown in Figure 3.5. The size of the particles can be calculated by measuring the rate of the intensity fluctuation using a component called a digital correlator which has the ability to measure the degree of similarity between two signals over a period of time. The digital correlator is part of the Zetasizer Nano system.

![Diagram shows the particles scatter the light towards the detector.](image)

Figure 3.5  Diagram shows the particles scatter the light towards the detector.
CHAPTER THREE CHARACTERISATION TECHNIQUES

Diffusion coefficient values are found due to the variations in the intensity of the scattered light. The diffusion coefficient can be calculated by Einstein’s equation, Eq.11:

\[ X = (2Dt)^{1/2} \]  

where: \( X \) = displacement of a particle along a given axis, \( D \) = diffusion coefficient and \( t \) = time of displacement from original position.

In fact, large particles move slowly, while smaller particles move quickly. According to Brownian motion, the Stokes-Einstein equation, Eq.12, can be used to demonstrate the relationship between water's molecular radius and the speed of particles [214].

\[ D = \frac{RT}{6\pi\eta rN_A} \]  

where: \( R \) = gas constant, \( T \) = absolute temperature, \( \eta \) = dynamic viscosity, \( r \) = water's molecular radius and \( N_A \) = Avogadro’s number.

In this study the Malvern instruments Zetasizer 1000 HS with a 10mm light bath was used. A 3 mL polystyrene cuvette was used to contain the diluted samples.

2.18.5 Inductively Coupled Plasma Spectroscopy (ICP)

The use of an Inductively Coupled Plasma - Optical Emission Spectrometer (ICP-OES) is a technique employed to determine element concentrations in a solution relative to a standard reference. In addition, this technique can be used to analyse a wide range of naturally occurring materials such as water, sediments, soils, rocks and minerals. A spectroscopic source is used to determine a wide range of major and trace elements in a single, short integration period with a dynamic linear range and moderate to low detection limits (~0.2-100 ppb). The main components of the ICP-OES are the nebuliser, spray chamber, ring torch, radio frequency generator and detector as seen in Figure 3. 6 [215].
Figure 3.6 Shows the major components and layout of a typical ICP-OES instrument [215].

The ICP has the ability to differentiate the sample into its component atoms or ions. This process is achieved by causing an electron to jump first to a higher orbital (absorbing electromagnetic radiation gives it a higher energy level) and then to return to its current orbital by emitting a photon (hv) at a characteristic wavelength. The process of excitation by high heat sources used in the OES enables it to mobilize a wide range of different energy levels from different elements concurrently. The radiation emission of these atoms or ions can be characterised at the approximately same time. This is considered one of the major advantages of the ICP-OES because it can measure more than one element at same time due to the excited atoms and ions producing a number of different emission wavelengths indicative of different elements. However, the increase of emission wavelengths can lead to an increase in the interference between very close wavelength values which would mean they should be measured separately. This is the main disadvantage for this technique. The content of each element in the analysed sample is determined in proportion to the rays' intensity [215].

Basically, the ICP-OES works based on the following steps [216]:
1- The solution is pumped into the nebuliser using a pump to convert it into small droplets (aerosol).

2- These aerosol droplets are carried through the spray chamber to the torch injector and then into the plasma (generated using argon gas) section respectively.

3- Then the atoms are excited using the high temperature of the plasma (ca. 8000 K) and then they emit light to return to their ground state (stable state).

4- The collected light is directed to the spectrometer and then amplified to measure the light intensity, the element concentration can then be determined by comparison with a calibration source, Figure 3. 7 shows the details. The calibration curve should be prepared before the sample measurement and should be suited to the instrument’s range (0-60 mg.L⁻¹).

Figure 3. 7 Shows the calibration curve of the ICP-OES presenting emission counts vs. concentration (mg.L⁻¹).

In this study calibration curves were prepared for two elements (Co²⁺ and Sr²⁺ ) from 1000 mg.L⁻¹ Aldrich ICP standard solutions and analysed using an ICP-OSE model Vista-MPX by Varian. Following a water treatment process, the samples were filtered to remove the fine particles of zeolite. 5 and 15 mg.L⁻¹ solutions of each elements ( Co²⁺ and Sr²⁺ )were prepared for the calibration curve from the 1000mg.L⁻¹ standard solutons. A pure water sample was measured, then the standard solution was measured to prepare the calibration curve, and finally the samples were measured to calculate the
concentration with a 228.3 nm wavelength for Co$^{2+}$ and 238.9 nm for Sr$^{2+}$. The calibration process was repeated after every 20 samples.

2.18.6 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is a technique used to measure the change (increase or decrease) of sample mass due to temperature or over time, at first in the presence an inert gas such as N$_2$ or Ar to slow down oxidation and then in air (controlled atmosphere). This analysis is used primarily to determine: the thermal stability at temperatures of around 1000°C; the approximate lifetime of a sample; the decay kinetics of materials, the moisture and volatiles content of materials; the composition of materials. A TGA involves a precision balance used to support a sample pan (ceramic or platinum) which is located inside a furnace to be heated or cooled as well as a reference balance pan out of the furnace [217], Figure 3. 8.

Temperature calibration is one of the most important steps to be done periodically for the thermo balance because it is considered to be the heart of the TGA analyser. Also important are the balance and furnace calibrations which are responsible for measuring the sample mass as a function of temperature and time [217].

**Equipment and Experimental Conditions**

Thermogravimetric analyses of samples were performed in this study using TGA (Q5000-0041 IR) to determine weight change of zeolite-carbon composites to estimate the amount of zeolite in samples due to the composition of carbon materials by taking the difference in sample’s weigh before and after TGA analysis. The sample, with a weight of between 2 and 50 mg (the sample should weigh at least 1mg to be run) was loaded into a ceramic crucible, then the sample was spread evenly over the bottom of the ceramic pan to increase the surface area of the sample. The samples were heated at a rate of 10°C/min in two ramps. The first ramp under an N$_2$ atmosphere (N$_2$ flow rate was 25 cm$^3$/min) raised the temperature from room temperature to 400 °C in order to study the change in zeolite-carbon composition due to water desorption. The second
ramp was programmed under an air atmosphere from 400 to 600 °C to determine the amount of zeolite in each sample due to the carbon being completely burned away, after that the temperature was dropped down to room temperature [217, 218].

Figure 3. 8 (a) - Schematic diagram for the TGA (b) - Top view of sample pan being loaded into furnace.
2.18.7 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM) was first developed in Germany in 1931 by Max Knoll and Ernst Ruska. It is a microscopy technique that uses electrons as an energy source instead of light to interact with a thin specimen. Electrons were suggested due to the limitations of the images given by the wavelengths of light. The wavelength of an electron is much smaller than wavelength of light, thus giving high resolution images a thousand times better than microscope images using light waves[209]. The high resolution and magnification of TEM images have resulted in this technique being used in physical, medical and biological sciences for many purposes, such as the study of morphology, crystallography and element composition [219]. Figure 3. 9 shows the TEM diagram. Electrons are emitted from the source located at the top of the microscope. The electrons travel through the microscope in a vacuum column. The very thin electron beam is focused by electromagnetic lenses and then passes through a very thin specimen before hitting a fluorescent screen which is positioned at the bottom of the microscope[209, 220]. Some electrons are be lost from the beam because the scattering due to the specimen’s density. The remaining unscattered electrons hit the fluorescent screen giving a shadow image of the sample [221]. TEM analysis was used during this research project to monitor the shape and size of the nano-particles of zeolite Y in a zeolite colloidal solution which was prepared to be used as a seed (next chapter).
2.18.8 Nitrogen adsorption (Physisorption)

Gas adsorption can be used to measure the specific surface area of materials and was published for the first time in a journal in 1938 by Stephen Brunauer, Paul Hugh Emmett and Edward Teller, referred to by the initials of their family names (BET). Furthermore, they extended the explanation for Langmuir’s theory of adhered gas molecules (adsorbate) for solid phases of the adsorbent for the new isotherm model which was developed by Irving Langmuir in 1916 [222]. Figure 3. 10Figure 3. 10 shows both ideas of adsorption: Langmuir (a) and BET (b). In his theory Langmuir made some assumptions for gas adsorption on solid surfaces: the surface area is uniform and all sites have the same adsorbent properties (equivalents); there is no interaction between the substances (adsorbates); these substances are deposited evenly onto the adsorbent; they create a monolayer at maximum adsorption, meaning the molecules are only found on the free sites of an adsorbent surface. The BET theory assumes that multilayer adsorption occurs [223].

Figure 3. 9 Transmission Electron Microscope (TEM) with all of its components [229].
Figure 3.10 The adsorption of gas onto the surface of a sample according to (a) the Langmuir theory (monolayer adsorption) and (b) the BET theory (multilayer adsorption model).

A specific surface area (SSA) is a very important factor which can give information about the material characterisation such as quality, structure, potential usage in applications and its formation. This can be obtained from the BET equation (13) which can be used to determine the specific surface area $m^2/g$ of materials [222]

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m} + \frac{c-1 P}{V_m C P_0}$$  \hspace{1cm} \text{Eq. 13}

where:
- $P$ is the absolute pressure,
- $P_0$ is the Saturation pressure,
- $V_a$ is the adsorbed volume,
- $V_m$ is the monolayer volume and
- $C$ is a constant.

Then, $V_m$ will be used to calculate the specific surface area ($S_{BET}$) using equation (14)

$$S_{BET} = \frac{V_m n_a a_m}{m V_L}$$  \hspace{1cm} \text{Eq. 14}

where:
- $n_a$ is Avogadro’s constant,
- $a_m$ is the cross-sectional area occupied by each nitrogen molecule (0.162 nm$^2$).
m is the weight of the sample and 

$V_L$ is the molar volume of nitrogen gas.

Adsorption isotherm graphs are usually used to study the adsorption process. These graphs describe the amount of the substance (adsorbate) on the solid surface (adsorbent) at a constant temperature as a function of its pressure or concentration. An inert gas is usually used in conducting physical gas adsorption, the most commonly used is $N_2$ due to its availability in high purity, its ability to interact strongly with a wide range of solids and to be adsorbed onto the outside of a solid surface. Samples are first pretreated in vacuum conditions or under a flowing gas before being measured at an elevated temperature to remove any wet or volatile contaminants. In addition, liquid $N_2$ is used to cool the solid surface of the adsorbent (because of the weak interaction between the gas molecules on the solid surface) in order to obtain detectable amounts of adsorption. Nitrogen gas is introduced gradually in known amounts (dosing) into the specimen cell. Through the use of a partial vacuum a point at which a relative pressure (less than atmospheric pressure) is reached, after attaining saturation pressure the adsorption will increase with increasing pressure. Adsorption layers will be formed. The sample, after being removed from the nitrogen atmosphere is then heated, increasing the temperature, in order to separate the nitrogen molecules adsorbed from the adsorbent surface (desorption) [224]. The collected data is shown in the form of a BET isotherm by plotting the volume of adsorbed gas versus relative pressure, Figure 3.11.

![Figure 3.11 N$_2$ adsorption–desorption at 77 K isotherms of Sextonia rubra[225].](image)

**Figure 3.11** N$_2$ adsorption–desorption at 77 K isotherms of Sextonia rubra[225].
There are six categories of the adsorption isotherm as illustrated and summarised in Figure 3. 12 [223-226].

A Type I isotherm is a monolayer adsorption obtained when the relative pressure \( (P/P_o) \ll 1 \) and the BET constant \( (C\text{-value}) \gg 1 \) which is presented in Equation (13). The curve shows that the inflection point occurs after a short interval of \( P/P_o \) due to the narrow pore size range followed by a horizontal section which gives an indication of very low adsorption and small external surface area due to the saturated pores on the outer surface. This is characteristic of microporous solids.

A Type II isotherm refers to multilayer adsorption and is characteristic of nonporous or macroporous adsorbents. Two inflection points occur in this type over the flatter region of the intermediate isotherm with no observation of a hysteresis loop. The first inflection point results from the coverage of the initial layer of surface and the second by the adsorption into multilayers. The BET constant \( (C\text{-value}) \) in the BET equation has to be \( > 1 \).

A type III adsorption isotherm corresponds to multilayer adsorption where not horizontally area is observed, which means no monolayer is formed. In this type the BET constant \( (C\text{-value}) \) in the BET equation is \( << 1 \) and is characteristic of nonporous sorbents with little affinity for adsorbent-adsorbate interaction.

A Type IV isotherm displays the same as behaviour as a Type II, while a Type V is similar to a Type III but at lower pressure. A hysteresis loop is presented in both cases due to the filling and emptying of pores. Types IV and V have two inflection points which means they have monolayer followed by multilayer adsorption. The horizontally regions in the isotherm graphs indicate monolayer formation. The phenomenon of the capillary condensation of gas occurs in both types and will lead to condensed gases in the tiny capillary pores of the adsorbent at pressures below the saturation pressure of the gas. These Types are characteristic of mesoporous systems.

A Type VI isotherm is a stepwise isotherm, not widespread and occurs only with highly homogeneous, nonporous solid surfaces.
Figure 3.12 Shows the six types of adsorption isotherm.

**Equipment and Experimental Conditions**

Nitrogen adsorption equipment (ASAP 2010 model) was applied to measure the specific surface area for zeolite samples in mg/m². Samples were first degassed overnight at 350 °C prior to any measurement. This removed unwanted vapours and gaseous containments and required a sample of minimum weight 0.1g to be placed in a glass cell. The dead space in glass cell was minimized by putting a glass rod inside it. After the degassing process the glass cell was transferred to the analyses port. The sample was cooled down using liquid N₂ dewar to maintain a constant low temperature for a good interaction between the adsorbate gas and the adsorbent sample. Then, the nitrogen gas is injected into the sample cell with a calibrated piston. The dead volume of the sample was used to calibrate the cell before and after each measurement using He gas because it does not interact with the sample. This process is carried out at 77K and the resulting N₂ adsorption and desorption graph is known as an adsorption-isotherm.
CHAPTER FOUR

PREPARATION OF CELATOM-ZEOLITE COMPOSITES
CHAPTER FOUR

PREPARATION OF CELATOM-ZEOLITE COMPOSITES

4. SYNTHESIS OF CELATOM/ZEOLITE-Y HIERARCHICAL POROUS MATERIAL

In this study, crystals of zeolite A and Y were incorporated onto celatom FW-14 surfaces, while zeolite A, Y and clinoptilolite were also deposited onto two types of carbon from two different sources- Iraqi Palm tree Leafs (IP) and Tamarind stones (TS) to build a hierarchical structure. The hierarchical structure of carbon-zeolite (C-Z) will be discussed in next chapter. These new composite structures of macropores/micropores, C-Z and Cel-Z, are suggested as a method to overcome the diffusivity problem of powdered zeolites [38, 39].

In this chapter celatom frustules were used to support two types of zeolite separately (A and Y) to build the hierarchical structure composite materials as mentioned in the previous chapters.

Zeolite type A and zeolite Y were successfully prepared in this study. XRD, SEM and EDAX characterisations of both zeolites were also carried out (see Appendix A and B for pure zeolite A and Y respectively).

4.1 CELATOM/ZEOLITE-Y COMPOSITE (CEL-ZY)

The synthesis of zeolite-Y was carried out in two main steps,

1- Syntheses of colloidal zeolite-Y as seeds using two methods,
   a- Colloids of zeolite-Y were made hydrothermally.
   b- Solution of fine crystal particles of zeolite-Y was made using a ball mill from a commercial zeolite-Y source.

2- Crystal growth of zeolite-Y onto celatom surfaces.

The synthesis of zeolite-Y on a diatomite surface reproduced the work by Anderson, Holmes and Hernandez [139, 157].
**4.1.1 Synthesis of Colloidal Zeolite-Y Seeds**

The molar composition of zeolite-Y seeding gel is shown in Formula 1 [139]:

\[
2.46 \text{ (TMA) } _2\text{O} : 0.032 \text{ Na}_2\text{O} : 3.4 \text{ SiO}_2 : 370 \text{ H}_2\text{O} : 13.6 \text{ EtOH} \quad \text{Formula 1}
\]

The calculation process was carried out to prepare the required amounts of chemical materials from the gel composition in Formula 1. Table 4.1 shows details of chemicals materials the suppliers and amounts.

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass (g)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td>0.13</td>
<td>Aldrich</td>
</tr>
<tr>
<td>TEOS (C(_8)H(_20)O(_4)Si)</td>
<td>35.5</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>TMA(_2)O (C(_4)H(_12)N.OH)</td>
<td>89.7</td>
<td>Aldrich</td>
</tr>
<tr>
<td>C(_9)H(_21)AlO(_3)</td>
<td>20.40</td>
<td>Aldrich</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>360</td>
<td>------</td>
</tr>
</tbody>
</table>

Sodium hydroxide pellets were used to prepare the alkaline media with the preparation procedure for the other types of zeolite. Tetraethoxysilane (C\(_8\)H\(_20\)O\(_4\)Si) TEOS, was used as silica source as shown below in Eq.15.

\[
\text{Si (OC}_2\text{H}_5)_4 + 2 \text{ H}_2\text{O} \rightarrow \text{SiO}_2 + 4 \text{ C}_2\text{H}_5\text{OH (EtOH)} \quad \text{Eq. 15}
\]

The aluminium source was provided by aluminium isopropoxide (C\(_9\)H\(_21\)AlO\(_3\)). While the template source was tetramethylammonium hydroxide TMA\(_2\)O (25Wt% solutions) (C\(_4\)H\(_12\)N.OH).

A template solution was then prepared by dissolving 90 g of (TMA)\(_2\)O in 360 mL of water. The template solution was divided into two equal halves. A 0.13g of NaOH was dissolved in one half of the template solution. This was then followed by adding 20.4 g of aluminium isopropoxide and it was also stirred to ensure good mixing. The second precursor was prepared by dissolving 35.5g of silica (TEOS) in the second half of the
template solution. The two solutions were mixed and stirred for 24h until a clear homogenous solution was obtained.

The Teflon-lined autoclave was prepared and the homogenous solution was transferred into it to fill two-third volume. The autoclave was sealed and put in an oven for six days at 100°C for synthesis to take place.

The solution was dialyzed in large excess of de-ionised water for two days as shown in Figure 4. The water was changed four times until a pH in the range of below 9 was obtained. A small sample of colloidal zeolite-Y was dried to determine the solid percentage (wt %). XRD analysis, SEM and TEM images of the samples were used to verify the crystalline structure.

![Image](image_url)

**Figure 4. 1 Dialyses Process for colloidal zeolite-Y for 2 days (Dialysis Tubing – Visking size 10 inf Dia. 1.25” - 31.7mm: 15m (approximately) MWCO-12-14000 Daltons).**

4.1.2 Seeding Process

An ultrasonic bath, shown in Figure 4. 2, was used for 6h to disperse and attach the fine particles of the colloidal zeolite-Y seeds evenly on the celatom FW-14 surfaces (supplied by Aldrich), using 20:1 Celatom/Zeolite-Y colloidal weight ratio. Figure 4. 3 shows the SEM of celatom image with organised distribution of pores.

This process (sonication) forces the particles in the mixture to move and can hit or attach the surface of celatom by electrostatic effects. This process can assist to create active sites to grow zeolite Y [38]. After that, the mixture of the seeded celatom was left to dry overnight at 50°C before the hydrothermal treatment.
Figure 4. 2 Schematic diagram ultra-sonic bath [227].

Figure 4. 3 Raw celatom FW-14 (Scale bar=20 µm).
4.1.3 Crystal Growth of Zeolite-Y onto Celatom Surfaces.

The growth gel of zeolite-Y was prepared from the initial composition of Formula 2 [139].

\[
14 \text{ Na}_2\text{O} : \text{Al}_2\text{O}_3 : 10 \text{ SiO}_2 : 798 \text{ H}_2\text{O} : 3 \text{ Na}_2\text{SO}_4 \quad \text{Formula 2}
\]

The silica source was sodium metasilicate. Sodium hydroxide and aluminium sulphate octadecahydrate were used respectively as alkaline and aluminium sources, of the gel composition. Table 4. 2 show the amount of each material for the formation of the growth gel.

**Table 4. 2 Shows crystal growth ingredients, amounts and suppliers.**

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass (g)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td>0.5</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Al₂(SO₄)₃·18H₂O</td>
<td>0.28</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Na₂SiO₃·9H₂O</td>
<td>0.24</td>
<td>Aldrich</td>
</tr>
<tr>
<td>H₂O</td>
<td>5.6</td>
<td>---------</td>
</tr>
<tr>
<td>Celatom FW-14 (seeded)</td>
<td>0.20</td>
<td>Aldrich</td>
</tr>
</tbody>
</table>

Celatom FW-14 was used as silica source due to its high silica content using Celatom: Silica molar ratio of 4:1. The estimate of Si content in celatom structure was approved using EDAX. It was assumed that celatom was made entirely of silica in the syntheses gel Formula 3:

\[
30 \text{ NaOH} : \text{Al}_2(\text{SO}_4)_3 : 18\text{H}_2\text{O} : 2\text{Na}_2\text{SiO}_3 : 9\text{H}_2\text{O} : 8\text{SiO}_2 : 747\text{H}_2\text{O} \quad \text{Formula 3}
\]

De-ionised water with 5.6 g was weighed and divided into two equal parts. 0.5 g sodium hydroxide was weighed and added into one of the water portion under stirring; 0.28 g of aluminium sulphate octadecahydrate powder was weighed and added to the
sodium hydroxide solution in a plastic bottle to make the first precursor. The plastic bottle was sealed and the mixture was stirred for 10-15 min. 0.24 g of sodium metasilicate was used to prepare the second precursor by dissolving in the second half of water. The first and second precursors were mixed and stirred for 2h in the plastic bottle. Then the mixture was transferred to the Teflon-lined autoclave for hydrothermally processes. At this stage 0.2 g of seeded celatom FW-14 was added to the each mixture. The mixture was added to fill two-third volume of the autoclave, sealed tightly and left in the oven for 75, 120 and 180 minutes at 100°C to investigate the gradual growth of the zeolite crystals.

Figure 4.4 Schematic diagram of preparation composite of Celatom/zeolite-Y.
This process is shown in the schematic diagram of zeolite synthesis in Figure 4. The autoclaves were taken out of the oven and left to cool down for 20 minutes. The autoclaves were opened and the content washed with de-ionised water until pH < 9, filtered and dried overnight at 50°C. The dried sample were analysed by powder diffraction (XRD) and Scanning Electron Microscopy (SEM).

**4.2 COLLOIDAL ZEOLITE-Y**

**4.2.1 Results and Discussion of Synthesis Colloidal Zeolite-Y.**

The gel composition remained inside the autoclave heated for 6 days. A cloudy solution was obtained, and then the product was dialysed for 2 days with a pH value of < 9. The concentration of dried particles in the mixture was 0.75% in average, after drying small amount of the colloids solution overnight at 50°C. The X-ray diffraction pattern for the dried colloid zeolite-Y showed reflection peaks of faujasite at 6.31°, 10.31°, 12.1° and 15.61° as shown in Figure 4.5. The hump in the 2θ° range between 20°-30° was the amorphous [39].

The Transmission Electron Microscopy (TEM) and Dynamic Light Scattering (DLS) were used to investigate the morphology of colloidal-Y, such as the particle size and uniformity. As shown in Figure 4.6, the average particle size was found to be about 80 nm using DLS. Figure 4.7 shows the TEM image of the colloid after putting small amounts of colloidal zeolite-Y on the sample holder and drying at room temperature for 24h. The TEM image showed uniformity in crystal size and has presented a good comparison with the result of DLS.
Figure 4. 5 Shows the XRD pattern of colloid zeolite-Y in comparison with pure zeolite-Y.

Figure 4. 6 Particle size distribution of colloidal zeolite-Y obtained through dynamic light scattering (DLS).
Figure 4.7 Colloidal zeolite-Y crystals in cubic shapes were observed through the TEM (scale bar =50 and 100 nm).

4.2.2 Seeded Celatom

The colloidal zeolite-Y mixture which prepared synthetically was used as seed solution, having a concentration of 0.5-1.00%. The 20:1 (Diatom/Colloidal zeolite-Y) weight ratio was suggested by Dr. Cundy [39]. It was found that 2% seeded ratio is too low to support the crystal formation, while 10% or more will not make an improvement to the crystal growth [139]. This ratio should be equivalent to 5% of the total weight of
celatom. It is used to encourage and improve the crystal growth on the Diatom surface (celatom FW-14).

Figure 4. 8a shows the SEM image for celatom FW-14 before sonication process. The SEM images appeared very uniform before hydrothermal process and the crystal of seeds were clearly can be noticed between the holes. According to the wide pores size of the celatom surfaces in comparison with the nano-particles colloidal zeolite-Y, these help the fine particles of the colloidal zeolite-Y which were used as a seed to pass inside the celatom body. In addition, the SEM images, Figure 4. 8b, shows that celatom surface have rough surface generated after sonication process for 6h (for additional images see appendix C). This may be due to the collision of the zeolite seeds on the celatom surface during sonication and it is suggested that these rough surfaces may assist to growth zeolite particles onto celatom surfaces as it may form points of attachment.

Figure 4. 8 Celatom FW-14 (a) - without seeded and (b) - with colloidal of zeolite-Y seeds after 6h of sonication using high resolution SEM (Scale bar=200 and 500nm).
4.2.3 Hydrothermal Growth of Zeolite-Y onto Celatom surface

The XRD pattern of pure celatom is shown in Figure 4.9 with the main peak at 22° of 2θ°. The XRD pattern of the Cel-ZY composite shows the characteristic reflections of zeolite-Y at 2θ°= 6.12°, 10.31°, 12.1° and 15.61°, while, the peak at 22° as shown in same figure is referring to celatom FW-14 (SiO₂). This peak still remained with good reflections after 75, 120 and 180 min of hydrothermal treatment at 100°C. This gives an idea that celatom is still found after hydrothermal treatment without damage to its structure.

The elements of pure celatom were identified using EDAX showing high quantity of silicon in its structure as shown in Figure 4.10. In addition, it is shown, after 75 minutes of hydrothermal treatment that the significant peaks of zeolite-Y have not clearly appeared. This indicates no growth of crystal was obtained, while good reflections of faujasite peaks have appeared clearly after 2h. This result demonstrated that the gradual growth of zeolite-Y happened between 75 to 120 min, this was also reported by Holmes and O. Hernandez [39, 139] which indicated that the gradual growth of zeolite-Y started nearly after 90 minutes. After 3 h of synthesis, the reflection peaks of zeolite-Y diminished as it outgrew the maximum stage of crystallization and started to dissolve. Holmes and Hernandez stated that the optimum time for synthesis 0.2 g of celatom is 2h [39, 139].

The SEM images show the morphology of pure celatom before the hydrothermal treatment (see Figure 4. 3) with uniform rows of pores. While Figure 4.11 shows the gradual growth of zeolite crystals after 75, 120 and 180 min at 100°C of synthesis process. Celatom retained its macropore structure, which can be seen clearly in SEM images.
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Figure 4.9 The XRD pattern shows the gradual growth of zeolite-Y combined with the diffraction pattern of Celatom. Samples treated in Teflon autoclaves at 100º C with different crystallization times 75 minutes, 2h and 3h respectively. (Silica: Celatom ratio= 2.3)

<table>
<thead>
<tr>
<th>Position [°2Theta]</th>
<th>Counts</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZYCaut3hr</td>
<td></td>
</tr>
<tr>
<td>ZYCaut2hr</td>
<td></td>
</tr>
<tr>
<td>ZYCaut75min</td>
<td></td>
</tr>
<tr>
<td>2hr</td>
<td></td>
</tr>
<tr>
<td>75 min.</td>
<td></td>
</tr>
</tbody>
</table>

Element  Wt %
---------  ------
OK        40.45
Na K      1.56
Al K      1.63
Si K      50.67
Ca K      0.47
Fe K      1.13
C K       4.08
Total     100.00

Figure 4.10 EDAX spectrum showing the high amount of Si in the Celatom-FW14 structure.
Figure 4.11 SEM images showing the gradual growth of zeolite-Y on the surface of celatom. Samples treated in Teflon autoclaves at 100°C with different crystallization times (a) 75 minutes (b) 2h and (c-d) 3h. (Scale bar=20 µm).
4.3 BALL MILLED ZEOLITE AS ALTERNATIVE SEEDING AGENT

4.3.1 Preparation of Zeolite A and Y Seeds Using Ball Mill Method

A ball mill was used to grind two types of commercial zeolite separately:

1. Commercial zeolite-A (0.5-5 micron diameter average supplied by PQ Corporation).

Ball mill is a very important apparatus and it is used in lots of industries such as food processing, fuel preparation and mineral preparation. In addition, it has a simple procedure to use [228, 229].

In this experiment ceramic bead (zirconium oxide) balls were used to reduce the size of crystal’s particles of zeolites. The ball mill, shown in Figure 4.12, rotate horizontally and the materials are ground together with grinding media. The mechanical treatment process was started by using 1mm diameter ceramic beads as a grinder media in order to prepare colloidal zeolite solution to be used as a seed to achieve growth of zeolite onto celatom surfaces. In addition, it was considered more economic than synthesis of the colloidal seeds in cost, time and energy as studied in the previous section (4.1.1) [38, 139].

A 125 mL bulk volume of commercial zeolite (equivalent to 62g) were mixed with a 125mL volume of water and placed into the grinder including 250 mL bulk volume of grinding media for 24h. The bulk of commercial zeolite and water is added so that it is a little bit more than the voids sandwiched between the balls (for proper grinding balls not exceeding 50% of the mill capacity are used). A 500 mL plastic bottle (3 cm inside radius) was used at speed of 173 rpm (the speed of the ball mill used in this study was calculated based on the empirical formula, Eq.16 [37, 38, 230].

\[ v = \frac{54.19}{\sqrt{r}} \]  

Eq. 16

where \( v \) is the speed ( rpm) and \( r \) is the mill radius (ft).
The product of fine particles of the zeolite was left to settle in solution for 3 days to give chance for the large particles to settle. Then the upper layers of solutions were collected due to suspension of the fine particles in it. The procedure of ball milled in case of zeolite-A is described in Figure 4.13. After that, the mixture was sieved to separate the grinding media. The remaining commercial zeolites were characterised using XRD powder diffraction and SEM after drying a small amount overnight at 50°C to investigate the effectiveness of the grinding on the crystallinity and morphology of the zeolite structure. The average size of the fine particles of each type of zeolite was measured using DLS.
Figure 4. 13 Shows the procedure for ball mill grinding of zeolite-A.

4.3.2 Seeding Process and Hydrothermal Treatment

A nano-crystal solution of zeolites were prepared by grinding a commercial zeolite-Y (supplied by PQ Corporation) for 24-38 h using 1 mm ceramic beads (zirconium oxide) ball mill grinders, while zeolite-A powder was grinding for 24 h.

The ground products of commercial zeolite-Y and A were left separately to settle down for more than 3 days, then the upper layer of the suspensions were taken out and diluted with deionised water to be used for seeding diatomite by using the same procedure of seeding which is mentioned in Chapter 4 (section 4.1.2), as well as reported in our previous work of seeded carbon [38]. Dynamic Light Scattering (DLS), XRD and SEM were used to characterise the fine particle size of ground zeolites in solution. BET
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surface area for the Cel-ZY composite was measured using nitrogen adsorption. For the seeding process the ground zeolites were distributed and attached onto celatom surface using 6h sonic-bath using 20:1 of Celatom: zeolite solution weight ratio.

4.4 RESULT AND DISCUSSION

4.4.1 Preparation of Zeolite-Y Crystals onto Celatom Surface

Hydrothermal treatment was applied using the same molar ratio of synthesised zeolite-Y solution (Formula 2) section 4.1.3 as seen below:

\[
30 \text{NaOH} : \text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} : 2\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O} : 8 \text{SiO}_2 \cdot 747\text{H}_2\text{O} \quad \text{Formula 2}
\]

The silica sources were sodium metasilicate and seeded celatom FW-14, while the sodium hydroxide and aluminium sulphate octadecahydrate were used as sources for the remaining elements. Sodium hydroxide was used to provide the alkaline medium and as cation source. Table 1 in section 3.6.3 shows the amount of each ingredient for the formation of the growth gel [138]. Figure 4.14 shows the XRD pattern of the ground zeolite seeds compared with the original of commercial zeolite-Y and the dried fine particles of suspension solution to study the structure of the ground product. This figure shows all peaks of zeolite-Y still appeared with good reflections and the crystals were not affected by the grinding and still had uniform shape.

The SEM images of the commercial zeolite-Y before and after milling are shown in Figure 4.15 and from this, it can be confirmed that the morphology of the crystals was not affected by grinding.
Figure 4.14 XDR for dried commercial zeolite-Y after 32, 38 hr and dried fine particles zeolite-Y (suspension) after 38h ball milled

Figure 4.15 SEM of (a) - Commercial zeolite-Y (b) – Bulk of the ball milled commercial zeolite-Y after 32 hr. (Scale bar=5µm).

The ball milled zeolite-Y was characterised using DLS (Figure 4.16) to estimate the particle size of zeolite crystals. The average particles size was obtained as 140nm. Similar study was performed by Hernandez (2009) [39] and the results showed particles size between (160-195) nm within average size 180nm for 24h grinding time. The difference between the two results can be attributed to increasing the grinding time in this study to 32-38h.
4.4.2 Hydrothermal growth and seeding of Celatom: Colloidal Zeolite-Y

A 4:1 Celatom: Silicon weight ratio was used in this experiment as a support and silica source, while Celatom: Zeolite-Y seed weight ratio was 20:1 [38, 39, 139]. The same procedure with synthesised colloidal zeolite-Y in the previous experiment was followed.

The XRD pattern of Cel-ZY composite using ball mill seeds, Figure 4.17a, shows slightly lower reflection of zeolite-Y at peak positions compared with Cel-ZY composite obtained from the synthesised seeds. This was suggested that the large particles were not attached onto celatom surface during sonication process. On the other hand, these peaks were proved that the successful seeding process due to incorporated zeolite-Y onto celatom surfaces. Comparing the XRD pattern with that from previous experiment, synthesised colloidal zeolite-Y after 3h hydrothermal treatment at 100°C as shown in same figure (Figure 4.17 a and b). The peaks of zeolite-Y are appeared similar to the peaks resulting from the ball mill process. Both methods were shown low intensity; these results may be due to the lower amount concentration of zeolite-Y.
From the SEM image of the celatom surfaces after sonication process as shown in Figure 4. 18, it cannot be easily recognised the crystals of fine particles of zeolite-Y.

Figure 4.17 XRD of celatom-zeoliteY composites after3h hydrothermal treatment at 100°C resulting from (a-) ball milled commercial zeolite-Y as seed (b-) synthesised colloidal zeolite-Y as seed

Figure 4. 18 Shows not clear surface to identify the fine particles of zeolite Y onto celatom surface after seeding process (Scale bar=20µm).
Both products of Cel-ZY composite were coated with zeolite-Y successfully. Figure 4.19 shows the SEM image of the composite after hydrothermal treatment for 3h at 100°C using ball milled process. Those crystals were completely coated on the some of celatom surfaces through the synthesised colloidal zeolite-Y as seen in previous experiments in Figure 4.11. The same result was noticed by O. Hernandez [39] where the experiment showed the crystals were grown in larger size through ball milling than the crystal yield from synthesised seeds due to the relationship between the size of seeds and the final product [39] While, in the same figure (Figure 4.19) some celatom surfaces in the composite product were not completely coated with zeolite-Y crystals. That was suggested due to distribute the fine crystal of zeolite-Y randomly onto celatom surfaces during seeding process.

BET surface area for the Cel-ZY composite was found to be 26.84 m².g⁻¹ as a type IV (see Chapter 2 Section 2.18.8) using nitrogen adsorption, this value was below the values of celatom-ZSM-5 composite (45.4 m².g⁻¹) which reported by Anderson and Holmes and later by Oscar and Holmes (29.2 m².g⁻¹) for Cel-ZY composite [139, 157]. While the BET surface area shows that pure synthesis zeolite Y has 327 m².g⁻¹. The lower values in the cel-ZY composite may be back to the lower amount of ZY onto celatom surfaces (~33% ZY). Figure 4. 20 shows the flat curves and the narrow hysteresis loop of sorption/desorption isotherm of the Cel-ZY composite.
Figure 4.19 SEM image for celatom/zeolite-Y after hydrothermal process using ball milled in different scale and different magnification (Scale =20 µm).
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4.5 ZEOLITE A GROWTH ONTO CELATOM SURFACE

The hydrothermal treatment was applied to prepare celatom/zeolite-A composite (Cel-ZA). The gel composition which is described in Formula 4 was used to prepare Cel-ZA composite using the same molar ratio of syntheses zeolite A (see appendix A).

In this experiment, Celatom FW-14 was also used for two purposes, first as silica source, second as a support material for zeolite-A using 4:1 Celatom:Silica molar ratio as mentioned in same Chapter, section 4.3.1 [39]. It was assumed that the silica in the celatom provides the some of the silica requirement for zeolite-A. The amount and ingredient of this batch is shown in Table 4.3. The silica molar ratio in Formula 4 [233] has been changed to be Formula 5.

\[3.1 \text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 1.9\text{SiO}_2 : 128\text{H}_2\text{O} \quad \text{Formula 4}\]

Changed to

\[3.1\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 0.385\text{Na}_2\text{SiO}_3 : 1.54\text{SiO}_2 : 128\text{H}_2\text{O} \quad \text{Formula 5}\]
The crystallization of zeolite-A was carried out in a Teflon-lined autoclave. The synthesis was carried out at 100°C in a stainless steel under autogenous pressure. Zeolite-A was synthesized hydrothermally using sodium aluminate as the alumina source. Sodium metasilicate was used as silica source and sodium hydroxide as alkaline and cation source. Zeolite-A was synthesized by adding 4.7 g of NaOH as a source of Na₂O to 150 g of distilled water (assume ρH₂O=1 g.m⁻³). The solution was then divided into two equal halves. The first half was mixed with 12.15 g of sodium aluminate which is used as a source of alumina, while, the second half (75 g NaOH solution) was used to dissolve 3.2 g of sodium metasilicate silicate. The solution containing the silicate was poured into the solution containing the aluminate. The seeded celatom (2.70g) was added to the mixture after transferring the gel composition inside the autoclave. The mixture was added to fill two-thirds of the volume of an autoclave, sealed tightly and left in an oven for 1.5, 4 and 6h at 100°C. Same gel composition was put into plastic bottle, sealed and left under same temperature for 2 and 6h. Vacuum filtration method was used to separate the solid from solution using a Whatman filter paper with 500 ml capacity of filter funnel. A pH meter was used to check the pH of solution as it washed with water; washing was finally stopped when pH was less than 9.

**Table 4.3 The amount of each ingredient for the formation of the growth gels for zeolite- A and Celatom/ZeoliteA composite.**

<table>
<thead>
<tr>
<th>Component</th>
<th>Zeolite-A Mass (g)</th>
<th>Celatom/Zeolite A Mass (g)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH (99.6%)</td>
<td>4.70</td>
<td>4.70</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Sodium aluminates (NaAl₂O₃)</td>
<td>12.15</td>
<td>12.15</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>55 wt % of Al₂O₃ and 45 wt % of Na₂O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium metasilicate Na₂SiO₃·9H₂O:47 wt % of SiO₂ and 52 wt % of Na₂O</td>
<td>16.12</td>
<td>3.20</td>
<td>Aldrich</td>
</tr>
<tr>
<td>H₂O</td>
<td>150</td>
<td>150</td>
<td>--------</td>
</tr>
<tr>
<td>Seeded Celatom</td>
<td>--------</td>
<td>2.70</td>
<td>Aldrich</td>
</tr>
</tbody>
</table>
The filter with separated solid was put in the oven at 50°C overnight for drying. The products were analysed by X-ray diffractometer to study the crystallinity of the composite Cel-ZA. In addition, Scanning Electron Microscopy (SEM) was used to determine the morphology of the zeolite structure.

The amount of zeolite A onto diatom surface for each sample was estimated by the celatom weight difference before and after hydrothermal process.

4.5.1 Results of the Product, Characterizations and Crystal Growth

The product of ground zeolite A was collected after 24h. The XRD pattern and SEM images of zeolite A showed that the structure of zeolite-A was not affected by the grinding process when compared with the commercial zeolite A pattern as shown in Figure 4.21 and Figure 4. 22, respectively. While the DLS shows the average diameter of the ground crystals was 158nm compared with the 0.5- 5µ commercial zeolite-A before the ball milled process as shown in Figure 4.23.

![XRD pattern of the suspension of dried ground and commercial zeolite-A using ball mill for 24h.](image)

**Figure 4.21** XRD pattern of the suspension of dried ground and commercial zeolite-A using ball mill for 24h.
Figure 4. 22 SEM images of the ground commercial zeolite-A after 24 h ball milled (Scale bar=5µm and 500 nm).

Figure 4.23 Dispersivity of ground zeolite A using DLS techniques on a Malvern.
CHAPTER FOUR

PREPARATION OF CELATOM-ZEOLITE COMPOSITE

Figure 4. 24 shows the XRD patterns for raw celatom material compared with commercial zeolite-A. While, Figure shows the XRD patterns of Cel-ZA composite after 1.5 and 4h using autoclaves and after 4 and 6h using plastic bottle. It was observed that zeolite-A was deposited onto celatom surfaces using XRD after the hydrothermal treatment using an autoclave and plastic bottle. The XRD patterns shows the characteristic reflections of zeolite-A at $2\theta = 7.18^\circ, 10.17, 12.46^\circ, 16.11^\circ, 22.85^\circ$ and $25.07^\circ$ [234] present in the Cel-ZA composite samples, while the strong reflection at $22^\circ$ is for SiO$_2$ of celatom.

It was noticed that the peaks a little bit higher in plastic bottle than the autoclave, which suggested faster heat transfer. The surface morphology of each samples were observed using SEM before and after the hydrothermal process as shown in Figure 4.26. The results show good organised porosity and the crystals of zeolite-A have been successfully grafted onto the celatom surfaces. The results show that celatom can be used successfully as a silica source in zeolitisation process with a shorter reaction time.

Figure 4. 24 The X-Ray diffraction pattern of (a) Pure celatom and (b) commercial zeolite-A.
Figure 4.25 The XRD patterns of Cel-ZA composite after different synthesis time (1.5, 4 and 6h) using bottle and autoclave (Zeolite-A 2θ°= 7.18°, 10.17, 12.46°, 16.11°, 22.85° and 25.07°).

Figure 4.26 Celatom FW-14 in conjunction with zeolite-A (Scale=5µm).
CHAPTER FOUR
PREPARATION OF CELATOM-ZEOLITE COMPOSITE

SUMMARY

The experiments showed that diatomite can be used as an alternative cost-efficient silica source due to its macroporous structure as well as to the presence of 80-90% of silica in its structure wall and widespread natural availability. In addition, it was successfully used in the zeolitisiation process as a scaffold material for the crystals of zeolites A and Y to prepare celatom-zeolite Y (Cel-ZY) and celatom-zeolite A (Cel-ZA) composite materials. The zeolitisiation processes for both zeolite A and Y were simple and involved a short reaction time.

In the case of Cel-ZY composite, the seeds of colloidal zeolite Y was synthesised hydrothermally. The main disadvantage of this method lies in the complexity of its operation, its cost with the need to use expensive source materials and the fact that any simple errors may lead to the product being damaged. Due to this limitation a ball mill method was used.

The ball method has two advantages of being simple and cost-effectiveness. Hence, the ball mill method was used to prepare zeolite seeds rather than the synthesis method. The average particle size of the seeds resulting from the synthesis and ball milled processes using Dynamic Light Scattering (DLS were found 80 and 140 nm, respectively). Both methods successfully produced particles within the nano-meter scale. However, the ball mill product was used successfully to prepare Cel-ZY composite, as it is cheaper and simple to manage than the synthesised method.

In the next chapter, carbons were suggested as alternative support materials to hold the zeolites particles for three types of zeolites (zeolite A, zeolite Y and clinoptilolite) to build the hierarchical structure materials.
CHAPTER FIVE

CARBONS AS ALTERNATIVE MATERIALS
5. CARBONIZATION

Two samples of raw plant wastes, obtained from the local shops, were tested and prepared carefully by carbonization. The raw materials were Iraqi Palm Tree Leafs (IP) and Tamarind Stones (TS). Both samples were washed with deionised water and dried at 50°C overnight in an oven. The carbonization in this study was a one step process consisting of heating the raw waste plant sample (Pyrolysis) at 900 °C for 2 h in a furnace (VECSTAR Furnaces) in an inert atmosphere of nitrogen gas to avoid oxidation which will result in a huge loss of the carbon sample. Pyrolysis is commonly use in the biomass conversion system [21]. Gases, liquids and solid are primary products in this process. Two isothermal steps were taken to improve the removal of these, as shown in Figure 5.1. The first step (250°C) was used to remove the moisture content, while the second step (600°C) was used to remove the volatile compounds. The temperature and heating time were chosen based on the most commonly seen conditions in the literature [21].

Both samples were crushed and converted to fine powder after the pyrolysis process. The characterization of the samples was performed using SEM for the samples before and after the carbonization process.

The percentage ratios of the carbon content in the plant samples which is used in this experiment were calculated using Eq. 17 [25].

\[
\text{Carbon Content} \% = \frac{m_1-m_2}{m_1} \times 100 \quad \text{Eq. 17}
\]

where \( m_1 \) and \( m_2 \) are the weight of the sample before and after carbonisation (mg), respectively.
Figure 5.1 Heating sequence applied for the pyrolysis of natural carbons.

5.1 SEEDING PROCESS
The suspension solution of fine particles of commercial zeolite A and Y prepared from the experiments in chapter 4 was used to seed both products of carbon materials (IP and TS) separately. While synthesised clinoptilolite was also prepared in this study and used to prepare the clinoptilolite fine particle’s solution (seeds) were following the same procedure of zeolite A and Y using ball mill method.

Carbons were seeded using 1:20 fine particle solution of zeolite: carbon weight ratio (5wt %) for each type of carbon and sonicated for 6 h in same procedure performed in Chapter 4 for all types of zeolites. Other batches of the carbon products were performed without seeding. All batches were dried overnight at 50°C.

5.2 EXPERIMENTAL. I
5.2.1 Preparation of Zeolite Y Crystal onto Carbon
Zeoite-Y was grown on carbon surfaces using hydrothermal treatment via the same molar ratio of the gel composition (Formula 2) in chapter 4 section 4.1.3 as shown below:

\[14 \text{Na}_2\text{O}: 10 \text{Al}_2\text{O}_3: 798 \text{SiO}_2: 3 \text{H}_2\text{O}: 3 \text{Na}_2\text{SO}_4\]  \text{Formula 2}
Silica source was supplied completely from sodium metasilicate in this experiment, while the sodium hydroxide and aluminium sulphate octadecahydrate were used as sources for the remaining elements. Sodium hydroxide was used to provide the alkaline medium. Table 5.1 shows the amount of each ingredient for the formation of the growth gel [26]. The same procedure in section 4.1.1 was performed to prepare zeolite-Y. The seeded carbons (IP and TS) were added at last stage before closing the autoclave in a 2:1 carbon: silica source weight ratio. Then the autoclave was put into oven for 17 h at 100ºC. In addition, pure zeolite-Y was prepared in same method using this formula (Formula 2) and the seed of fine particles of zeolite-Y (5%) was added to the mixture and transferred to the autoclave.

Table 5.1 The crystal growth ingredients, amounts and materials suppliers.

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass (g)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td>0.2</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Al$_2$(SO$_4$)$_3$.18H$_2$O</td>
<td>0.25</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Na$_2$SiO$_3$.H$_2$O</td>
<td>1</td>
<td>Aldrich</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>4.4</td>
<td>------</td>
</tr>
<tr>
<td>Seeds Carbon</td>
<td>0.5</td>
<td>------</td>
</tr>
</tbody>
</table>

After that the sample was cooled and washed with water until pH ≤ 9, filtered and then dried overnight at 50ºC. The product was characterised using XRD and SEM to investigate the structure and morphology, while TGA (Q5000-0041 IR) was used to estimate the loading of zeolite-Y on the carbon surface by take the difference between the initial and final weight.

EDAX was applied to estimate the chemical composition of the carbon/zeolite-Y (C-ZY) products as well as to determine the Si/Al ratio. Nitrogen adsorption was used to measure the surface area of samples.
5.3 EXPERIMENTAL. II
5.3.1 Preparation of Zeolite - A /Carbon Composites.

The same procedure of seeding process in section 5.3 of zeolite synthesis for zeolite-Y was performed to prepare C-ZY composite for zeolite-A. The gel composition formula for zeolite-A and the ingredients were described in Formula 5 and Table 4.3 section 4.5.

Zeolite-A \[3.1 \text{Na}_2\text{O}: \text{Al}_2\text{O}_3: 1.9\text{SiO}_2: 128\text{H}_2\text{O}\] \hspace{1cm} \text{Formula 5}

The gel compositions of zeolite-A were poured into an autoclave then the seeded carbon powders (IP and TS) were added separately to the each mixture as same procedure in section 4.5. The autoclaves were sealed tightly and put inside the oven for 3 h at 100°C. The samples were characterised as the same method of C-ZY composite in section 5.3 using XRD, SEM, EDAX and TGA.

5.4 EXPERIMENTAL. III (CLINOPTILOLITE)
5.4.1 Synthesis of Clinoptilolite

The clinoptilolite used in this study was synthesised from aluminoslicate gel under hydrothermal conditions at 140°C at autogenous pressure for 1, 3 and 6d. A molar batch composition as described in Formula 7 which reported by Chi and Sand [98] aided by seed crystals was used to prepare this type of zeolite.

\[2.1\text{Na}_2\text{O}: 10\text{SiO}_2: \text{Al}_2\text{O}_3: 110.1\text{H}_2\text{O}\] \hspace{1cm} \text{Formula 7}

A 10 wt% of dry material in the batch was used as a seed. The calculation for material was prepared according to the gel composition (Formula 7) to get the required amount of each substance; the amounts of required reactants are given in Table 5.3.
Table 5.2 Shows clinoptilolite zeolite, ingredients, amounts and suppliers.

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass (g)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>27</td>
<td>---</td>
</tr>
<tr>
<td>Sodium hydroxide, NaOH 99.6%</td>
<td>2</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Ludox-HS-40 (40% SiO$_2$ and 60% H$_2$O)</td>
<td>48.5</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Sodium aluminates, anhydrous, 55 wt% of Al$_2$O$_3$ and 45 wt% of Na$_2$O</td>
<td>6.00</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Natural clinoptilolite as seed</td>
<td>2.8g</td>
<td>Shop Holistic</td>
</tr>
</tbody>
</table>

5.4.2 Batch Composition

27 g of water was mixed with 2 g NaOH (used as cation source) in a plastic bottle and magnetically stirred on a hot plate. 6.00 g of sodium aluminate (used as alumina source) was added to the NaOH solution and mixed for 15 min using magnetic stirrer until a clear solution was obtained. Then Ludox-HS40 (48.5 g) was poured slowly into the clear solution under continuous stirring and a gel was obtained immediately. Ludox-HS40 was used as colloidal silica. The gel was mixed strongly for 1 h at room temperature until creamy milk was obtained. After that a 2.8 g (10 wt% of dry material in batch composition) of natural clinoptilolite crystals was added to the mixture under stirring and mixed for 5 min. Then the mixture was transferred to the autoclaves for 1, 3 and 6 days under 140ºC at autogenous pressure. After the autoclaves were cooled, vacuum filtration method used to separate the solid from solution using a Whatman filter washed until under pH < 9. Finally, the filter with separated solid was put in the oven at 50ºC overnight in an oven for drying.

Two types of syntheses were studied in this experiments, one of them was seeded using natural clinoptilolite crystals while the other was a without seeded system. The products were analysed by X-ray diffractometer for qualitative purposes. The product of synthesised clinoptilolite was compared with the natural clinoptilolite material to study the phase identification and crystallinity of clinoptilolite as well as to find out whether all peaks are in the right place or not by comparing the product patterns with the pattern...
of natural clinoptilolite. The crystallinity of the clinoptilolite product was determined by intensity summation method of the XRD pattern for selected peaks (see Eq.9).

In addition, SEM and EDAX were used to determine the morphology of clinoptilolite crystals and Si/Al ratio, respectively. The previous studies show that the SEM of the natural clinoptilolite crystal images in sedimentary rocks were found as sheets or as needles agglomerated together, it is found in several microns in length and 1-2 micron thick. While, the Si/Al ratio is found ≥ 4.0 [98, 235].

5.5 RESULTS AND DATA ANALYSIS
5.5.1 Carbonisation

Two types of carbon were prepared using pyrolysis method. The surface morphology of each product (IP and TS) was observed using SEM before and after the carbonisation process, and these showed good and organised porosity. Figure 5.2 shows carbonised samples after the pyrolysis process for each type of samples, showing the original shape of each type of carbon is not affected by the high temperature.

Table 5.3 illustrated the %carbon content to give an idea about the change in weight and surface area (m².g⁻¹) for both samples.

The Nitrogen isotherm of the pyrolysed IPC carbon sample is shown in Figure 5.3. Carbon - ZeoliteY (C-ZY) composite adsorbents for IPY was also analysed using the nitrogen adsorption-BET method to examine the effect of the preparation on the surface area is shown in Figure 5.4. The surface area calculated from the isotherms for the pyrolysed and composite adsorbents are listed in Table 5.3 (see appendix D). The isotherms obtained are classified as adsorption-desorption isotherm type IV according to the International Union of Pure and Applied Chemistry (IUPAC) for porous materials[56]. The surface area of the composite adsorbent is less than that of the pyrolysed precursors may due to the grafting of the zeolite Y onto the carbon structure of the pyrolysed carbon as well as the amount of zeolite onto carbon surfaces may affected.
Figure 5.2 Shows the product of the two types of carbons (TS and IP) after 2h carbonisation at 900°C (Scale bar=1cm).

Table 5.3 Shows the BET surface area m$^2$.g$^{-1}$ and the % carbon content for each material of carbon media (TSC and IPC).

<table>
<thead>
<tr>
<th>Materials</th>
<th>BET surface area m$^2$.g$^{-1}$</th>
<th>% Carbon yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSC</td>
<td>202</td>
<td>26.48</td>
</tr>
<tr>
<td>TSY</td>
<td>139.8</td>
<td>-------</td>
</tr>
<tr>
<td>IPC</td>
<td>257.43</td>
<td>17.40</td>
</tr>
<tr>
<td>IPY</td>
<td>196</td>
<td>-------</td>
</tr>
</tbody>
</table>
Figure 5.3 Sorption/desorption isotherm for IPC.

Figure 5.4 Sorption/desorption isotherm for IPY.
The SEM of images as seen in Figure 5. 5 shows pores on the carbon surfaces are arranged like tubes such as IP sample and honeycombs through the TS sample. Whereas, most pores with a variety of sizes and shapes were also found in comparison with the raw materials before the carbonisation. In addition, the observed SEM images for the same sample for both materials showed different shapes such as hollows or rod shapes agglomerated together. The SEM images in both samples show that there is satisfactory prospect on the surface of the carbon to hold zeolite crystals. In addition, elements of each type of carbons were specified using EDAX (see appendix G); Figure 5.6 a and b shows the EDAX for the pyrolysed IPC and TSC, respectively.

Figure 5. 5 The (A and B) SEM images present the raw materials of IP and TS, while (C and D) SEM images represent the materials after carbonization process for IP and TS, respectively (Scale bars =50µm).
Figure 5.6 Shows the EDAX for pyrolysed (a) Iraqi Palm Tree Leafs (IPC) and (b) Tamarind stones.
5.5.2 Results of Seeding Process

Both carbon samples (IP and TS) were seeded separately with ground zeolite solution fine particles of zeolite A, Y and clinoptilolite. The seeded carbon for each type was investigated by SEM. It was difficult to indicate the fine particles of zeolite on the carbon surfaces because of the irregular nature of the surfaces and the small debris on all types of sample surfaces. This observation was noticed with the seeded celatom in Chapter 4.

5.5.3 Crystal Growth of Zeolite/Carbon Composite

5.5.3.1 Carbon/Zeolite-Y Composite (C-ZY)

It was observed that zeolite-Y growth has taken place on the carbon surfaces using XRD for both types of carbons as shown in Figure 5. 7. The XRD measurements show good zeolite-Y peaks for both types of composite. The products were obtained after 17h of hydrothermal growth, the XRD patterns show the characteristic reflections of zeolite-Y at 2θ°= 6.12° and 11.86° are presented clearly with the carbon/zeolite-Y composite samples (C-ZY). In addition, Figure 5. 8 (a and b) shows the SEM images for the products from IP and TS respectively, good morphology and crystals distribution within and on the carbon surfaces were observed. The EDAX presented the Si/Al ratio between 2.1-2.5 on the C-ZY composites for both type of carbon surfaces as shown in Figure 5. 9 a and b.
Figure 5.7 Shows the X-Ray diffraction pattern of pure zeolite-Y, TSY and IPFY for 17h hydrothermal treatment at 100°C.

The amount of zeolite-Y onto carbon surfaces in the composites of carbon/zeolite-Y (IPY and TSY) was estimated from the Thermogravimetric (TGA).

There was a weight loss first between 25-400°C for all types of samples which were used in this study. An inert atmosphere was used in the first 100 min to study the composite weight behaviour under high temperature due to removal of moisture and volatile compounds. From Figure 5.10 it can be seen clearly that the weight of TSY gradually dropped at this stage from 100 to 85%. While, the major weight loss was observed between 100 to 120 min at temperature between 400 to 600°C in an air atmosphere from 85 to 37.3%, indicating that the carbons were burned to oxidized carbon element direct after cutting the N₂ gas. The same behaviour was observed with the TGA behave for IPY. The loading of zeolite-Y in the composite were 37.36% and 35.32% for TSY and IPY, respectively.
Figure 5.8 SEM images for TSY (A) and for IPY (B) after hydrothermal treatment.
Figure 5.9 Shows the EDAX pattern for (a-) IPY and (b-) TSY.
Figure 5.10 Thermogravimetric analysis (TGA) curves of (a) - TSY and (b) - IPY carbon/zeolite composites at 600°C show the loading of zeolite onto carbon surfaces were 37.36% and 35.32% respectively.
5.5.3.2 Carbon/ Zeolite-A Composite (C-ZA)

Novel zeolite-A/carbon composites (C-ZA) were made-up through an incorporated process of zeolite-A onto the surfaces of plant waste of IP and TS after carbonisation at 900°C for 2 h in an inert atmosphere (N₂ gas) followed by seeded and hydrothermal treatment. The XRD patterns and SEM images show that the commercial zeolite-A was not affected by the ball mill process as mentioned in Chapter 4. The XRD, Figure 5.11, shows that the structures of the composite for both type of carbons (IPA and TSA) had good crystallinity and this is in line with the peaks of commercial of zeolite-A. While, SEM show that the crystals of zeolite-A were deposited successfully in both types of carbon surface as show in Figure 5.12 and Figure 5.13 for IPA and TSA , respectively. The crystals were distributed uniformly for each type on the carbon surfaces. The type of zeolite was also identified by the EDAX through calculation of the Si/Al ratio for the products which was found to be nearly 1 as presented in Figure 5.14.

![Figure 5.11 The XRD patterns for Zeolite-A/Carbon composite (C-ZA) for a- IPA and b- TSA.](image-url)

![Graph showing XRD patterns for Zeolite-A/Carbon composite (C-ZA) for IPA and TSA.](image-url)
Figure 5.12 Shows the SEM for zeolite-A/carbon composite for IPA. (Scale bar=20 µm) with different magnifications.
Figure 5.13 The SEM for TSA with different scale and magnification (Scale bar=20 and 50 µm).

However, the content of zeolite-A on the carbon surfaces was determined by TGA in the same technique of Carbon-ZY. It was observed that the weight loss was gradual for TSA during first 10 min in an inert atmosphere from 100 to nearly 87%, then the weight stay in this range until dropped significantly between 100-120 min under air atmosphere from 87 to 46.35%. After that, there was no further weight change indicating that the residue left was a zeolite as the carbon was completely burned. The TGA process of the IPA sample behaved in the same way as the TSA sample as shown in Figure 5.15. The loading of zeolite-A in the composite were 46.35 and 30.35 % for IPY and TSY.
Figure 5.14 The EDAX pattern for (a-) TSA and (b-) IPA.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>30.52</td>
</tr>
<tr>
<td>O</td>
<td>36.61</td>
</tr>
<tr>
<td>Na</td>
<td>2.80</td>
</tr>
<tr>
<td>Si</td>
<td>12.74</td>
</tr>
<tr>
<td>Al</td>
<td>13.44</td>
</tr>
<tr>
<td>Ca</td>
<td>0.78</td>
</tr>
<tr>
<td>Fe</td>
<td>0.37</td>
</tr>
<tr>
<td>Mg</td>
<td>0.13</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>36.69</td>
</tr>
<tr>
<td>O</td>
<td>27.56</td>
</tr>
<tr>
<td>Na</td>
<td>8.97</td>
</tr>
<tr>
<td>Si</td>
<td>11.99</td>
</tr>
<tr>
<td>Al</td>
<td>12.34</td>
</tr>
<tr>
<td>Ca</td>
<td>1.95</td>
</tr>
<tr>
<td>Fe</td>
<td>0.37</td>
</tr>
<tr>
<td>Mg</td>
<td>0.13</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
</tr>
</tbody>
</table>
Figure 5. 15 TGA for (a-) IPA and (b-) TSA, the loading of zeolite onto carbon surfaces were 46.35% and 30.31% respectively.
5.5.3.3 Synthesis of Clinoptilolite

The gel composition in Formula 7 was used to prepare clinoptilolite for different times at 140°C.

\[ 2.1\text{Na}_2\text{O}:10\text{SiO}_2: \text{Al}_2\text{O}_3: 110.1\text{H}_2\text{O} \quad \text{Formula 7} \]

The gel composition was hydrothermally treated for 1, 3 and 6 days to prepare clinoptilolite. This zeolite was prepared in two ways, first with seeds using natural clinoptilolite crystals and secondly without seeds crystals. The XRD pattern shows there was no phase of any crystal without seed system even after 6 day and the resulting sample was totally amorphous. All the peaks related to clinoptilolite prepared using 10wt% seeded system of natural clinoptilolite crystals appeared clearly after 1, 3 and 6 days of hydrothermal treatment. However, highly amorphous product was observed at the earlier stage after 1 day for the same gel composition.

The XRD patterns data collection was conducted in the 2θ range 3-50° followed by characterisation using SEM to identify the structure and morphology of the product. The XRD patterns for clinoptilolite, synthesised after 3d has similar peak positions to the pattern for clinoptilolite after 6d as shown in Figure 5. 16 and both are similar to the pattern for natural clinoptilolite.

The main peaks were selected to calculate the percentage of crystallinity. The relationship between the percentage crystallinity versus crystallization time is shown in Figure 5. 17.
Figure 5.16 Show XRD of clinoptilolite synthesised after 1, 3 and 6 days compared with the natural zeolite.

Figure 5.17 The crystallinity relationship ($I/I_0$) between the percentages degree of crystallinity of clinoptilolite samples and their crystallization times.
In addition, EDAX was used to investigate the bulk chemical compositions in the samples of zeolite as shown in Figure 5. 18; the amounts of Si and Al were used to calculate the Si/Al ratio and compared with the natural clinoptilolite in the literature. The Si/Al ratios were found to be 4.1 to 5.7 for all samples from five spots chosen randomly for each sample. In the literature the Si/Al ratio for clinoptilolite is found to be 4.0-7.0 [235]. The SEM images show that the crystals of clinoptilolite appeared mostly as tubular crystals. Some other forms such as fibrous crystals appear in layers similar to the way plywood is layered, as shown in Figure 5. 19. In addition, the SEM showed that the vitreous matrix and glass shards are lengthily changed in synthesis samples.

![EDAX spectrum of clinoptilolite after 6 days crystallization time (Si/Al ratio 4.8)](image)

<table>
<thead>
<tr>
<th>Elem</th>
<th>Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>OK</td>
<td>44.38</td>
</tr>
<tr>
<td>Na K</td>
<td>4.47</td>
</tr>
<tr>
<td>Al K</td>
<td>8.80</td>
</tr>
<tr>
<td>Si K</td>
<td>42.35</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure 5. 18 EDAX spectrum of clinoptilolite after 6 days as crystallization time (Si/Al ratio 4.8).

The results from XRD, SEM and EDAX show the synthesis of clinoptilolite was successful and good crystallinity was achieved. The results from this study are in line with those found in the literature [101, 235].
Figure 5. 19 SEM images are shown the crystal of clinoptilolite after 6 days as crystallisation time, respectively (Scale= 5 µm).
5.5.3.1 Carbon/ Clinoptilolite Composite (C-Clinp)

Novel hierarchical porous structures of Clinoptilolite/Carbon composites were prepared through a conjunction process of clinoptilolite crystals onto the surfaces of plant wastes of IP and TS using same procedure of deposited zeolite A and Y after carbonisation at 900°C for 2h. The SEM images, Figure 5. 20, show that the clinoptilolite was not affected by the ball milled process as mentioned in the previous chapter while it is clear to see small parts of crystals were resulted after this process. Figure 5.21 shows the EDAX of pure clinoptilolite, the Si/Al ratio is 4.5 after ball milled process. The gel composition in Formula 7 was used to prepare the Clinoptilolite: Carbon composite for each type of carbon. Both types of carbon (IP and TS) were sonicated with seeds of ball milled clinoptilolite for 6h using 5% of fine particle solution of clinoptilolite: Carbon ratio for both types of carbon TS and IP as shown in Table 5.4 for 140h at 140°C. Synthesised clinoptilolite was ball milled for 24h to prepare fine particles size solution. Figure 5. 22 shows the average diameter particle size has reduced from 220 to 120nm in the solutions resulting after 24h ball milled using same process of zeolite A and Y.

![Figure 5.20](image-url) 

Figure 5. 20 The SEM image showing the crystals of clinoptilolite after 24h ball milled.
CHAPTER FIVE  CARBON AS ALTERNATIVE SUPPORT MATERIALS

Figure 5.21 The EDAX spectrum of pure clinoptilolite.

Figure 5.22 The average particles size of clinoptilolite after 24h ball milled.
Table 5.4 The clinoptilolite ingredients, amounts and suppliers (10:4 ratio Si source: carbon ratio).

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass (g)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>12.25</td>
<td>---</td>
</tr>
<tr>
<td>Sodium hydroxide, NaOH 99.6%</td>
<td>0.9</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Ludox-HS-40 (40% SiO₂ and 60%H₂O)</td>
<td>21.85</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Sodium aluminates, anhydrous, 55 wt % of Al₂O₃ and 45 wt % of Na₂O</td>
<td>2.7</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Seeded carbon</td>
<td>3.5</td>
<td>---------</td>
</tr>
</tbody>
</table>

To investigate the ability of carbons to support this type of zeolite due to its high silica, different Si source: TS ratios were studied at 140°C for 3d as shown in Table 5.5. The yields of products were calculated via Eq. 18

\[
\%Yield = \frac{W_p}{W_b} \times 100 \quad \text{Eq. 18}
\]

where \(W_b\) is the weight of the batch and \(W_p\) is the weight of the product.

Each type of Carbon: Clinoptilolite composite (C-Clinp) was identified through the XRD and the amounts of clinoptilolite were estimated via TGA as shown in same Table (5.3). It was observed that the deposited amount (layer) of clinoptilolite decrease with increasing the amount of carbon as support layer (see appendix F). Figure 5.23 shows the XRD pattern of C-Clinp composites for each mixture.
Table 5. 5 Shows the different Si: Carbon ratio of TS: Clinp composites, the weight of batch and the weight of the product.

<table>
<thead>
<tr>
<th>Carbon: Clinp Si:Carbon ratio</th>
<th>Empty Teflon (g)</th>
<th>Teflon +batch (g)</th>
<th>Wb Weight of batch (g)</th>
<th>Wp weight of product (g)</th>
<th>Yield %</th>
<th>%Clinoptilolite (TGA)(1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure clinoptilolite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10:0</td>
<td>158.43</td>
<td>197.93</td>
<td>39.5</td>
<td>10.27</td>
<td>26</td>
<td>100</td>
</tr>
<tr>
<td>10:1</td>
<td>161.4</td>
<td>197.23</td>
<td>35.83</td>
<td>10.88</td>
<td>30.36</td>
<td>74.42</td>
</tr>
<tr>
<td>10:2</td>
<td>157.43</td>
<td>195.72</td>
<td>38.29</td>
<td>10.87</td>
<td>32.38</td>
<td>70.78</td>
</tr>
<tr>
<td>10:3</td>
<td>165.96</td>
<td>196.1</td>
<td>30.14</td>
<td>10.47</td>
<td>34.37</td>
<td>65.91</td>
</tr>
</tbody>
</table>

(1) The TGA figures of each type are presented in the appendix F.

Figure 5.23 The XRD for clinoptilolite with different Si: TS ratio after 70h at 140°C.
The 2.5:1 (Si: Carbon) ratio was used to prepare a hierarchical structure of C-Clinp composite of each type of carbon (IP and TS) at 140°C for 6d suggested the ability to obtain a thinner layer of clinoptilolite onto carbon surfaces than the other prepared ratios in Table 5.4. The XRD shows that the structures of the composite for both type of carbons (Iraqi Palm Tree- Clinoptilolite (IPClinp) and Tamarind Stones-Clinoptilolite (TSClinp)) have had a good crystallinity as shown in Figure 5.24 and this going in same tuning with the peaks of commercial of clinoptilolite (2θ° = 10.1, 14.0, 17.4 and 21.8) [101, 235].

![XRD patterns for clinoptilolite/carbon composite for 140h at 140°C](image)

**Figure 5.24** The XRD patterns for clinoptilolite/carbon composite for 140h at 140°C (a-) IPClinp and (b-) TSClinp.

Figure 5. 25 and Figure 5.26 shows that the images of SEM show that the crystals of clinoptilolite were deposited and distributed successfully in both types of carbon surface for IPClinp and TSClinp, respectively (for additional images, see appendix E).
Figure 5.25 The SEM of IP-Clinp composite after 140h hydrothermal treatment at 140°C (Scale bar= 50 µm).
Figure 5.26 Shows the SEM images of TS-Clinp composite after 140h hydrothermal treatment at 140°C (Scale bar= 20 and 50µm).
Clinoptilolite was identified by measuring the element compositions for each type (IP-Clinp and TS-Clinp) by the EDAX through calculation of the Si/Al ratio for the products which was found to be > 4.0 which is belonging to the clinoptilolite as mentioned in chapter two, this presented in Figure 5.27 a and b. However, the quantity of clinoptilolite on the both of carbon surfaces was determined by TGA using the same procedure for zeolite-Y and A.

It was observed that the weight loss was gradual for TS Clinp in similar way of zeolite A and Y during 10-100 min in an inert atmosphere from 100 to 87% and then the weight dropped significantly between 100-120 min under air atmosphere from 87 to 63.91% for TS Clinp. After that, there was no further weight change indicating that the residue left was a zeolite as the carbon was completely burned.

IP Clinp sample in the TGA process behaved in the same way as the TS Clinp sample as shown in Figure 5.28. The loading of clinoptilolite in the composite were 63.91 and 64.76 % for TS Clinp and IP Clinp.
Figure 5.27 The EDAX for (a-) TS Clinp and (b-) IPClinp (Si/Al > 4.0).
Figure 5.28  TGA for (a-) TS-Clinp and (b-) IP-Clinp, the loading of zeolite were 63.91% and 64.76% respectively.
SUMMARY

Two types of macroporous carbon materials of the natural carbons readily available agricultural residues in the Middle East were obtained from the carbonisation process of Iraqi palm tree Leaves (IP) and Tamarind stones (TS). These types were selected as scaffolds for the three types of zeolites: A, Y and clinoptilolite in order to prepare the hierarchically structured materials in micro/macro porosity (zeolite/carbon) composite materials.

The carbon materials were prepared through a Pyrolysis process at 900°C for 2h under nitrogen atmosphere with two isothermal steps of 250°C and 600°C. By weighing the natural carbon before and after the Pyrolysis process, the carbon content of each material was found to be 26.48 for TS and 17.4% for IP.

Fine particle zeolite solutions for each type of zeolite (Y, A and Clinp) were prepared via ball mill method to seed the carbon surfaces to avoid using the synthesised colloidal method. Hydrothermal treatment was employed to build the Carbon/Zeolite hierarchical structure materials. Using the commercial zeolite of each type, after 24 hours grinding using zirconium oxides balls, the average particle size of zeolite A and clinoptilolite were 150nm and 120nm, respectively. After seeding the carbon surface for 6h using a sonication bath, the crystals of each type of zeolite were successfully grown and attached to the carbon surfaces of both the IP and TS carbons. This was confirmed by the SEM images and the XRD patterns show that the peaks of each composite product correspond closely to the peaks of the commercial zeolites (A, Y and clinoptilolite) which serve as a reference point. In addition, using the EDAX measurement the Si/Al ratio was calculated for all the composite materials to verify the identity of each zeolite type (Si/Al=1, 2.3 and > 4 for ZA, ZY, and clinoptilolite, respectively).

In case of Carbon-Clinoptilolite composite, from the XRD and EDAX measurement it was confirmed that IPClinp and TSClinp composites was successfully prepared and this study provides insight into a new type zeolite composite as there is no evidence in literature of this being carried out before.
CHAPTER SIX

APPLICATION OF WASTEWATER TREATMENT
CHAPTER SIX

APPLICATION OF WASTEWATER TREATMENT

6.1 INTRODUCTION

The main aim of the water treatment process was to study the capacity of the synthesised hierarchical porous materials, the preparation of which is outlined earlier in this study, to remove undesirable ions from the synthesis wastewater.

In the tests, Co\(^{2+}\) and Sr\(^{2+}\) ions were selected in order to study the ability of synthesised hierarchical porous materials to remove these non-radioactive elements as a model to remove radioactive elements of Co-60 and Sr-90. The influence of a range of parameters such as the effect of pH, temperature and initial concentrations were investigated with the objective of identifying the behaviour of the materials listed in Table 1.6 during the water treatment processes.

The sorption data have been analysed using the Langmuir and Freundlich sorption isotherm models. These models were used to evaluate the theoretical data with the experimental results obtained in this study. The residue of the adsorbent materials, which were produced as a result of water treatment processes, were vitrified at 1200 °C for 2 hours in order to study the immobilisation of captured Co\(^{2+}\) ions. The vitrification process was applied to the Co\(^{2+}\) ions due to their possession of a high melting point of 1400°C. It is not possible to apply this process to Sr\(^{2+}\) ions which have a much lower melting point (777°C).

6.2 EXPERIMENTAL WORK

6.2.1 Preparations of Synthesised Materials

The pure and composite materials (Carbon-Zeolite (C-Z) and Celatom-Zeolite (Cel-Z)) were prepared using the methods described in the previous chapters. For the Co\(^{2+}\) and Sr\(^{2+}\) elements, a small amount of each composite material (0.1g) was mixed with the synthesised wastewater (50mL) in 100mL capacity plastic bottles. As a reference point, the three types of pure zeolite (A, Y and clinoptilolite) were treated separately under same conditions in order to test their ability to remove these ions. To maintain similar Si/Al ratio and properties, pure zeolites were prepared from the same gel compositions.
as the synthesised hierarchical porous materials. Table 6.1 shows all the ion exchanger materials which were employed in this study. This table shows each sample with its abbreviation and the proportion of zeolite loaded measured using the TGA instrument.

Table 6.1 The samples materials were used in this study with its abbreviations

<table>
<thead>
<tr>
<th>Material descriptions</th>
<th>Abbreviation</th>
<th>Loading Zeolite (TGA) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Zeolite-A</td>
<td>PZA</td>
<td>100</td>
</tr>
<tr>
<td>Iraqi palm tree Leafs-ZeoliteA</td>
<td>IPA</td>
<td>46.35</td>
</tr>
<tr>
<td>Tamarind Stone-ZeoliteA</td>
<td>TSA</td>
<td>30.31</td>
</tr>
<tr>
<td>Celatom-ZeoliteA</td>
<td>Cel-ZA</td>
<td>33.66</td>
</tr>
<tr>
<td>Pure ZeoliteY</td>
<td>PZY</td>
<td>100</td>
</tr>
<tr>
<td>Iraqi palm tree Leafs-ZeoliteY</td>
<td>IPY</td>
<td>35.32</td>
</tr>
<tr>
<td>Tamarind Stone-ZeoliteY</td>
<td>TSY</td>
<td>37.36</td>
</tr>
<tr>
<td>Celatom-ZeoliteY</td>
<td>Cel-ZY</td>
<td>33.66</td>
</tr>
<tr>
<td>Pure Clinoptilolite Zeolite</td>
<td>PClinp</td>
<td>100</td>
</tr>
<tr>
<td>Iraqi palm tree Leafs-Clinoptilolite</td>
<td>IPClinp</td>
<td>63.91</td>
</tr>
<tr>
<td>Tamarind Stone-Clinoptilolite</td>
<td>TS Clinp</td>
<td>64.76</td>
</tr>
</tbody>
</table>

6.2.2 Batch Sorption and Ion exchange Studies

The batch experiments were performed under kinetic and equilibrium conditions. 0.1g of each composite media listed in Table 6.1 was mixed in the Co²⁺ and Sr²⁺ solutions in a 100 ml capacity plastic bottle containing 50mL of ion solution with a given concentration (Co²⁺ ≈250mg.L⁻¹ and Sr²⁺≈450mg.L⁻¹) at pH 6.5 and room temperature. A shaker was used to blend the mixtures which were subsequently left to rest in a horizontal position for 3 hours at room temperature and rotated at 250 rpm. For this purpose 0.025M CoCl₂.6H₂O was used to prepare the Co²⁺ solution, while 0.06M SrCl₂ was used to prepare the Sr²⁺ solution. Each solution was diluted a number of times to generate a range of different solutions of Co²⁺ and Sr²⁺ concentrations. All runs were conducted at room temperature and the mixing speed and pH parameters were controlled. 0.6 mL of each sample removed from the solution using a fine micro-pipette after intervals of 30 minutes, 1.5 hours, 2 hours and 3 hours and then filtered through a 12.5 mm diameter Whatman filter. The samples were diluted with water and the
concentration of each ion was measured before and after the batch operation process with an ICP-OES model Vista-MPX by Varian. All mixed media were dried overnight at 50°C after the ion exchange process for the leaching and vitrifaction study.

Both the support media (carbon and celatom without zeolite) and the pure zeolites in powder form without support were mixed separately with the Co\(^{2+}\) and Sr\(^{2+}\) solutions under identical conditions to observe the effect of composite zeolite supported by the carbon or celatom surfaces. After the ion exchange process, the samples were measured by XRD, SEM and EDAX to explore the integrity of the micro/macroporous structure, surface morphology and bulk elements composition. The ICP-OES was used to measure the concentrations of Co\(^{2+}\) and Sr\(^{2+}\) ions. The instrument was calibrated with two standard solutions of 5 and 10 mg. L\(^{-1}\) of Co\(^{2+}\) and Sr\(^{2+}\) ions. All samples were diluted to be within this range of concentration before the analysis. To determine the concentration, wavelengths of 228.3 and 231.160 nm were used for Co\(^{2+}\), while 238.9 and 460.733 nm were used for Sr\(^{2+}\).

The number of adsorbed ions \(q(t)\) mg. g\(^{-1}\) at time \(t\) was calculated using equation 31[26].

\[
q(t) = \frac{C_0 - C_i}{m} \times V \quad \text{Eq.(31)}
\]

where \(V\) and \(m\) are the volume of Co\(^{2+}\) or Sr\(^{2+}\) ions solution (L) and the amount of the adsorbent (g) respectively, and \(C_0\) and \(C_i\) are the initial and any time concentrations of Co\(^{2+}\) or Sr\(^{2+}\) respectively.

### 6.2.3 Effect of pH, Initial Concentration, Binary and Temperature on the Uptake of Co\(^{2+}\) and Sr\(^{2+}\)

To study the effect of pH variation on the uptake of each ion, different Co\(^{2+}\) and Sr\(^{2+}\) solutions with varying pH (2, 4 and 6) for Co\(^{2+}\) and (2, 4, 6 and 10) for Sr\(^{2+}\) were prepared. As an initial concentration, plastic containers of 100 mL were filled separately with 25mL from the stock solution of each ion. 1M HCl and 1M NaOH were used to adjust the pH value of the solutions. Then 0.05g of selected media was added to the solutions and they were left to stand for 3 hours at room temperature to ensure that the system reached at state of equilibrium. The experiment was conducted with two different types of zeolites (ZA and ZY) test on one support media (IP), the zeolite Y was tested with another support media, celatom, for the purposes of comparison.
To study the effect of temperature on the uptake of Co\(^{2+}\) and Sr\(^{2+}\) ions, three different temperatures (20-25\(^{\circ}\)C, 45-50\(^{\circ}\)C and 65-70\(^{\circ}\)C) were used to conduct this experiment and the Co\(^{2+}\) and Sr\(^{2+}\) ions were stirred in thermostat mixer with 0.05g of each media at pH 5-6.

The effect of the intensity of the initial concentration was also studied under the conditions noted above by varying the concentrations between 100 to 480 mg.L\(^{-1}\).

To investigate the capacity to take up both ions in one solution, 1:1 volume ratio was used to prepare a binary component sorption solution, 250 mg.L\(^{-1}\), of Co\(^{2+}\) and Sr\(^{2+}\) ions for each solute. The same ion exchange procedure for the single solute was used in the bi-solute.

### 6.3 ISOTHERM MODEL (LANGMUIR AND FREUNDLICH EQUATIONS)

According to the results of kinetic experiments outlined in 6.2.2, 3 hours was the period applied to study the isotherms for IPA, IPY, IPClinp and Cel-ZY using the Langmuir and Freundlich models. These samples of IPA, IPY, IPClinp and Cel-ZY were selected to study the different types of zeolite based on one supporter type (IP), while Cel-ZY was selected to study the behaviour of zeolite using another type of supporter (celatom). For this purpose, 25 mL Co\(^{2+}\) and Sr\(^{2+}\) solutions with a range of different concentrations (75- 480 mg.L\(^{-1}\)) were mixed with a 0.05g of each selected adsorbent medium at 20\(^{\circ}\)C and pH 5-6. Equations 5 and 7 describe the non-linear Langmuir and Freundlich models, which are stated in Chapter 2 section 2.6 [17].

\[
q_e = \frac{K_L b \cdot C_e}{1 + K_L \cdot C_e} \tag{Eq.5}
\]

\[
q_e = K_F (C_e)^{\frac{1}{n}} \tag{Eq.7}
\]
6.3.1 DETERMINING ISOTHERM PARAMETERS

The coefficients of determination $r^2$ were calculated to study the best fitting isotherms for the theoretical data of the two models to the experiment data by using Eq. (17) [30].

$$ r^2 = \frac{\sum (q_e,\text{model} - q_e,\text{av.})^2}{\sum (q_e,\text{model} - q_e,\text{av.})^2 + \sum (q_e,\text{model} - q_e,\text{exp.})^2} \quad \text{Eq. (17)} $$

Where: $q_e,\text{model}$ is the equilibrium capacity obtained from the isotherm model, $q_e,\text{exp.}$ is the equilibrium capacity obtained from experiment and $q_e,\text{av.}$ is the average $q_e,\text{exp.}$.

The constants in the Langmuir and Freundlich equations are calculated using the nonlinear optimizing procedure solver add-in with Microsoft’s spreadsheet, Microsoft Excel [236, 237]. An error function is required to be selected in order to estimate the fit value of the theoretical data which results from the equilibrium isotherm model to the experimental data. Thus, the coefficient of determination $r^2$, will be maximised, while the respective error function will be minimised across the choice of concentrations studied by varying the value of the isotherm parameters [238].

The values of the separation factor $R_L$ were used to indicate the range most conducive to maximum adsorption using Langmuir constant $K_L$ (L.mg$^{-1}$) as described in Equation 6 as mentioned in Chapter 2 [19].

$$ R_L = \frac{1}{1 + K_L C_0} \quad \text{Eq.6} $$
6.4 RESULTS OF THE ION EXCHANGE PROCESS

6.4.1 Adsorption of Co$^{2+}$ and Sr$^{2+}$ Ions

The adsorptions of Co$^{2+}$ and Sr$^{2+}$ ion onto different adsorbents, listed in Table 6.1, were performed separately at room temperature. In the batch operations, the absorbent types were varied, while other parameters such as temperature, solution volume, stirring time and initial concentration of each solution remained constant. As shown in Figure 6.1 (a and b) the results for the experiments carried out with 0.1g of each type of pure zeolites (zeolite A, zeolite Y and clinoptilolite) show that the concentration of Co$^{2+}$ and Sr$^{2+}$ ions decreased more significantly through the use of pure zeolite A (PZA) than through pure zeolite Y (PZY) and pure clinoptilolite (PClinp). For each ion, as shown in Figure 6.2 (a and b), PZA achieved a higher adsorption capacity ($q_e$ = 61.15 mgCo.$g_z^{-1}$ and $q_e$ = 204.55 mgSr.$g_z^{-1}$) than PZY (53.1 mgCo.$g_z^{-1}$ and 118.2 mgSr.$g_z^{-1}$) and PClinp (28.5 mgCo.$g_z^{-1}$ and 91.5 mgSr.$g_z^{-1}$). A higher removal capacity of Co$^{2+}$ and Sr$^{2+}$ ions was observed with PZA and PZY. This may be due to the high ion-exchange capacity (low Si/Al ratio), larger framework channels and higher number of ion-exchange sites characteristic of zeolite. For each type of adsorbent the first 30 min of the initial stage of the contact time registered the fastest reduction of both ions. This could be due to the availability of vacant sites on the adsorbent solid surfaces at the beginning of the contact with the initial concentration of solutions [37, 239]. This was also reported by A.M. El-Kamash who observed that for zeolite-A, 80-90% of the sorption of Cs$^+$ and Sr$^{2+}$ ions occurred within the first 30 min [240]. In addition, it was noticed that the uptake of Sr$^{2+}$ and Co$^{2+}$ ions was significantly increased by increasing the mixing time until reaching the equilibrium state [38].
Figure 6.1 Effect of contact time on the concentration of (a) Co$^{2+}$ and (b) Sr$^{2+}$ ions at pH 5.5-6.5, 25°C, interaction time (0.5, 1, 2 and 3h), initial Sr$^{2+}$ ions concentration ~480mg.L$^{-1}$, 50mL volume and 0.1g of Pure zeolite-A(PZA), Pure zeolite-Y(PZY) and Pure clinoptilolite(PClinp).
Figure 6.2 Effect of reaction time on the adsorption of (a-) Co\(^{2+}\) and (b-) Sr\(^{2+}\) ions with each type of adsorbent (Pure zeolite-A (PZA, Pure zeolite-Y (PZY) and pure Clinoptilolite (PClinp)).
6.4.1.1 Adsorption of Co$^{2+}$ and Sr$^{2+}$ ions onto Carbon-Zeolite Composites

The adsorption of Co$^{2+}$ and Sr$^{2+}$ ion onto carbon-zeolite composites media is listed in Table 6.1. Zeolites (ZA, ZY and Clinp) with two types of carbon materials (IP and TS) were tested at 20°C by varying the adsorbent types. The hierarchical structures (IPA, TSA, IPY, TSY, IPClinp ,TSClinp ,Cel-ZY and Cel-ZA) and the non-corresponding carbons IPC and TSC or diatomite (Celatom-FW14 ) without zeolite were used in order to study the uptake of Co$^{2+}$ and Sr$^{2+}$ ions from the solutions. The other conditions such as temperature, volume, shaking time and initial concentration of Co$^{2+}$ and Sr$^{2+}$ ion solutions were fixed. Using SEM it was found that, after the completion of the adsorption process for all types of zeolites, zeolite crystals remained attached to the carbon surfaces, Figure 6. 3 (see appendix G).

Figure 6. 4 shows the decrease in the Co$^{2+}$ and Sr$^{2+}$ concentrations after each has been mixed with composite materials (Carbon-Zeolite (C-Z) and Celatom-Zeolite (Cel-Z)). It can be observed that both composite materials have minimised the Co$^{2+}$ and Sr$^{2+}$ ion concentration in the solutions. Experiments with Iraqi Palm Tree Leafs carbon (IPC), Tamarind Stones carbon (TSC) media and Celatom-FW14 without zeolite did not significant indicate result in the removal of any Co$^{2+}$ and Sr$^{2+}$ ions (low negligible values from 3-8 mg.g$^{-1}$).
Figure 6. 3 SEM images showing that the crystals of all used zeolite types still stuck onto carbon surfaces even after 3h of adsorption process (Scale bar=20 and 50 µm) with different magnifications.)
Figure 6.4  Preliminary screening analyses of adsorbents of (a) Co$^{2+}$ and (b) Sr$^{2+}$ ions . 
(IPA= Iraqi Palm Tree Leafs-Zeolite A, TSA= Tamarind Stone-Zeolite A, IPClinp= Iraqi Palm Tree Leafs- Clinoptilolite and TSY= Tamarind Stone-Zeolite Y (See Table 6.1) in respect to the total mass of carbon-zeolite.)
Figure 6.5a shows that the increase in the adsorption capacity (uptake of ions) increased significantly, with respect to the total mass of carbon/zeolite (C-Z) composite materials, of both ions (mg_{ion}/g_{(C-Z)}) with an increase in the contact time until reaching the state of equilibrium between 2-3h for both ions. This has also been observed in previous studies [24].

Figure 6.5b, shows the adsorption rate of Co^{2+} ions in relation to the zeolite mass onto composite materials listed in Table 6.1. They are arranged in descending order in term of their ability to the uptake of Co^{2+} ion as TSA >IPA>TSY>IPY>TSClinp>IPClinp. The highest adsorption rate was achieved by TSA (120 mgCo.g_{z}^{-1}), while the lowest adsorption capacity was with observed with IPClinp (42.1 mgCo.g_{z}^{-1}).

For the Sr^{2+} ion, Figure 6. 6a depicts the decrease in the Sr^{2+} ion concentration for each composite material. It shows clearly that each composite material has minimised the Sr^{2+} ion concentration in the solutions. With the loading of zeolite masses aided by the presence of scaffold for each type of zeolite listed in Table 6.1. The results show that TSA has the highest adsorption capacity q_{e}(290 mgSr.g_{z}^{-1}) (Figure 6. 6b), whilst the other adsorbent media show that TSA>IPA> IPY > TSY > TSClinp > IPClinp.

Figure 6. 7 and Figure 6. 8 clearly shows that Co^{2+} ion in IPY and Sr^{2+} ion in TSClinp composites appear in the EDAX spectrum which were measured for the adsorbent samples before and after the ion exchange process.
Figure 6.5 Effect of reaction time on the adsorption capacity of Co\(^{2+}\) ions in respect to the (a) total mass of C-Z composite and (b) zeolite mass only at pH5.5-6.5, 25°C, interaction time (0.5, 1, 2 and 3h), initial Co\(^{2+}\) ions concentration 250-300 mg.L\(^{-1}\), 25 ml volume and 0.05g of IPA, TSA, IPY, TSY, IPClinp and TS Clinp as adsorbent materials.
Figure 6.6 Effect of reaction time on the adsorption capacity of Sr\(^{2+}\) ions in respect to the (a) total mass of C-Z composite and (b) zeolite mass only at pH 5.5-6.5, 25°C, interaction time (0.5, 1, 2 and 3h), initial Sr\(^{2+}\) ions concentration 480 mg.L\(^{-1}\), 25 ml volume and 0.05 g of IPA, TSA, IPY, TSY, IPClinp and TSClinp as adsorbent materials.
Figure 6.7 Shows the EDAX for IPA showing the peak of Co\(^{2+}\) ion appeared clearly in each pattern after adsorption processes.

The results of the Sr\(^{2+}\) ions uptake in Figure 6.8 show that the peak of Sr\(^{2+}\) was appeared unclearly at 1.806 KeV in an interference with the peak of silicon at 1.740 KeV in the EDAX spectrum. (see Table 3.1). The weight percent (wt\%) of elements of TSClinp adsorbent after treatment process was used as an evidence to approve that Sr\(^{2+}\) ion has taken place onto composite materials after treatment process.
6.4.1.2 Adsorption of Co$^{2+}$ Ions onto Celatom-Zeolite (Cel-Z)

The adsorption of Co$^{2+}$ and Sr$^{2+}$ ion onto the Celatom-Zeolite (A and Y) composites was performed at room temperature. For the batch operation, the Cel-ZY and Cel-ZA adsorbent types were alternated, while other variables such as temperature, solution volume, shaking time and initial concentration of both Co$^{2+}$ and Sr$^{2+}$ solution were controlled (230-250 mg.L$^{-1}$ Co$^{2+}$ and 450-480 mg.L$^{-1}$ Sr$^{2+}$) using the same procedure for carbon-zeolite composite outlined in section 6.2.2. The SEM images show that the zeolite crystals still adhered to the celatom surfaces after the adsorption process. The results show that Cel-ZA achieved a maximum adsorption capacity of $q_e$ 154.2 mgCo.g$^{-1}$ and $q_e$ 263 mgSr.g$^{-1}$ for both ions in comparison with $q_e$ 110.1 mgCo.g$^{-1}$ and $q_e$ 250.3 mgSr.g$^{-1}$ for the Cel-ZY composite (Figure 6. 9 a and b respectively). This could be due to the low Si/Al ratio of zeolite-A (Si/Al=1) which, as mentioned in Chapter two, creates greater amounts of the exchangeable ions.
Figure 6.9 Effect of contact time on the amount of (a) $\text{Co}^{2+}$ and (b) $\text{Sr}^{2+}$ ions adsorbed (pH 5.5-6.5, 25°C, interaction time (0.5, 1, 2 and 3h), 50 ml volume and 0.1g of Celatom-Zeolite A (Cel-ZA) and Celatom-zeolite Y (Cel-ZY) as adsorbent materials.
Figure 6. 10 clearly show that Co\(^{2+}\) ion in Cel-ZY composite appear in the EDAX spectrum, the EDAX for the adsorbent samples were measured after the ion exchange process.

![EDAX spectrum](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt%</th>
</tr>
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</tr>
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<tr>
<td>Fe</td>
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<td>Total</td>
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</tbody>
</table>

Figure 6. 10 Shows the EDAX for Cel-ZY showing the peak of Co\(^{2+}\) ion appeared clearly in its pattern after adsorption processes.

### 6.5 RESULTS OF THE EFFECT OF pH, INITIAL CONCENTRATION AND TEMPERATURE

The effect of pH on the sorption of Co\(^{2+}\) and Sr\(^{2+}\) ions using the prepared hierarchical materials was investigated. For the Co\(^{2+}\) solution, the pH range from 2.0 to 6.5 was employed to avoid the Co\(^{2+}\) precipitating in the solution, as evidence from literature indicates that Co\(^{2+}\) (OH)\(_2\) is formed when the pH is above 7 [241]. In this study the result indicates that there was no evidence of hydroxide precipitation in the 2.0-6.5 range. Conversely, a stock solution of Co\(^{2+}\) was prepared at pH 7, 8 and 10 it was observed that the blue Co\(^{2+}\) solution had precipitated and that there was a clear distinction between the upper layer and bottom (blue) layer forming in the upper layer as can be seen in Figure 6.11.
Figure 6.11 Shows the chemical precipitation of Co^{2+} ion started from pH7 to pH10.

For the Sr^{2+} solution, a pH range of 2 to 10 was used. Within this range the Sr^{2+} formed in solution has insignificant amounts of Sr (OH)^+ up to pH11 [240, 241]. In the literature , the amount of Sr(OH)^+ starts to predominate after pH 13 [242]. Thus, the pH range which was used in this study between 2 to 10.

The results in Figure 6.12 and Figure 6.13 shows respectively that the uptake of both ions (Co^{2+} and Sr^{2+}) was positively correlated with the pH values in the solution. It was clearly observed that the sorption of Co^{2+} and Sr^{2+} ions increases with an increase in the pH level. The trend may be explained by the effect of the acids on the zeolites, as at low pH levels the acids will attack the zeolite framework. Zeolites have two types of bonds in their frameworks: Si-O-Si and Si-O-Al as mentioned in Chapter 2. The former bond is stronger than the latter. Due to the low and intermediate Si/Al ratio in the framework structure of zeolite-A and zeolite-Y (ZA=1 and ZY=3.2), H^+ ion can easily attack the Si-O-Al bonding leading to a collapse of the structure[238].

The results at pH 2 show a minimum uptake of both metals (Co^{2+} and Sr^{2+}) because of the higher sorption of H^+ ions, while the uptake values of both metals increased as the pH was increased.

At pH levels of 2 to 4 both H^+ and metal (Co^{2+} ions) were sorbed onto the composite material. However, at pH levels 6-7 sorptions was mostly occurring only for Co^{2+} ions. On the other hand, the sorption of Sr^{2+} continued even up to pH value 10-12. This gives a clear indication of the role of elemental Co^{2+} and Sr^{2+} respectively, in this part of pH.
range. The same result was reported by Park, Y., et al using ammonium molybdophosphate–polyacrylonitrile (AMP–PAN) to remove Co$^{2+}$, Sr$^{2+}$ and Cs$^+$ from wastewater released from nuclear power plants [241, 243]. Yusan, S. and S. Erenturk also reported this result by using PAN/Zeolite composite to adsorb Sr$^{2+}$ ion from aqueous solution [242].

The effect of temperature on the adsorption process was studied through the application of three different temperatures: 20, 50 and 70°C., the results Figure 6. 14 and Figure 6. 15 show respectively that the uptake of Co$^{2+}$ and Sr$^{2+}$ ions slightly reduced as the temperature was raised from 45-50 to 65-70 °C. The highest uptake occurred between room temperature (20°C) and 50°C. Inglezakis and other [243], Panayotova and others[244], observed that the typical zeolite isotherm for Pb$^{2+}$, Cr$^{2+}$, Fe$^{3+}$, Cu$^{2+}$ was achieved at room temperature indicating an exothermic characteristic of the adsorption process and then decreased slightly between 50-70°C. A similar result was observed by M. Uğurlu and others with Ni (II) ions in an aqueous solution[245]. The weakness of the bonds between Co$^{2+}$ and Sr$^{2+}$ ions and the active sites of adsorbents under increasing temperatures may led to the reduction in the adsorbent rate for each ion [241].

Figure 6. 16 and Figure 6. 17 respectively show the effect of initial concentration strength of Co$^{2+}$ and Sr$^{2+}$ versus the increase in contact time on composite adsorbent media. It illustrates that the strength of the initial concentration plays an important role in increasing the uptake of Co$^{2+}$ and Sr$^{2+}$ ions, this may be due to an increase in the collision of the ions onto the adsorbents materials. In all the experiments, the equilibrium time was attained between 120 and 180 minutes. Varying the initial concentrations of Co$^{2+}$ and Sr$^{2+}$ ion did not alter the equilibrium time.

From the results of all experiments it can be seen that the most of Co$^{2+}$ and Sr$^{2+}$ ions were adsorbed onto the surface of media within the first 30 minutes. Subsequently, the adsorption rate remains constant and does not alter as a result of changes in the conditions of the experiment. In addition, it was recognized that the time required to reach the equilibrium remained between 120-180 minutes and the pH value in the solutions were increased for all samples after adsorption processes.
Figure 6. 12 plot of pH Vs $q_e$ (mg/gz) for IPA, IPY and Cel-ZY for Co$^{2+}$ (Initial conc. = 250(mg.L$^{-1}$) and range of pH from 2.0 to 6.5).

Figure 6. 13 plot of pH Vs $q_e$ (mg/gz) for IPA, IPY and Cel-ZY for Sr$^{2+}$ (Initial conc. = 480(mg.L$^{-1}$) and range of pH from 2.0 to 10.0 for Sr$^{2+}$)
Figure 6. 14 plot of Temp. Vs qe (mg/gz) for IPA, IPY and Cel-ZY for Co$^{2+}$ (Initial conc. = 250(mg.L$^{-1}$))

Figure 6. 15 plot of Temp. Vs qe (mg/gz) for IPA, IPY and Cel-ZY for Sr$^{2+}$ (Initial conc. = 480(mg.L$^{-1}$))
In the binary solute system, the capacity for adsorption may be affected by mixing the Co\(^{2+}\) and Sr\(^{2+}\) ions in one solution. All the composite materials listed in Table 6.1 were treated separately to remove the Co\(^{2+}\) and Sr\(^{2+}\) ions. The ions were included in one
mixture with the same volume (~250 mg.L\(^{-1}\) of each ion type) under the same conditions: pH5-6, room temperature, reaction time and solution volume. The results show that for all types of composite adsorbent materials the uptake of Sr\(^{2+}\) ions were higher that for the Co\(^{2+}\) ions (Sr\(^{2+}\) > Co\(^{2+}\)), same result was reported in literature using natural clinoptilolite to remove these ions from aqueous solution (Serbia) by batch technique [243]. The maximum adsorption capacities for the Co\(^{2+}\) and Sr\(^{2+}\) ions in the mixed solutions were lower than the maximum adsorption capacities of the same composite materials for the single solution. In addition, with all of composite materials listed Table 6.1, the uptake of Sr\(^{2+}\) ions was higher than the uptake of Co\(^{2+}\) ions, as shown in Figure 6.18 to Figure 6. 23. This may be because of two factors that affect the two metal ions in solution, the first being the reactivity of the two ions in aqueous solution and the second being the effect of the ionic radius of the element. The reactivity of the two ions may also be an important factor at influences the ionic system in involving Sr\(^{2+}\), Co\(^{2+}\) and the Na\(^+\) that balances the charge on the zeolite structure. Sr\(^{2+}\) is higher than Na\(^+\) and Co\(^{2+}\) on the activity series, so it can readily displace Na\(^+\) in an aqueous system so it is presented that it can take up the place of Na\(^+\) on the zeolite framework structure. However, Co\(^{2+}\) is lower than Na\(^+\) on the activity series and the ease of ion-exchange of Co\(^{2+}\) with Na\(^+\) on the zeolite framework is lower than that of Sr\(^{2+}\). So because the mechanism is that of ion-exchange, the reactivity series position of the two metals means that Sr\(^{2+}\) will have a higher removal capacity than Co\(^{2+}\) by the composite adsorbents (Sr\(^{2+}\) =215 mg.L\(^{-1}\) and Co\(^{2+}\) = 125 mg.L\(^{-1}\)). Sr\(^{2+}\) ion showed higher removal capacity than the Co\(^{2+}\) because it has a larger ionic radius and this larger size helps it in reducing the amount of repulsive forces that can hinder its transport across the bulk of the solution onto the surface of the adsorbent. The model proposed by Sverjensky and co-workers explains this surface-ionic interaction as follows; that in an aqueous solution system, ions of larger ionic radius are less affected by the repulsive solvation effects when approaching the adsorbent/aqueous interface [246]. Thus the Sr\(^{2+}\) ion transport will have a higher success than the Co\(^{2+}\) thereby increasing its ability reach the adsorbent surface and increase the probability of ion-exchange to occur. All results were respect to zeolite A, Y and clinoptilolite mass in carbon and zeolite A and Y onto celatom surface samples. In Figure 6.18, the trend
order of the different zeolites supported by IPC is arranged as IPY>IPA>IPClinp in case of Co$^{2+}$ ions, whereas for Sr$^{2+}$ ions the trend follows the sequence IPA>IPY>IPClinp as can be seen in Figure 6.19. For the TSC, which was used to hold separately the same type of zeolites (A, Y and Clinp), the trend for Co$^{2+}$ ions is arranged as shown in Figure 6.20 as TSA=TSY>TSClinp. However, for Sr$^{2+}$ ions (Figure 6.21), it is arranged in the order TSA>TSY>TSClinp. In addition, as shown in Figure 6.22, for both ions Cel-ZA performed better than Cel-ZY. The trend order of the maximum adsorption capacity of Sr$^{2+}$ ion based on different supporter materials (IP, TS and celatom) is: TSA> Cel-ZA >IPA, whilst for Co$^{2+}$ ions it is IPA≥ Cel-ZA >TSA.

Figure 6.18 plot of $q_e$ (mg/g.) Vs time for Iraqi Palm Tree Leaves – Zeolite composites (IPA , IPY and IPClinp for Co$^{3+}$ (Initial conc. = 250(mg.L$^{-1}$)) .
Figure 6.19 Plot of $q_e$ (mg/g) Vs time for IPA, IPY and IPClinp for Sr$^{2+}$ (Initial conc. = 250 (mg.L$^{-1}$)).

Figure 6.20 Plot of $q_e$ (mg/g) Vs time for Tamarind Stones–Zeolite composites (TSA, TSY and TSClinp) for Co$^{3+}$ (Initial conc. = 250 (mg.L$^{-1}$)).
Figure 6.21 Plot of $q_e$ (mg/g) Vs time for TSA , TSY and TSClinp for Sr$^{2+}$ (Initial conc. = 250(mg.L$^{-1}$)).

Figure 6.22 Plot of $q_e$ (mg/g) Vs time for Celatom-Zeolite composites( Cel-ZA and Cel-ZY for Co$^{2+}$) (Initial conc. = 250(mg.L$^{-1}$)).
6.6 RESULTS OF LANGMUIR AND FREUNDLICH ISOTHERM MODELS

The isotherms obtained for the adsorption of Co$^{2+}$ and Sr$^{2+}$ onto selected composites media (IPA, IPY, IPClinp and Cel-ZY) were investigated using Freundlich and Langmuir models. Both models were used to reconcile the theoretical data with the experimental data for each composite adsorbent. A non-linear method was calculated using the solver add-in program in Microsoft Excel for this purpose. The results of the model analysis are presented in Figure 6. 24 for Langmuir model and Figure 6. 25 for Freundlich isotherm model in case of Co$^{2+}$ ion. The data obtained from these models is presented in Table 6.2.
Figure 6. 24 Sorption isotherms of Co\(^{2+}\) ions sorbed onto different composite adsorbents (IPA, IPY, IPClinp and Cel-ZY) at room temperature. The dashed and pointed lines show the fitting between the theoretical data and experimental data by Langmuir model.

Figure 6. 25 Sorption isotherms of Co\(^{2+}\) ions sorbed onto different composite adsorbents (IPA, IPY, IPClinp and Cel-ZY) at room temperature. The dashed and pointed lines show the fitting between the theoretical data and experimental data by Freundlich model.
The coefficients of determination $r^2$ were calculated to study the best fitting isotherms to the experiment data by using Eq. (17). From the results based on an analysis of the $r^2$ values obtained, it can be seen that for Co$^{2+}$ adsorption, the IPClinp composite fits the Langmuir model more closely than the other adsorbents. For Co$^{2+}$ adsorption using the Langmuir model, the order of $r^2$ value for the adsorbents is IPClinp $>$ Cel-ZY $>$ IPY $>$ IPA. $b$ which equals the trend in the sorption capacity, is IPA $>$ Cel-ZY $>$ IPY $>$ IPClinp. This is a measure of the maximum sorption capacity in the Langmuir model corresponding to complete monolayer coverage for the composite adsorbents. $K_L$, the trend in the adsorption coefficient, is IPY $>$ IPA $>$ Cel-ZY $>$ IPClinp as indicated in Table 6.2. $K_L$ is a measure of the apparent sorption energy for the composite adsorbents.

With the Freundlich model, for analysis of Co$^{2+}$ adsorption, the IPClinp composite adsorbent shows the best fit for the model based on the $r^2$ value analysis, Figure 6.25. The order of $r^2$ value of composite media is given as IPClinp $>$ Cel-ZY $>$ IPA $>$ IPY.

Table 6.2: Freundlich and Langmuir parameter for adsorption of Co$^{2+}$ and Sr$^{2+}$ ions at 20°C (adsorbent media 0.05g/25mL; initial ions concentration from 100 to 480 mg.L$^{-1}$; pH 6 and 180 min as contact time)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>IPA</th>
<th>IPY</th>
<th>IPClinp</th>
<th>Cel-ZY</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Langmuir Co$^{2+}$</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$b$</td>
<td>1.122</td>
<td>0.023</td>
<td>0.00206</td>
<td>0.0327</td>
</tr>
<tr>
<td>$K_L$</td>
<td>139.29</td>
<td>181.65</td>
<td>113.679</td>
<td>124.39</td>
</tr>
<tr>
<td>$R_L$</td>
<td>0.004-0.23</td>
<td>0.15-0.5</td>
<td>0.65-0.9</td>
<td>0.118-0.45</td>
</tr>
<tr>
<td>$r^2$</td>
<td>0.919</td>
<td>0.944</td>
<td>0.985</td>
<td>0.953</td>
</tr>
<tr>
<td><strong>Freundlich Co$^{2+}$</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_F$</td>
<td>102.78</td>
<td>31.24</td>
<td>0.803</td>
<td>26.58</td>
</tr>
<tr>
<td>$n$</td>
<td>15.8</td>
<td>3.379</td>
<td>1.38</td>
<td>3.71</td>
</tr>
<tr>
<td>$r^2$</td>
<td>0.939</td>
<td>0.867</td>
<td>0.989</td>
<td>0.967</td>
</tr>
</tbody>
</table>
The Freundlich isotherm parameter $n$ measures the adsorption intensity of Co$^{2+}$ on the composite adsorbents and the trend of this constant is given as IPA > Cel-ZY > IPY > IPClinp. While the trend of $K_F$, which is relates to the adsorption capacity, is given as IPA > IPY > Cel-ZY > IPClinp.

For the adsorption of Sr$^{2+}$ onto the composite adsorbents the isotherm Langmuir isotherm analysis is presented in Figure 6. $26$ was use to determine the best fit for the isotherm the $r^2$ values. The results indicate that the IPA composite is the closest and the trend is as follows; IPA > IPY > Cel-ZY > IPClinp.

![Figure 6. 26 Adsorption isotherms for Sr$^{2+}$ on different adsorbent composites (IPA, IPY, IPClinp and Cel-ZY) at 25°C and pH 6.5. The lines show the Langmuir isotherm equation fitted to the experimental data using a least squared error method.](image-url)
While for the Freundlich isotherm the best fitting composite adsorbent is the IPClinp based on the r² value with the trend order being IPA>IPClinp>Cel-ZY>IPY, as shown in Figure 6.27. Examination of the isotherm constants for the composite adsorbents as shown in Table 6.3 indicates that for the Langmuir isotherm the trend for the b constant is Cel-ZY> IPClinp> IPA > IPY, and for KL the trend is IPA> IPY > Cel-ZY >IPClinp. For the Freundlich isotherm constants the trend for the n parameter is indicated as Cel-ZY> IPClinp > IPY > IPA, while for the constant KF the trend is Cel-ZY> IPY > IPA >IPClinp.

Figure 6.27 Adsorption isotherm for Co²⁺ on (IPA, IPY, IPClinp and Cel-ZY) at 25°C and pH 6.5. The lines show the Freundlich isotherm equation fitted to the experimental data using a least squared error method.
Table 6.3 Freundlich and Langmuir parameter for adsorption of Co\(^{2+}\) and Sr\(^{2+}\) ions at 20°C (adsorbent media 0.05g/25mL; initial ions concentration from 100 to 480 mg.L\(^{-1}\); pH 6 and 180 min as contact time):

<table>
<thead>
<tr>
<th>Parameters</th>
<th>IPA</th>
<th>IPY</th>
<th>IPClinp</th>
<th>Cel-ZY</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Langmuir Sr(^{2+})</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b)</td>
<td>0.043</td>
<td>0.0392</td>
<td>0.258</td>
<td>2.33</td>
</tr>
<tr>
<td>(KL)</td>
<td>354.8</td>
<td>292.91</td>
<td>101.43</td>
<td>238.02</td>
</tr>
<tr>
<td>(RL)</td>
<td>0.057-0.219</td>
<td>0.0472-0.192</td>
<td>0.029-0.122</td>
<td>0.001465-0.0065</td>
</tr>
<tr>
<td>(r^2)</td>
<td>0.994</td>
<td>0.863</td>
<td>0.722</td>
<td>0.920</td>
</tr>
<tr>
<td><strong>Freundlich Sr(^{2+})</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(KF)</td>
<td>59.37</td>
<td>73.854</td>
<td>37.21</td>
<td>239.53</td>
</tr>
<tr>
<td>(n)</td>
<td>3.28</td>
<td>4.399</td>
<td>4.17</td>
<td>1.46</td>
</tr>
<tr>
<td>(r^2)</td>
<td>0.968</td>
<td>0.7107</td>
<td>0.965</td>
<td>0.7402</td>
</tr>
</tbody>
</table>

Overall, an examination of the isotherms indicates that for the description of Co\(^{2+}\) adsorption IPClinp was the best fit for both isotherms with \(r^2\) values of 0.989 (Freundlich) and 0.985 (Langmuir). For Sr adsorption, IPA was the best fit for the Langmuir model with an \(r^2\) value of 0.994 and also for the Freundlich model with an \(r^2\) value of 0.968.

As described in, Chapter 2 section 2.16.1, Langmuir model is only valid for single-layer adsorption. In addition, it depends on the supposition that the highest adsorption corresponds to a saturated monolayer of adsorbate molecules on the solid surface, that the energy of adsorption is constant. While, the Freundlich model has capable of being used with non-ideal sorption on heterogeneous surfaces as well as for multilayer sorption.

The Langmuir and Freundlich models can be applied on a wide range of adsorbents to investigate the one that describes the adsorption process better for a known contaminant. Both models can be demonstrated to estimate the amount of a contaminant which can be adsorbed from wastewater using an adsorbent as shown in Table 6.4.

Different parameters can be affected by the concentration of contaminants remaining in the wastewater at the equilibrium point such as adsorbate properties, nature of
adsorbent, and type of contaminant. Since unique parameters can be obtained with each condition using the models they can be evaluated to determine which model is better.

Table 6.4 Shows the comparison between the favourable models in case of different composite material for both ions (Co\(^{2+}\) and Sr\(^{2+}\)) based on the coefficient of determination r\(^2\).

<table>
<thead>
<tr>
<th>Adsorbent type</th>
<th>Favourable model (Langmuir / Freundlich)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr</td>
<td>Co</td>
</tr>
<tr>
<td>IPA</td>
<td>Langmuir</td>
</tr>
<tr>
<td>IPY</td>
<td>Langmuir</td>
</tr>
<tr>
<td>IPClinp</td>
<td>Freundlich</td>
</tr>
<tr>
<td>Cel-ZY</td>
<td>Langmuir</td>
</tr>
</tbody>
</table>

The performance of the adsorbents can be compared using the separation factor \(R_L\) obtained, which is based on the Langmuir isotherm. As shown in Figure 6. 28 a and b, respectively for both the Co\(^{2+}\) and Sr\(^{2+}\) ions the favourable sorption isotherms were indicated for the composites media (Cel-ZY, IPClinp, IPY and IPA) due to the range of \(R_L\) values which were found between 0 and 1 (0 < \(R_L\) < 1). For the Co\(^{2+}\) ion (Figure 6. 28), the separation factor \((R_L)\) for IPA was between 0.65 and 0.9, while for IPY and Cel-ZY the \(R_L\) ranged from 0.1 to 0.5 and for the IPClinp values fell within the 0.004 to 0.23 range. As shown in Figure 6. 28b, for the Sr ions the \(R_L\) for IPA was between 0.057 and 0.22, while for Cel-ZY it was between 0.0014 and 0.0061. The separation factor for IPY was between 0.047 and 0.19 and for IPClinp and it ranged from 0.029 to 0.122. The separation factor (\(R_L\)) was used to express the essential characteristics of the Langmuir isotherm terms equilibrium parameter using Eq. (6).
Figure 6. 28 Separation factor (RL) for the adsorption of (a) Co\textsuperscript{2+} and (b) Sr\textsuperscript{2+} onto (IPA, IPY, IPClinp and Cel-ZY) was calculated using equation 15 and the equilibrium constant obtained from the fit of the Langmuir isotherm equation to the experimental data.
6.7 VITRIFICATION AND LEACHING

Vitrification can be defined as a method to convert material into glassy substances [247]. Due to the particular features of the vitrification process, it is considered a very attractive technique to use in the treatment of different types of wastes, such as High Level Radioactivity Waste (HLW) and/or heavy metals. The process of vitrification can be performed through heating (above 800°C) and without heating through gel formation which can also form glass-like material. This product can withstand both chemical and biological environments [248].

In the process of vitrification, organic substances can be broken down through pyrolysis process or combustion. While the vitrification process is more stable with inorganic materials with which immobilization can occur via integration within the structure of the glass or encapsulation within the glass. The ability to integrate glass with metals has a long history, selenium is found in transparent glass, and has also been found that chromium can give a green colour to glass [249].

Silica, alumina and oxides of alkali (silicate glass) are the primarily components of glass. It is rigid and has relatively low porosity. The Si-O tetrahedron is the basic structure of the SiO₂ network. As shown in Figure 6.29, the silicon atom is surrounded by four oxygen atoms, these tetrahedrons have the ability to link with the other tetrahedron (some or all of them) at the corner by sharing oxygen atoms (called oxygen bridge) to form a 3-D network (Figure 6.30). The main factors that are responsible for the failure of the composition of a crystalline network are an extended irregular three-D network and a random configuration of Si-O-Si bonds.
As in all treatment methods there are advantages and disadvantages to the use of the vitrification process. The main advantages of this method can be summarised in four main points.

Firstly, the durability of the waste glasses product and its ability to contain the contaminants (vitrification products are classified as recycling materials due to their physical and chemical properties). Secondly, the flexibility of the waste glass to integrate with many of the contaminated materials. The vitrified entity has the capacity to integrate the waste materials within its structure without having any effect on the quality of the product. Thirdly, vitrification processes have the capacity to
accommodate organic and inorganic materials in different quantities. Finally, it entails the possibility of reducing the volume of contaminated materials.

There are two main drawbacks to the use of vitrification. Firstly, the large amount of energy required by this process, which is expensive compared with other therapeutic methods. Secondly, there is the potential for organic and inorganic pollutants to be volatilized during the treatment process. Despite these limitations, EPA has endorsed vitrification processes as the Best Demonstrated Available Technology (BDAT) for High level waste (HLW) [250]. When nuclear wastes or heavy metals are confined within a glass matrix, there are able to remain stable for a longer period of time. This technique has been used for several decades in many countries such as China and France. In general, vitrification is capable for use with organic and inorganic materials due to its ability to immobilize inorganic materials and destroy the organic phase. In addition, it is suitable method to treat wide range of waste types, such as:

- Radioactive Wastes and sludges
- Contaminated soils and sediments
- Incinerator ashes
- Industrial wastes and sludges
- Medical and asbestos wastes

Table 6.5 shows clearly that zeolites are highly conducive to the vitrification process due to the fact they contain SiO$_2$ and Al$_2$O$_3$. The same table also highlights that these media possess the ability to increase the durability of the product [251]. Zeolites are considered one of the media most conducive to the process of vitrification. They are widely used to immobilise radioactive isotopes due to their exceptional capacity for the reduction of the diffusion of ions via the leaching process even after periods of time as long as 3 years [252].
Table 6.5 Effects of waste-components on processing and product performance [251].

<table>
<thead>
<tr>
<th>Waste Component</th>
<th>Processing</th>
<th>Product Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>Increases viscosity and has tendency to devitrify</td>
<td>Increases durability</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>Reduce viscosity; is hard to dissolve</td>
<td>Increases durability</td>
</tr>
<tr>
<td>U₃O₈</td>
<td>Reduce tendency to devitrify</td>
<td>Reduces durability</td>
</tr>
<tr>
<td>NiO</td>
<td>Is hard to dissolve; increase tendency to devitrify</td>
<td>Reduces durability</td>
</tr>
<tr>
<td>MnO</td>
<td>Is hard to dissolve</td>
<td>Increases durability</td>
</tr>
<tr>
<td>Zeolite</td>
<td>Is slow to dissolve; produce foam</td>
<td>Increases durability</td>
</tr>
<tr>
<td>Sulphate</td>
<td>Is an antifoam, melting aid; increases corrosion of processing equation</td>
<td>Too much causes foam or formation of soluble second phase</td>
</tr>
</tbody>
</table>

6.7.1 Vitrification and Leaching

6.7.1.1 Cobalt

The vitrification process was performed for the composite samples after the ion exchange process for the removal of Co²⁺ ions. The samples were heated at 1200°C for 2h using a muffle type furnace. The rate of temperature increase was 5°C/min. Each sample was put inside a quartz vessel as can be seen in Figure 6.20. These vessels have the capability to resist the high temperatures.

Different weight of each vitrified cobalt sample was mixed with a 0.05M NaCl solution as 1:50 weight ratio to study the extent of the leaching of Co²⁺ ions from the media. Some of the other non-vitrified (powder form) media were subjected to the same conditions of the treatment. For all the Co²⁺ samples (vitrified and non-vitrified), samples were collected after 90 and 120 days of leaching time. ICP was used to analyse the concentration of Co²⁺ ions in the solution using 5 and 10mg.L⁻¹ Co²⁺ prepared from 1000mg.L⁻¹ standard solutions to prepare the calibration curve. An identical procedure was employed by preparing 0.05 and 2.5 mg.L⁻¹ to prepare the calibration curve to study Sr²⁺ leaching using non-vitrified samples. The main reason to not vitrify the composite samples, which being used to remove Sr²⁺ ions from wastewater in this study, was to the low melting point for this ion. The melting point of the strontium ion is 777°C which is...
below the vitrification temperature (1200°C for 2h) required to vitrify the silica within the zeolite structure.

6.8 RESULTS AND DISCUSSION

The vitrification processes were performed at 1200°C for 2h under air atmosphere. As shown in Figure 6.31, all vitrified media were converted into glassy forms. Some of the vitrified samples have a blue colour resulting from the natural Co²⁺ colour. This indicates that cobalt ions has are present inside the media even after vitrification at 1200°C (Co²⁺ melting point is 1495.0°C and boiling point is 2870.0°C).

The volume of all the vitrified samples was reduced by more than 50% due to the removal of carbon through conversion to dioxide carbon (CO₂). While the volumes of Celatom-Zeolite were reduced due to the conversion of silica material on the diatomite wall into glass resulting in the collapse of its structure. In addition, the volumes were reduced due to the vaporization of void gas and water present in the samples during the vitrification process as well as the combustion of organic materials.

The end product of each type (Carbon-Zeolite (C-Z) and Celatom-Zeolite (Cel-Z)) was a hard crystalline fragment and which retained the same solidified form after mixing with a 0.05M NaCl solution even after 120 days for the leaching test. Table 6.6 shows the concentrations of Co²⁺ ions (mg.L⁻¹) which were measured in the solutions after 90 and 120 days mixing time for both vitrified and non-vitrified samples. The results show that the leaching of the Co²⁺ ions were in the order of 0.01-0.09 mg.L⁻¹, while the leaching from the non-vitrified samples were in the order of 22-44 mg.L⁻¹.

The results revealed that after leaching, the non-vitrified samples have higher values of released Co²⁺ ions than the vitrified samples. In the case of most of the vitrified media, the concentrations of released Co²⁺ in the presence of Na⁺ ions were found to be low even after 120 days. This indicates that Co²⁺ ions have been trapped within the structure of the glass, encapsulated and rendered suitable for long-term storage.
CHAPTER SIX
APPLICATION OF WASTEWATER TREATMENT

Figure 6. 31 Different composite’s samples (a-) before and (b-) after vitrification process at 1200°C for 2h.

Table 6. 6 Shows the leaching of Co$^{2+}$ ion using vitrified and non-vitrified media in 1:50 ratio of 0.05M NaCl solution: adsorbed media.

<table>
<thead>
<tr>
<th>Media</th>
<th>Vitrified media (g) 90d(mg.L$^{-1}$)</th>
<th>Vitrified media (g) 120d(mg.L$^{-1}$)</th>
<th>Non-vitrified mg.L$^{-1}$ after 90days</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSY</td>
<td>0.106</td>
<td>0.110</td>
<td>49</td>
</tr>
<tr>
<td>IPY</td>
<td>0.310</td>
<td>0.280</td>
<td>44</td>
</tr>
<tr>
<td>IPClinp</td>
<td>0.240</td>
<td>0.234</td>
<td>39</td>
</tr>
<tr>
<td>TSA</td>
<td>0.196</td>
<td>0.189</td>
<td>76</td>
</tr>
<tr>
<td>IPA</td>
<td>0.159</td>
<td>0.187</td>
<td>65</td>
</tr>
<tr>
<td>TSClinp</td>
<td>0.327</td>
<td>0.33</td>
<td>24</td>
</tr>
<tr>
<td>PClinp</td>
<td>0.10</td>
<td>0.15</td>
<td>22</td>
</tr>
<tr>
<td>Cel-ZA</td>
<td>0.226</td>
<td>0.231</td>
<td>95</td>
</tr>
<tr>
<td>Cel-ZY</td>
<td>0.273</td>
<td>0.277</td>
<td>78</td>
</tr>
</tbody>
</table>

The leaching test results for the Sr$^{2+}$ ion are presented in Table 6.7. It can be seen that the highest Sr$^{2+}$ values leaching from the powder of composite samples are around 137mg.L$^{-1}$ for 0.5g of each media.
Table 6.7 shows the leaching of Sr$^{2+}$ ion using non-vitrified media in 1:50 ratio of 0.05M NaCl solution: adsorbed media.

<table>
<thead>
<tr>
<th>Media</th>
<th>Sr$^{2+}$ ion (mg.L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cel-ZY</td>
<td>122</td>
</tr>
<tr>
<td>P-Clinp</td>
<td>78</td>
</tr>
<tr>
<td>IPA</td>
<td>137</td>
</tr>
<tr>
<td>Cel-ZA</td>
<td>132</td>
</tr>
<tr>
<td>IPY</td>
<td>94</td>
</tr>
</tbody>
</table>

**SUMMARY:**

All the types of the composite materials IPA, TSA, IPY, TSY, IPClinp, TSClinp, Cel-ZA and Cel-ZY and the pure zeolites A, Y and clinoptilolite without scaffold, were treated separately in order to remove Co$^{2+}$ and Sr$^{2+}$ ions from an aqueous solutions. This work serves as a model for the removal of Co-60 and Sr-90 radionuclides from the radioactive wastewater in the Al-Tuwaitha site in Iraq. All the composite materials demonstrated a high level of efficacy in the removal both the Co$^{2+}$ and Sr$^{2+}$ ions in more than 50% of each type of the pure zeolites (A, Y and clinoptilolite). Hence, it can be interpreted that the composite process increases the efficiency of the removal of the metal ions. All the adsorbents were modelled using the Langmuir and Freundlich isotherms to describe the fitting of the theoretical with the experimental results.

The Co$^{2+}$ was subjected to vitrification process at 1200°C for 2h and the residue encapsulated. Thereafter, the encapsulated composites were leached for 90 and 120 days and no significant Co$^{2+}$ was recorded in the leached solution. The results show that the composite materials can be used effectively to remove the radioactive ion of Co-60 and Sr-90 ion as they display the same chemical behaviour as Co-59 and Sr-89 studied in this work and the residue can be contained using encapsulation without leaching into the environment.
CHAPTER SEVEN

CONCLUSIONS AND FUTURE WORK
CHAPTER SEVEN

CONCLUSION AND FUTURE WORK

7. CONCLUSIONS

In this study, three types of zeolite composites were successfully prepared: zeolite A, zeolite Y and clinoptilolite with diatomite and carbon. These zeolites were selected due to their possession of qualities such as the capacity for ion exchange. Zeolites (A and Y) were successfully incorporated onto diatomite surface (as can be seen in Chapter 4), while zeolites (A, Y and clinoptilolite) were incorporated onto two different types of carbons (Iraqi palm tree Leaves (IP) and Tamarind stones (TS)), as can be seen in Chapter 5. These materials were used as scaffold in order to create hierarchical materials through a compotation of microporous zeolite crystals with macroporous materials (diatomite and carbon). The aim was to use this method to overcome the diffusivity problem incurred in the use of zeolites powder as ion exchange materials. Zeolites were used in this study to remove two types of non-radioactive ions (Cobalt-59 (Co$^{2+}$) and Strontium-89 (Sr$^{2+}$)) from wastewater. This was designed to model the use of ion-exchange technique to remove radioactive Co-60 and Sr-90 from low level wastewater from Al-Tuwaitha site. Al-Tuwaitha site is a nuclear research in Iraq was used for radio-medical and radio-chemical purposes before 1990.

7.1 CELATOM - ZEOLITES COMPOSITES (CEL-Z)

In the case of diatomite (celatom FW-14), high quality products of Cel-ZY composite prepared via both methods was obtained using a fine particle solution containing seeds. The Cel-ZY composites had uniform distributions of zeolite-Y crystals onto diatomite frustules surfaces. The SEM shows that some of these frustules were completely coated with the highly crystalline zeolite, while others were poorly coated as a likely consequence of the large size of some of the seed particles. This also was supported by the results obtained using XRD.

The products of ball milled commercial zeolite were used as seeding agents and their success in the results with the initial composite materials proved the efficiency of this method for the preparation of the other types of composite materials. This was applied using other types of zeolites such as zeolite A and clinoptilolite.
The Cel-ZA composite was also successfully prepared using the ball mill method following the same procedure used for Cel-ZY. A high quality zeolite A with a uniform distribution of crystals onto surface of the frustules was obtained. This was also characterised by SEM and XRD.

7.2 CARBON - ZEOLITES COMPOSITES (C-Z)
Due to its availability, low cost, high surface area and macroporosity, carbon was employed in order to build hierarchical structure materials. Two types of macroporous carbon materials of the natural carbons readily available agricultural residues in the Middle East were obtained from the carbonisation process of Iraqi palm tree Leafs (IP) and Tamarind stones (TS) were selected as scaffolds for the three types of zeolites: A, Y and clinoptilolite in order to prepare the hierarchically structured materials in micro/macro porosity (zeolite/carbon) composite materials.

The carbon materials of of Iraqi palm tree Leafs (IP) and Tamarind stones (TS) were prepared through a pyrolysis process at 900°C for 2h under nitrogen atmosphere with two isothermal steps of 250°C and 600°C in order to build hierarchical structure materials. By weighing the natural carbon before and after the pyrolysis process, the carbon content of each material was found to be 26.48 for TS and 17.4% for IP.

Hydrothermal treatment was employed to build the Carbon/Zeolite hierarchical structure materials. After 24 hours grinding of the commercial zeolite using zirconium oxides balls to prepare seeds, the average particle size of zeolite A and clinoptilolite were 150nm and 120nm, respectively.

After seeding the carbon surface for 6h using a sonication bath, the crystals of each type of zeolite were successfully grown and attached to the carbon surfaces carbons. The products of both the Carbon/Zeolite (IP-zeolite and TS-zeolite) were confirmed by the SEM images and the XRD patterns show that the peaks of each composite product correspond closely to the peaks of the commercial zeolites (A, Y and clinoptilolite) which serve as a reference point. In addition, using the EDAX measurement the Si/Al ratio was calculated for all the composite materials to verify the identity of each zeolite type (Si/Al=1, 2.3 and > 4 for ZA, ZY, and clinoptilolite, respectively).
In case of Carbon-Clinoptilolite composite, from the XRD and EDAX measurement it was confirmed that successfully prepared of IPClinp and TSClinp composites was obtained in this study as there is no evidence in literature of this being carried out before.

7.3 APPLICATION OF COMPOSITE MATERIALS IN THE WASTEWATER TREATMENT

In the application of wastewater treatment, all types of the composite materials IPA, TSA, IPY, TSY, IPClinp, TSClinp, Cel-ZA and Cel-ZY and the pure zeolites A, Y and clinoptilolite without scaffold, were treated separately in order to remove Co\(^{2+}\) and Sr\(^{2+}\) ions from an aqueous solutions. This work serves as a model for the removal of Co-60 and Sr-90 radionuclides from the radioactive wastewater in the Al-Tuwaitha site in Iraq. All the composite materials demonstrated a high level of efficacy in the removal both the Co\(^{2+}\) and Sr\(^{2+}\) ions in more than 50% of each type of the pure zeolites (A, Y and clinoptilolite). Hence, it can be the interpreted that the composite process increases the efficiency of the removal of the metal ions.

Ion exchange processes undertaken proved that the attachment of zeolite crystals to macroporous surfaces improved the adsorption capacity of each type of zeolite. In addition, the tests carried out proved that diatomite and carbons can be used to overcome diffusivity problem and function effectively as a scaffold to hold the crystals of zeolite and enable the formation of a hierarchically structured material. The results of the characterisation using SEM indicated that the zeolite crystals were still allocated onto zeolite crystals to carbon and diatomite surfaces even after the manipulations of the ion exchange processes.

Generally, good uptakes of both Co\(^{2+}\) and Sr\(^{2+}\) ions were achieved by all types of the composites materials. For both ions, in terms of the adsorption rate the performance of the pure zeolites could be ranked as follows: PZA>PZY>PClinp. The maximum capacity achieved by the PZA was 61.15mgCo.g\(^{-1}\) and 200mgSr.g\(^{-1}\). 53.1mgCo.g\(^{-1}\) and 118mgSr.g\(^{-1}\) was recorded for PZY, while the pure clinoptilolite achieved the lowest uptake of both ions with 28.51mgCo.g\(^{-1}\)and 91.51mgSr.g\(^{-1}\). The zeolite-A composite materials achieved the highest degree of adsorption with the order in terms of
performance being: Carbon-ZA>Carbon-ZY>Carbon-Clinoptilolite and Cel-ZA>Cel-ZY. It is likely that this could be due to the low Si/Al ratio of zeolite-A (Si/Al=1).

7.4 STUDYING OF DIFFERENT CONDITIONS ON THE UPTAKE OF Co$^{2+}$ AND Sr$^{2+}$ IONS

In order to study the behaviour of the composite materials in the process of adsorption the variables pH, temperature, and initial concentration were altered for both the Co$^{2+}$ and Sr$^{2+}$ ions. The results show that for both ions the adsorption rate was positively affected by an increase of the pH and an increase in the initial concentration. Increasing the temperature from 20 to 50°C had a slight impact on the uptake of both ions and efficiency was slightly decreased by raising it from 45-50 to 65-70°C.

The highest adsorption capacities were realised with TSA in the order 120mgCo.gz$^{-1}$ and 290mg.g$^{-1}$ for Co$^{2+}$ and Sr$^{2+}$ ions, respectively. The tests show that equilibrium occurred between 2 to 3 hours for all types of composites materials. Kinetic studies indicates that majority of the uptake took place between 30-60 minutes even with the manipulation of the experiment parameters by changing the pH, initial concentration and temperature solution.

The Sr$^{2+}$ and Co$^{2+}$ ions were prepared in single solution and mixed separately under same conditions in terms of volume, temperature, concentration and pH. The results demonstrate that all of the composite materials possess the ability to adsorb more Sr$^{2+}$ ions than the Co$^{2+}$ ions. The trend of the adsorption using A, Y and clinoptilolite zeolites supported by IP carbon, was IPY>IPA>IPClinp in case of Co ions, IPA>IPY>IPClinp for the Sr ions. For TS carbon, which was used to support the same three type of zeolites, rank order for the Co$^{2+}$ ions adsorption was TSY=TSA >TSClinp. However, for Sr ions the sequence is TSA>TSY>TSClinp. In addition, for both ions Cel-ZA exhibited a superior uptake than Cel-ZY.

In general, the trend order of the maximum adsorption capacity of Sr$^{2+}$ ion, based on the different the support materials IP, TS and Celatom, is TSA> Cel-ZA >IPA, while in case of Co$^{2+}$ ion it as IPA≥ Cel-ZA ≥TSA. The highest uptake was achieved by the composite-zeolite-A with results in the order of 78mg.g$^{-1}$ for the Sr and 40mg.g$^{-1}$ for the Co$^{2+}$ ions.
7.5 LANGMUIR AND FREUNDLICH MODELS

The isotherms obtained for the adsorption onto selected composites media (IPA, IPY, IPClinp and Cel-ZY) of Co$^{2+}$ and Sr$^{2+}$ were investigated using Freundlich and Langmuir models. Both models were used to fit the theoretical data to the experimental data for each composite adsorbent. Based on an analysis of $r^2$ values (determination of coefficient) obtained, it can be seen that for Co$^{2+}$ adsorption, the IPClinp composite works significantly better as an adsorbent under the Langmuir model than the other adsorbents. In case of Co$^{2+}$ adsorption, the order of the $r^2$ values for the adsorbents is IPClinp>Cel-ZY>IPY>IPA for the Langmuir model. In the analysis of Co$^{2+}$ adsorption via the Freundlich model, based on the $r^2$ value analysis the IPClinp composite adsorbent shows the best fit of the model with the experimental data. The order of $r^2$ value of composite media is given as IPClinp> Cel-ZY>IPA>IPY.

Under the Langmuir isotherm analysis for the adsorption of Sr$^{2+}$ onto the composite adsorbents the $r^2$ values indicate that the IPA composite is the best match to the model and the trend is as follows; IPA>IPY>Cel-ZY>IPClinp. While for the Freundlich isotherm the best fitting composite adsorbent according to the $r^2$ values is IPClinp, with the trend order being IPA>IPClinp>Cel-ZY>IPY.

Overall, the data indicates that for both isotherms IPClinp was the best fit for the description of Co$^{2+}$ adsorption with $r^2$ values of 0.989 recorded for the Freundlich model and 0.985 for the Langmuir. For Sr$^{2+}$ adsorption, IPA was the best fit for both the Langmuir model with an $r^2$ value of 0.994 and the Freundlich model with an $r^2$ value of 0.968.

The separation factor $R_L$ was analysed to indicate the favourable sorption isotherms, based on the Langmuir isotherm, for the adsorbents. The favourable sorption isotherms were indicated for the composite media (Cel-ZY, IPClinp, IPY and IPA) by the range of $R_L$ values achieved: between 0 and 1 (0 < $R_L$ < 1) for both Co$^{2+}$ and Sr$^{2+}$ ions.
7.6 LEACHING OF Co$^{2+}$ AND Sr$^{2+}$ FROM THE COMPOSITES MEDIA

In order to study the Co$^{2+}$ leaching, all composite materials were vitrified by heating for 2h at 1200°C under air atmosphere. Then the products of vitrified and non-vitrified samples were mixed with a 0.05M NaCl solution. The main reason not to vitrify the composite samples that were being used to remove Sr$^{2+}$ ions from wastewater was the low melting point for this ion (777°C), which is below the vitrification temperature (1200°C for 2h) required to vitrify the silica within a zeolite structure. The results show that the leaching of Co$^{2+}$ ions was in the order 0.01-0.09 mg.L$^{-1}$, while the leaching from the non-vitrified samples, even after 120 days, was in the order of 22-44 mg.L$^{-1}$. The leaching tests confirmed that the Co$^{2+}$ ion had been encapsulated. The volumes of all the vitrified samples were reduced by more than 50% after the vitrification process, and there was an increase in the product density.

7.7 IN THE SUMMARY, THE FOLLOWING POINTS CAN BE CONCLUDED FROM THE PRESENT STUDY

1- The composite materials are more effective to remove Co$^{2+}$ and Sr$^{2+}$ from synthetic wastewater than pure zeolites media used in batch system.

2- The uptakes of the adsorbent media have increased with the increase of pH.

3- The removal efficiency (the uptake) of the clinoptilolite is less than of zeolite-A and zeolite-Y for both ions (Co$^{2+}$ and Sr$^{2+}$) but it is more effective in removal of Sr$^{2+}$ ion.

4- The take up of all adsorbent materials were increased with the increase of contact time (until equilibrium concentration) and initial ion concentrations, while it is slightly decreased with the increasing the temperature of solutions above 50°C.

5- The equilibrium isotherm for the system all composite media is of a favourable type for both ions (Co$^{2+}$ and Sr$^{2+}$).

6- The equilibrium isotherm modelling for the systems used indicates that they were well represented by Langmuir and Freundlich equations.
7.8 THE ADVANTAGE OF USING HIERARCHICAL COMPOSITE MATERIAL.

1- It is a relatively cost effective method for the removal of Co$^{2+}$ and Sr$^{2+}$ ions from aqueous solution.
2- This method could be applied to any industry to treat the wastewater because it is easy to operate and to maintain. It may be proven efficiency in removing a large number of other effluent compounds.
3- It does not need a large number of operators.

7.9 CORRELATION OF Co-59 AND Sr-89 AS A MODEL TO REMOVE RADIOACTIVE Co-60 AND Sr-90

The results from this research have shown a favourable removal of the non- radioactive Co$^{2+}$ and Sr$^{2+}$ from aqueous solutions and binary systems. Generally, the optimum conditions for the adsorption of the two metal ions were found to be as follows:

- Tamarind stones – zeolite A composite (TSA) was the most effective adsorbent
- Temperature of 45-50°C gave the highest adsorption
- The time required for reaching the equilibrium adsorption was between 120-180 minutes
- The optimum pH for adsorption of Co$^{2+}$ was in the range of 5-6 while for strontium it was at pH 10.
- The maximum adsorption was at the highest initial concentration for both materials.

The above stated optimum conditions for the two non-radioactive metals can be extrapolated and utilized for the adsorption of the radioactive Co-60 and Sr-90 due to their chemical similarities. Thus the TSA adsorbent can be recommended for utilisation in the removal of the radionuclide from radioactive waste water systems.
7.10 FURTHER WORK

Three types of zeolites: A, Y and clinoptilolite were prepared in this study. The potential for other types of zeolite to be used as ion exchanger media could be investigated, such as zeolite X and P due to their low Si/Al ratio. There suitability for the deposition process also makes them appropriate for use in wastewater treatment processes. In addition, due to its widespread availability, other types of plant waste could be proposed to hold the zeolite crystals in order to build hierarchical structure materials. Plant waste is suitable because of its high cellulose content (a high cellulose content provides a high surface area) and its natural availability. One example is date palm stones and there are more than 30 million palm trees in Iraq and 18 million in the Kingdom of Saudi Arabia.

In this study, two types of carbon: Iraqi palm tree Leaves (IP) and Tamarind stones (TS) were used. It was observed that the TS product was very hard to crush after Pyrolysis. This quality of robustness makes it a suitable means of holding the zeolite crystals in the packed columns employed in wastewater treatment works. Hence column operation studies using this composite material should be under taken.

Using the 2.5-1 Si-Carbon weight ratio (section 5.5.3.3.1 Chapter 5), clinoptilolite loading onto carbon surfaces was recorded at 63.9 and 64.7% for IPClinp and TSClinp (using TGA), respectively. This dense amount can be reduced by utilising other Si-Carbon ratios for depositing a thinner layer of zeolite onto the support media.

According to the results of this study further work could be suggested using the hierarchical materials such as determining:

1- The loading of these adsorbents (the composite materials) can be examined to remove other types of pollutants (organic or inorganic pollutants).

2- Carbon and diatomite are organic materials which could encourage bacteria growth in wastewater treatment station. Further study is required to study the effect of grown these bacteria on properties of the support materials (carbon and diatomite).
3- Due to the vitrified the residue of the adsorbent composite materials after the ion exchange process different gases were evolved because of the high temperature (1200 °C). Further study is required to capture these gases and study its effect on the environment.
REFERENCES

43. Michael D. Rosenthal, L.L.S.-M., Frank Houck and George Anzelon,, Review of the negotiation of the model protocol to the agreement(s) between state(s) and the international atomic energy agency application of safe guards national nuclear security administration 2010. I/iii(infcirc/540 (corrected), 2010. bnl-90962-2010.
103. Castellanos, O., Ríos Reyes, C.A and Williams, C.D., Tratamiento hidrotermal a baja temperatura de una toba rica en clinoptilolita en soluciones de NaOH, KOH y Ca (OH) 2. 2011.
References

142. Hassan, M.S., Ibrahim I.A and Ismael, I.S., Diatomaceous deposits of Fayium, Egypt:


162. ICRP.31 (Recommendation of the international commission on radiological protection), “Biological Effects of Inhaled Radionuclides” ICRP publication 31, (1980), vol. 4, No.112.,


APPENDIX A

SYNTHESES OF ZEOLITE-A

The crystallization of zeolite-A was carried out in a Teflon-lined autoclave. The initial composition of the reactant mixture is described in the below formula.

\[ 3.1 \text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 1.9\text{SiO}_2 : 128\text{H}_2\text{O} \]

The XRD pattern of commercial of zeolite-A compared with synthesised zeolite-A, which has supposed a 100% crystalline zeolite.
The crystallinity relationship (I/IO) between the percentages degree of crystallinity of zeolite-A samples and their crystallization times.

Table: Show the rate of crystal size with increasing crystallization time

<table>
<thead>
<tr>
<th>Crystallizations time (h)</th>
<th>2h</th>
<th>2.5h</th>
<th>3.5h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range of crystal size (nm)</td>
<td>760-1325</td>
<td>875-1565</td>
<td>1315-1600</td>
</tr>
</tbody>
</table>
SEM images shown the gradually growth of crystal of a zeolite-A after 30min, 1.5, 2, 2.5 and 3.5h with 6000 magnification. (Scale bar= 20 µm).
EDAX spectrum of zeolite a after 3.5 h crystallization time, Si/Al ratio was found 1.08 for this spectrum.

Shows the EDAX spectrum of commercial zeolite-A, the Si/Al ratio was found 1.09.
APPENDIX B

Synthesis of Zeolite-Y

The aim of this experiment was to reproduce the work by D. M. Ginter, A. T. Bell and C. J. Radke which was reported in the verified synthesis handbook (2001) for zeolite Na-Y type FAU. The chemical compositions for the synthesis procedure are described in Formula

\[ 4.62\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 10\text{SiO}_2 : 180\text{H}_2\text{O} \]

The XRD patterns of synthesis zeolite Y for 4, 5, 24 and 45h compared with commercial zeolite Y, which has supposed a 100% crystalline zeolite.
The crystallinity relationship (I/IO) between the percentages degree of crystallinity of zeolite-Y samples and their crystallization times during various times from 4 to 45hrs.

EDAX spectrum of synthesised zeolite Y showing (Si/Al) ratio between 2.31-2.46 for five spots
SEM images shown the gradually growth of crystal of a zeolite-Y after 4, 20, 24 and 45h. (Scale bar= 5µm).
APPENDIX C

Additional Images of A- celatom FW-14 and B- Celatom seeded with zeolite-Y

Celatom FW-14

Celatom seeded with colloidal zeolite-Y
APPENDIX D
Nitrogen Adsorption/Desorption Isotherms

Tamarind Stone Carbon (TSC)

Tamarind Stone-Zeolite Y (TSY)
APPENDIX E

SEM images for synthesis Clinoptilolite with different scales (2 and 5µm) and magnifications after 70h at 140°C.
APPENDIX F

THERMO-GRAVIMETRIC ANALYSIS

(a) TS Clinp (Tamarind Stone-Clinoptilolite) 10:1 Si: carbon weight ratio

(b) TS Clinp (Tamarind Stone-Clinoptilolite) 10:2 Si: carbon weight ratio
APPENDIX G

Additional EDAX and SEM images for the raw carbon and carbon-zeolite composites before and after ion exchange process.

Iraqi Palm Tree Leaves (IP) Raw and Carbon

Tamarind Stone (TS) Raw and Carbon
APPENDIX G  ADDITIONAL EDAX AND SEM IMAGES FOR CARBON

**TSA Co (After 3h of Adsorption Treatment)**

![TSA Co EDAX and SEM Image]

**TSY Co (After 3h of Adsorption Treatment)**

![TSY Co EDAX and SEM Image]

**IPA Co (After 3h of Adsorption Treatment)**

![IPA Co EDAX and SEM Image]
APPENDIX G
ADDITIONAL EDAX AND SEM IMAGES FOR CARBON

IPClinp Co (After 3h of Adsorption Treatment)

TSClinp Sr (After 3h of Adsorption Treatment)

IPClinp Co (After 3h of Adsorption Treatment)
APPENDIX H

Publications

A- Conferences

1. Post Graduate conference in Manchester University, CEAS June, 2010 - Poster.
2. Post Graduate conference in Manchester University, CEAS June, 2011 - Poster.
3. Engineering and Science conference, London 1\textsuperscript{st}-2\textsuperscript{nd} Oct, 2011 Poster.
4. Post Graduate conference in Manchester University, CEAS June, 2012 - Oral presentation.

B- Papers

1- **Salam K. Al-Nasri and SM Holmes**

“Effect of Different Conditions on the Sorption Behaviour of Co\textsuperscript{2+} Using Celatom ZeoliteY Composite”

World Academy of Science, Engineering and Technology 81 2013 (WASET), International Journal of Chemical Science and Engineering Vol: 7 No: 9, 2013

Online article  http://www.waset.org/journals/waset/v81/v81-41.pdf

2- **Oscar Hernandez-Ramirez, Salam K. Al-Nasri and Stuart M. Holmes**

“Hierarchical structures based on natural carbons and zeolites”

Journal of Materials and Chemistry, Received 17th August 2010, Accepted 25th August 2011.

DOI: 10.1039/c0jm02710c
Effect of Different Conditions on the Sorption Behavior of Co$^{2+}$ Using Celatom-Zeolite Y Composite

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Abstract—Celatom-Zeolite Y (Co-ZY) was used to remove cobalt ions from aqueous solution by batch mode. Zeolite Y has successfully supersorbed on Celatom FW-14 surface using hydrothermal treatment. The product was synthesized as a novel of hierarchical porous material. It was observed from the results that Co-ZY has higher ability to remove cobalt ions than the pure Zeolite Y powder (ZY) synthesized under the same conditions. Several parameters were studied in this project to investigate the effect of removal cobalt ions such as pH and initial cobalt concentration. It was clearly observed that the uptake of cobalt ions was affected with increase these parameters. The results proved that the product can be used effectively to remove Co$^{2+}$ ions from wastewater as an environmentally friendly alternative.

Keywords—Adsortion, Celatom-Zeolite, Cobalt ions, isomelar media.

I. Introduction

Several techniques are being used for treating industrial and domestic wastewater such as chemical precipitation, sedimentation, ion exchange, thermal evaporation and reverse osmosis membranes. These techniques (along with others) aim to release discontaminated effluents into the environment and allow the conditioning of waste concentrates for disposal [1], [2]. Adsorption is widely used and considered a most powerful technique according to the low cost, easy technique, efficiency, abundance and availability [2]. Activated carbon is considered as the most competitive media to the sorbent materials as a powder or granular due to its properties such as porous structure, meso and micro porous which give high surface area and capacity for the sorption of undesirable ions and organics molecules. On the other hand, the high cost production and regeneration processes are considered the main drawbacks from the industries and looking for more economic, easier and efficient sorbent materials.

The cost and efficiency of purification techniques have become increasingly important in implementing industrial waste disposal of alternative ion exchange media [3], [4].

Disodium, are mesoscopic size, which are found in every aquatic environment, formed by fragments of water (skeletone) of disodium algae. Disodium rock belongs to the group of surface-containing materials. It has special properties, such as low density, high porosity, low thermal conductivity [6], high melting point (1400 °C to 1750 °C depending on impurities) being chemically inert [7], high permeability and high surface area [8], [9]. These properties make it very useful for a wide range of applications.

Zeolites are considered one of the most important and naturally abundant ion exchange media [10], [11]. Zeolites are tetrahedral aluminosilicate framework with very open three dimensional structure. Zeolites are principally comprised of [SiO4] and [AlO4] [10], have pores of uniform sizes from 5 to 12 Å [12]. Cations and anions are found within Zeolite structures; they form about 50% of the total volume allowing cations such as Na+, K+, Ca2+ and Mg2+ and water molecules to be held within Zeolite frameworks. These cations have a high degree of mobility and affinity to exchange with other cations. In addition, the internal structure of the Zeolite allows for regular arranged pores. These structural properties make it a useful adsorbent for metallic ions and water vapour [11], [12]. However, due to the diffusivity problem of small particles of Zeolite powder, this has caused an inhibition of Zeolite use in the industry.

In this work, Zeolite crystals were superimposed onto Celatom surfaces in this experiment to build a hierarchical structure. This new composite structure of mesoporous Celatom microporous Zeolite Y is suggested as a method to overcome the diffusivity problem of Zeolite powder [14].

II. Experimental Work

A. Seeding Process

A nanocrystal solution of Zeolite Y was prepared by printing a commercial Zeolite Y (supplied by PQ Corporation) for 2h using 1mm ceramic beads (zirconia oxide) ball mill grinding as the grinder media. The ground product was used for seeding Dacronate using the same procedure reported in our previous work with different kind of seeded carbon [14]. This method is considered more economic in time, energy and cost than the expensive and complex synthesis of colloidal Zeolite seeds [15].

Dynamic Light Scattering (DLS) and Transmission Electron Microscopy (TEM) were used to characterize the fine particle size of ground Zeolite Y in solution.

For seeding process the ground Zeolite Y was distributed and attached onto Celatom surface using 0a semi-vulc and 201 Celatom-Zeolite Y weight ratio.
Hierarchical structures based on natural carbons and zeolites

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Received 17th August 2010, Accepted 25th August 2011
DOI: 10.1039/e002710c

Hierarchical porous structures have been widely synthesised to provide the most beneficial flow and surface area characteristics for a range of liquid and gas phase processes. We present three novel hierarchical porous structures based on carbonised olive stones, coconut shells and coconut fibres coupled with zeolite Y. The structures are synthesised using a new seeding technique based around milling commercially available zeolite Y to provide nano-seeds for the growth step. The efficacy of the structures for the removal of ionic cobalt and arsenic contaminants is demonstrated with complete arsenic removal at simulated pollution levels. In addition, the verification of the structures to completely encapsulate cobalt ions, allowing no detectable release, is also described. All steps of the synthesis are tailored to produce the most economically viable materials using inexpensive starting materials and replacing, costly, colloidal seeds of zeolite Y with ball milled replacements.

Introduction

The production of hierarchically porous materials has been extensively studied. A material that combines several levels of porosity can encompass the positive properties each array offers. Highly ramified networks of micro- and macro-pores are desirable, so that an easy, rapid access to the active sites on a given surface becomes possible. Zeolites are aluminosilicate crystalline compounds possessing microporous and ion exchange properties suitable for a wide range of applications in catalysis and separation of liquid and gaseous mixtures.

In current industrial applications, such as petroleum refining, zeolites are used in the form of pellet compacts, usually melted with a clay binder, which is an inexpensive alternative but involves the loss of active area. During the past two decades there have been many attempts to avoid this problem. Zeolite films have been deposited on stainless steel and alumina. Other suggested alternatives include synthetic carbon fibres, multilayer films of bacteria and polymer spheres. Although these efforts have generated interesting and elegant structures, they all involve complex techniques which would lead to high production costs; this is caused mainly by the need to use templates which are expensive or hard to synthesize, (for most of the cases, these templates must be removed before use). Often, the synthesis of zeolite structures using macroscopic templates or supports utilises colloidal seeding to facilitate zeolite growth, the production of colloidal seeds can be a difficult and time consuming process. In addition, the majority of the previous studies involve silicate or ZSM-5, which are readily synthesised zeolite species but offer low acid site density and consequently limited ion-exchange/catalytic properties.

Many of the processes in which such aggregated materials will ultimately benefit are, by their nature, bulk procedures; hence it is crucial to have simple and inexpensive production routes. Here, we develop for the first time a family of porous materials based on zeolites supported on carbon generated from readily available natural structures. The structures are generated using a process which is simple and inexpensive enough to be compatible with large-scale use and incorporate a zeolite which is highly reactive. Additionally, we study the efficiency of these materials for the removal of two hazardous ions, arsenic and cobalt. Finally, the ability to encapsulate metal ions by vitrification (high temperature glass formation) of the alumino-silicate is demonstrated for cobalt.

The concepts derived from our previous research in which zeolite Y, one of the most widely used zeolites in industry, was successfully incorporated onto diatom frustules forming a hierarchically structured composite. Having more exposed active sites, this novel material proved to dramatically enhance the adsorption efficiency of its zeolite content. Despite these properties, the zeolite Ydiatom composite still involves high production costs, related mainly to the colloidal nano-zeolites which must be synthesised to seed the diatom surface prior to growth of the zeolite film. Patent literature has reported the possibility of using wet ball-milling to reduce zeolite particle size and using the crushed particles as synthesis seeds to manufacture MFI (ZSM-5 and silicalite) and zeolite A.

Complex synthetic carbon structures have proved useful as zeolite supports, so this study examined naturally occurring