# Synthesis and Characterization of Ternary Composite from Zeolite/ZnO/$Fe_3O_4$ for the Removal of Methylene Blue Dye

**Misikir Tamiru Asefa**

**A Thesis submitted to The Department of Materials Science and Engineering**

**School of Chemical, Mechanical and Materials Engineering**

**Presented in Partial Fulfillment of the Requirement for the Degree of Master's in Materials Science and Engineering**

**Office of Graduate Studies**

**Adama Science and Technology University**

**July 2021**

**Adama, Ethiopia**

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# Declaration and Recommendation

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I hereby declare that this Master Thesis entitled " **Synthesis and Characterization of Ternary Composite from Zeolite/ZnO/$Fe_3O_4$ for the Removal of Methylene Blue Dye**" is my original work. That is, it has not been submitted for the award of any academic degree, diploma, or certificate in any other university. All sources of materials that are used for this thesis have been duly acknowledged through citation.

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# ACKNOWLEDGMENTS

First of all, I praise the Lord God Almighty for providing me with the power and grace to carry out this work. Foremost, I would like to express my gratitude to my advisor Dr. Gebisa Bekele for his patience, guidance, and very constructive criticism. His guidance helped me all the time with this thesis work. I would like to express my gratitude to my co-adviser Dr. Osman Ahmed and Dr. Temesgen Debeo for their valuable advice and insightful comments. I would like to express my gratitude to ASTU/SM-R/211/21 for given me this opportunity and I would like to thank Dr. Dinsefa Mensur and the Technical Staff of the Material Science and Engineering program, Mr. Demeke Tesfaye, Ms. Bruktawit Ayele, and Mr.Henok Mekonen for their support and motivation. I am extremely grateful to my parents for their love, prayers, support, guidance, and patience in educating and preparing me for my future. I am very much thankful to Mr. Abenezer Ashenafi for his endless support, kind and understanding spirit. Last but not least, I would like to thank my long-time class meats, relatives, and others who in one way or another shared their support.

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# ACRONYM

| | |
|---|---|
| DTA | Differential thermogravimetric analysis |
| EDS | Energy-dispersive X-ray spectroscopy |
| FTIR | Fourier transforms infrared spectroscopy |
| MB | Methylene blue |
| M Z-A/Z5 | Magnetic Sodalite octahydrate zeolite with 5wt% Zinc Oxide |
| M Z-B/Z5 | Magnetic Zeolite LTA with 5wt% Zinc Oxide |
| PBUs | primary building units |
| SBUs | Secondary building units |
| SCBA | Sugar cane bagasse Ash |
| SEM | Scanning Electron Microscopy |
| UV–Vis | Ultraviolet-visible spectroscopy |
| TGA | Thermogravimetric analysis |
| XRD | X-Ray Diffraction |
| Z-A | Sodalite octahydrate zeolite (hydrothermal) |
| Z-A/Z5 | 5wt% Zinc Oxide on Sodalite octahydrate zeolite |
| Z-B | Zeolite Linder type A (sol-gel) |
| Z-B/Z3 | 3wt% Zinc Oxide on Zeolite LTA (Linder type A) |
| Z-B/Z5 | 5wt% Zinc Oxide on Zeolite LTA (Linder type A) |
| Z-B/Z7 | 7wt% Zinc Oxide on Zeolite LTA (Linder type A) |

## *ABSTRACT*

*The enormous expansion of industrialization across the world has been accompanied by discharging of large amounts of waste materials such as organic dyes that resulted in water pollution. Zeolite is among the porous materials used for the absorption of pollutants in wastewater. However, Zeolite is a non-magnetic material, it had been often synthesized by the hydrothermal method, and it has limited absorption active sites. In this work, we have synthesized a magnetic zeolite/ZnO composite with high adsorption performance, recyclability, and a new magnetic separation way by co-precipitation method for Methylene blue (MB) removal from wastewater. Sugar cane bagasse ash was used as a low-cost silica source and waste food packaging aluminum foil as an alumina source to synthesized zeolite adsorbent by using hydrothermal (Z-A) and sol-gel method (Z-B). The synthesized materials were characterized by using XRD, SEM, FTIR, TGA–DTA, and UV-Vis spectroscopy. The XRD's results confirmed that Z-A was Sodalite octahydrate zeolite and Z-B was Zeolite LTA type. In addition to this, the Peak of ZnO did not appear on the XRD pattern of both Z-A/5% of ZnO (Z5) and Z-B/Z5 due to its small quantity. The SEM results showed the porous and spherical nature of Z-A and Z-B, and the formation of composites was also confirmed by FTIR's peak shift from 357 $cm^{-1}$ to 353 $cm^{-1}$. TGA–DTA analysis concluded that synthesized zeolites and their composites were stable up to 800°C. The removal of MB from wastewater using both composites was checked by UV-Visible spectroscopy. The results revealed that the optimum absorption was observed at PH of 7, an adsorbent dosage of 3g/l, contact time 30min, and MB concentration of 10ppm. The absorption results were compared with Langmuir and Freundlich models then first and second-order kinetics were studied. The removal efficiencies of Z-A/Z5 and Z-B/Z5 were greater than Z-A and Z-B by 28.9% and 37.14 % respectively and contact time was also reduced from 150min to 30min due to additional adsorption sites of ZnO. The addition of $Fe_3O_4$ to Z-A/Z5 and Z-B/Z5 make them magnetic materials named MZ-A/Z5 and MZ-B/Z5 but their adsorbance was reduced insignificantly. The composites also showed outstanding stability for three-round tests, and it was observed that the removal efficiency of MZ-A/Z5 and MZ-B/Z5 is comparable. Therefore, MZ-B/Z5 is a promising absorbent for removal of MB due to its safety, synthesized without using autoclave and cost-wise.*



***Keywords: Magnetic Zeolite/ZnO composite, Adsorption, Methylene blue, and Wastewater.***

# CHAPTER ONE

## 1. Introduction

### 1.1. Background of the Study

Water is the most essential substance for all living things to survive. In the absence of water, life cannot be sustained beyond a few days [1, 2]. Water is used for different applications such as drinking, washing, sanitary, bathing, irrigation, air-conditioning, and also it has a major role in industries [3]. However, it's polluted by different pollutants or contaminants bring severe threats to the health of the environment and the societies [4]. These contaminants may be released from different sources into water bodies [5]. The growth of civilization, population, and industrialization have led to a steady worsening in the purity of available water resources [6]. Processing industries are the main sources of these pollutants [7]. Industrial waste is waste that generates by industrial activity, and some of them are chemical solvents, dye effluents, industrial by-products, heavy metals, and radioactive wastes [8]. Due to their unfavorable effects, the presence of dyes in wastewater is a major concern to many forms of life [9]. The discharges of dyes to the environment have both toxicological and esthetical effects. Many Industries use dyes to color their products and also consume substantial volumes of water the common industries are Dyeing, printing, rubber, cosmetics, textile, leather, paper, and plastics [10, 11]. Those industries generate a large amount of colored wastewater and approximately there are around 100,000 commercially available dyes that produced more than $7\times10^5$ tons of dye stuff annually. Thus the colors would highly influence the public perception of water quality. Color is the principal pollutant to be detected in wastewater because of the existence of dyes even insignificant amounts are easily seen and undesirable [10].

Dyes can be classified as anionic, cationic, and non-ionic dyes. Methylene Blue (MB) is a cationic dye most commonly used substance for Dying [10]. MB leads to diseases such as vomiting, shock, increase heart rate, Heinz body formation, cyanosis, jaundice, tissue necrosis in humans, and quadriplegia [12]. Those coloring compounds and the effluent requires proper treatment before it discharged to any water body to save lives and protect the environment [13]. There are several techniques to eliminate or minimize the level of these pollutants from wastewater like chemical precipitation [14], ion exchange [15], chemical coagulation [16], and rivers osmosis [17], electro dialysis [18], flocculation [19], bioremediation [20], and adsorption

[21]. From these methods, adsorption has been commonly considered as a highly efficient technique for the elimination of organic dyes from wastewater due to its low cost, effective and cheap operation, easy and various designs, and high capacity [22]. Adsorption is the deposition and adhesion of ions or molecule species onto a surface [23]. It is based on two fundamental parameters namely the adsorbent and the adsorbate. The adsorbent is the surface at which ions or molecules are adsorbed whereas; the adsorbate is the species that is adsorbed. The surface where adsorption occurs is provided by adsorbent and the species which is adsorbed on the surface is adsorbate [24]. The adsorbent uptake capacity depends on the adsorption properties such as porosity, specific surface area, pore-volume, cation exchange capacity, interaction time, and adsorbent dose [24]. Different adsorbents were obtained from several sources such as charcoal [25], clays [26], sands [27], zeolites [28], and other waste resources. Adsorbents derived from wastes used coconut shell [29], eggshell [30], sugar cane bagasse [31], rice husk [32], petroleum wastes [33], coffee husk [34], sawdust [35], industrial wastes [36], fertilizer waste [37], fly ash [38] , chitosan [39], algae [40], bacteria [41], yeasts [42], fruit wastes [43], etc.

There are various adsorbents used before as we have discussed above to remove dyes, while due to the complex nature and stability of these organic pollutants further study is required [44]. Researchers still searching for high removal efficiency and low-cost adsorbents used for the removal of dyes from wastewater [45]. Zeolite is belonging to porous materials which have high absorption efficiency [46]. However, Zeolite is non-magnetic properties so that it is hard to recycle it easily, usually; zeolite has been synthesized by the hydrothermal method. But, the hydrothermal method needs expensive autoclaves, safety issues, and hard to observe the reaction process.

In this study, magnetic zeolite/ ZnO composite was synthesized by non-hydrothermal and hydrothermal methods to compare the effect of synthesized methods on the absorption efficiency of Zeolite materials. ZnO has interesting and promising uses due to its high selectivity and capacity to dyes from wastewater besides this property its size also helps it to penetrate the contamination zone where bulk materials cannot [47] [48]. Iron oxide particles were used for magnetism because of their ability to separate suspended adsorbents easily and rapidly using an external magnetic field [47]. In addition to this, the raw materials for synthesizing zeolite are industrial by-product sugar cane Bagasse Ash and waste food packaging aluminum foil.

The food packaging aluminum foil is a waste that pollutes the environment so that utilizing it is helpful not only in synthesizing zeolite but also reduces the burden of environmental pollution. Figure 1.1 shows sugar cane bagasse ash and food packaging aluminum foil wastes.

*Figure 1.1: sugar cane bagasse ash and Waste food packaging aluminum foil*

**In this work**

- Zeolite was synthesized by a new low-cost synthesis method,
- The adsorption capacity of zeolite was increased by loading zin oxide,
- Iron oxide nanoparticles were used for easy separation way of adsorbent,
- recyclability of the composite was increased by using strong acid and,
- Parameters that affect the performance of the adsorption process were investigated.
- Adsorption isotherm models and adsorption kinetics were studied.

Thus zeolite was synthesized by using waste products that are environmental pollutants by using a new low-cost synthesis method (sol-gel). The adsorption capacity of both zeolites types Sodalite octahydrate zeolite (hydrothermal) and zeolite LTA (sol-gel) increased highly from removal efficiency (66.7% to 95.3%) and (57.9% to 95.04%) respectively. In addition to that Iron oxide nanoparticle was added to make the composite magnetic for easy separation way of adsorbent from aqueous solution. Subsequently, Parameters that affect the performance of the adsorption process namely contact times, pH, adsorbent dosage, and initial concentration of methylene blue were studied not only this but Adsorption isotherm models and adsorption kinetics were also thoughtful. Moreover, the recyclability of adsorbents was performed for three rounds and confirmed with outstanding stability though out the three rounds for the acid-treated adsorbent.

## 1.2. Statement of the problem

The synthesis of zeolite was needed an autoclave for the hydrothermal method. In the absence of autoclaves, there was no proposed method before to synthesize zeolite. However, in this study different types of zeolite were obtained by using hydrothermal and sol-gel methods so the study opens another way to produce zeolite without using an autoclave.

In addition to the above problem recycling of wastes are a top issue and leading research area[48]. Even there were some works done by using wastes for the production of zeolite there was no research have done before by using waste for both sources of silica and aluminum oxide. In this work, SCBA was used as a silica source and waste food packaging aluminum foil as aluminum oxide source which makes the synthesis of zeolite less costly and safe for the environment.

Even zeolite is one of the best and efficient adsorbents for the removal of dyes [49] it is difficult to separate zeolite material after the adsorption process thus its industrial applications are highly limited due to the separation process, which results in the need for additional process either filtration or centrifuge. Using the additional process after adsorption is a waste of labor and cost so this makes zeolite material very limited in the adsorption process [50].

To full fill, this gap in this work, magnetic particles ($Fe_3O_4$) were added to zeolite as a solution for the separation problem due to the easy separation of magnetic zeolite by a magnetic field. Despite the advantage of $Fe_3O_4$ for magnetic separation way it could occupy available active sites on the surface of zeolite which leads to lower adsorption performance. This can be outdone by incorporating ZnO particles into the magnetic zeolite composite and produce ternary composite to enhance adsorption of methylene blue dye.

Again, as we know adsorbents have to use several cycles in the adsorption-desorption cycle while zeolites have very limited cycles due to the occupation of the pores by the adsorbate [50]. This is also another limitation on the usage of zeolite which was overcome in this work by using strong acid to dissolve the triggered adsorbate in the pore of the adsorbent.

## 1.3. Objectives

### 1.3.1. General objective

- Synthesis and Characterization of magnetic composite from zeolite/zinc oxide for the removal of methylene blue dye with high adsorption performance, recyclability, and easy magnetic separation way.

### 1.3.2. Specific objective

- Extracting sodium silicate solution from sugar cane bagasse ash and aluminum oxide from food packaging Aluminum foil.
- Synthesizing zeolite with a hydrothermal and sol-gel method.
- Scrutinizing the effect of iron oxide and zinc oxide on the adsorption capacity of Zeolite for the removal of Methylene blue.
- Characterizing the synthesized materials by using different materials and also examine isotherm models as well as adsorption kinetics for the synthesized zeolite.
- Investigating the effect of the surface area of adsorbent, the effect of pH, contact time, adsorbent dose, and initial concentration of impurity on the adsorption process of magnetic zeolite/ZnO composite.

## 1.4. Scope of the study

This study covers the synthesis of a magnetic composite of zeolite/ZnO by using sugar bagasse ash wastes to obtained sodium silicate solution, and food packaging aluminum foil as a starting material for zeolite production. It further focuses on the application of synthesized magnetic ternary composite for the adsorption of Dyes from wastewater.

## 1.5. Significance of the study

In this work, easy and inexpensive methods for the production of synthetic zeolite without using autoclaves were used. Zeolite was synthesized by using sugar cane bagasse ash and waste food packaging aluminum foil as raw material. This helps to minimize the cost of precursors for mass production of zeolite and is environmentally friendly. In addition to that this study was introduced a new Magnetic nanocomposite material for adsorption of Methylene blue with high adsorption capacity, an easy separation method, and a proposed way for the regeneration of material after the adsorption process which eliminates additional processes like filtration and centrifugation. So, the work can be effectively used for manufacturing industries to treat large amounts of contaminated water because the material is cost-effective, can be synthesized in mass production and the method is easy to perform.

# CHAPTER TWO

## 2. Literature Review

### 2.1 Water

Water is the most abundant and uses a full compound that is found in nature [51]. Water is life in the absence of water, life cannot be sustained beyond a few days [52]. Water is used for different applications such as drinking, washing, sanitary, bathing, irrigation, air-conditioning, and also it has a major role in industries [51]. However, the distribution of water on the Earth's surface is extremely uneven. Freshwater on the surface is only around 3% (less than 1% is located in lakes, rivers, and swamps, 69% resides in glaciers, 30% underground) the remaining 97% resides in the ocean [51].

In this chapter water, source of water contamination, industrial wastes mainly organic dyes, and the effect they had on humans and the environment are discussed. Several ways this contaminant is removed from the wastewater and the techniques used for the treatment of the water are mentioned. Among those techniques, the adsorption process is discussed briefly in this chapter with its working mechanism and the factors affecting the mechanism. The main focus of this chapter is to show promising adsorbents like zeolites, metal oxide nanoparticles, and composite materials in the adsorption process. We will cover a synthesis of zeolite for heavy metal removal, works that have been done before were mentioned with their gap, and finally discussed metal oxide nanoparticles with their special function to develop them as a composite material. In addition to this removal capacity of the adsorbents mentioned from the work done before. In the final portion of this chapter Parameters affecting the adsorption process are discussed in detail.

#### 2.1.1 Source of contaminated water

Water is usually contaminated by different types of impurities from different sources. The Major sources of water pollution are Domestic sewage, Population growth. Pesticides and fertilizers, Plastics and polythene bags, Urbanization, and Industrialization [51]. Different industrial wastes are drained into a river without treatment is the major cause of water pollution. The discharges from the industries are responsible for surface water and groundwater contamination [53].

### 2.1.2 Industrial wastes

Industrial waste is waste that generates by industrial activity some of them are chemical solvents, industrial by-products, dyes, heavy metals, and radioactive wastes [54]. Roughly speaking, 25% of the water pollution is caused by industrial wastes and heavy metals are the most toxic metals that enter into water and reduced the quality of water [55].

### 2.1.3 Organic Dyes

A dye is a colored substance that is bond chemically to the substrate to which it is being applied [56]. Dyes used in industries are classified into three: (i) anionic dyes those are direct, acid, and reactive dyes, (ii) cationic dyes which include all basic dyes, and (iii) nonionic dyes those are dispersed dyes [57]. Dye effluents, discharged with waste water from manufacturing, dyeing, printing, and textile industries, contain chemicals those leads toxic effect toward microbial and carcinogenic to mammals [28].

## 2.2 Methods to remove Dyes

Due to the increase in disposal of wastewater, there are many methods proposed for wastewater treatment. The most common methods for dyes removal are chemical precipitation [14], flotation [58], flocculation [59], ion exchange [15], chemical oxidation [16], reverse osmosis [17], ultrafiltration [60], electro dialysis [18], and adsorption [61, 62] as shown in Fig 2.1. Adsorption technologies have several advantages over the methods listed above due to their easy operation, low cost, flexibility in design, high efficiency, availability, high-quality treated effluent, and recyclability [63].

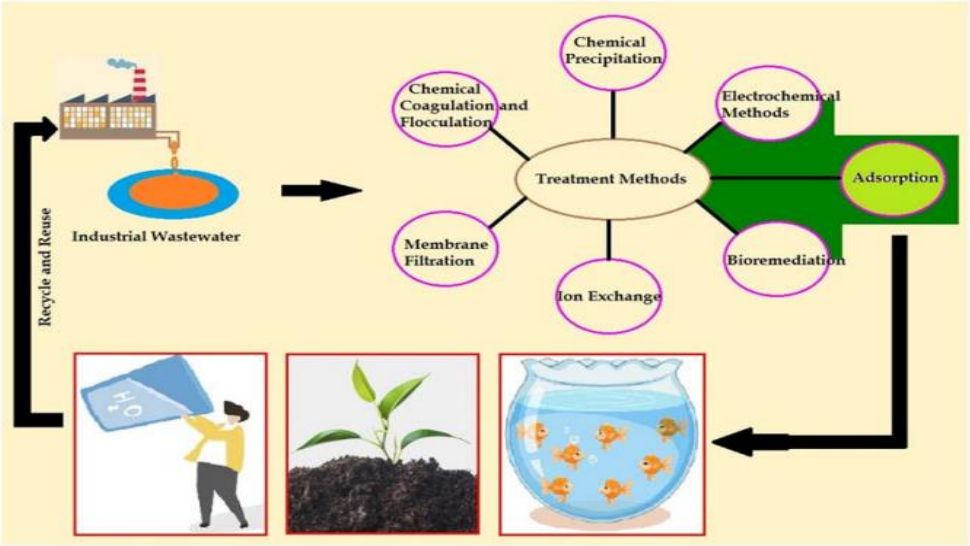


*Figure 2.1: Waste water treatment techniques [64]*

### 2.2.1 Adsorption process

The term Adsorption implies an excess concentration of molecular species present at the surface of the adsorbent [65]. The process was first invented in 1881 by a physicist named Heinrich Kayser. It is a process in which something takes in another substance which means impurities take by the absorbent material. The molecular species that gets adsorbed on the surface is known as adsorbate while the surface on which adsorption occurs is known as adsorbent [65]. Figure 2.2 shows the adsorption process.

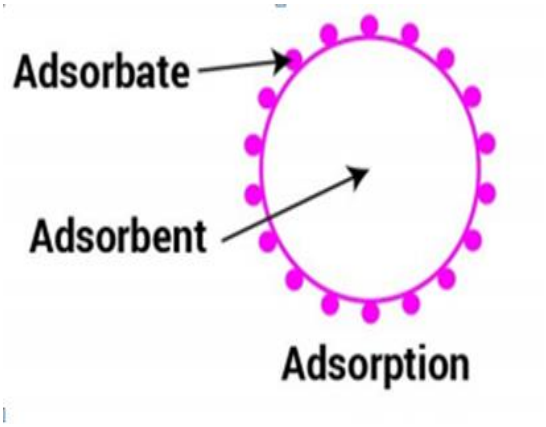


*Figure 2.2: Adsorption process [65]*

Nowadays, adsorption is considered an efficient as well as low-cost technique for removing wastes from water [66]. This process is flexible in design and operation and allows for producing high-quality treated effluents. Furthermore, since the adsorption is reversible in some cases, adsorbents can be regenerated through desorption [61].

There are two types of adsorption called physical and chemical adsorption. Physical adsorption is in which the increase in the adsorbate concentration at the interface is due to non-specific van der Waals forces and it is weakly specific, reversible and its thermal effect is small while chemical adsorption is caused by chemical reactions between the adsorbate and the adsorbent which create covalent or ionic bonds it is selective, usually irreversible and heat ranges from tens to hundreds of kJ/mol [67, 68].

### 2.2.2 Materials used for adsorption

There are various adsorbents as shows in Fig 2.3 below which are available either naturally or commercially that are used to remove organic dyes from wastewater in the last decades [69]. Adsorbents are classified as conventional and nanostructured adsorbents based upon their size and efficiency in the removal of impurity from wastewater [70].

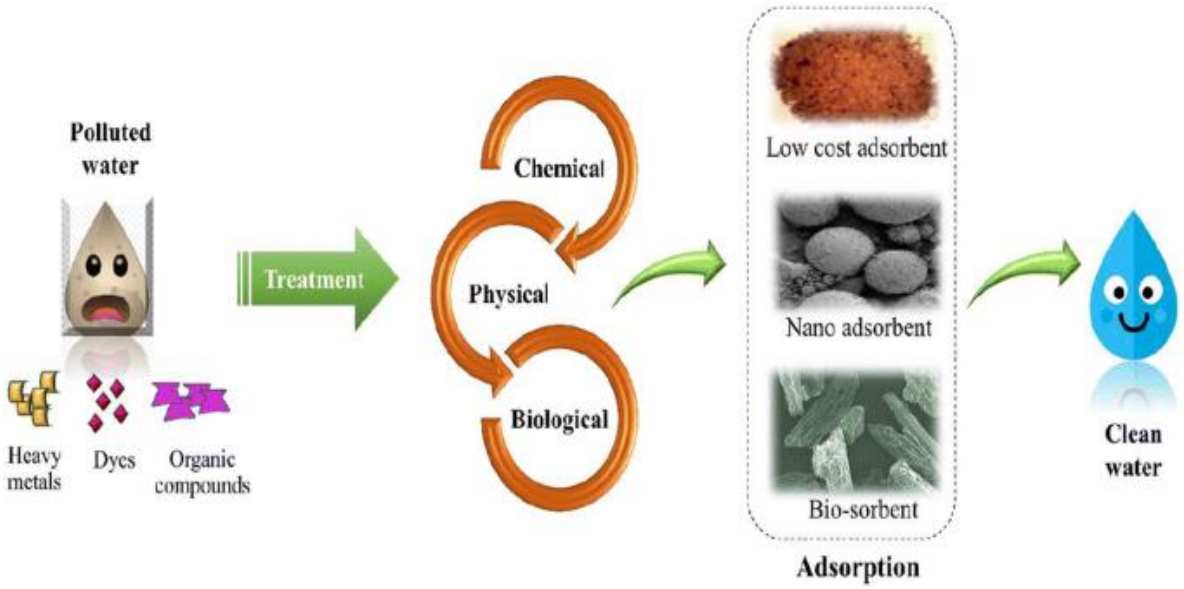


*Fig 2.3: Different types of adsorption methods [71]*

### 2.2.3 Conventional absorbent

Conventional absorbents are inexpensive and available either naturally or easily synthesized from waste materials [72]. Some of the conventional adsorbents are activated carbon [73], bio adsorbents obtained from non-living biomass [74, 75], algal biomass and microbial biomass [76], clay materials [77], and zeolite [78].

**Zeolite**

Zeolites are among the best adsorbents because they are composed of three-dimensional crystalline, hydrated alumino silicates made from the interlinked tetrahedra of silica $(SiO_4)^{4+}$ and alumina $(A1O_4)^{5+}$ [79]. Figure 2.4 shows the chemical model of a zeolite structure. Zeolites crystal structures are normally categorized into primary building units (PBUs) and secondary building units (SBUs). Those are the $(SiO_4)^{4+}$ and $(AlO_4)^{5+}$ tetrahedral respectively.

The secondary building units come in a variety of forms such as single rings, double rings, polyhedral, or even more complex units that are linked together in a variety of ways to produce a unique system of channels and cages. The differently sized holes in the figure represent channels and cages [80].

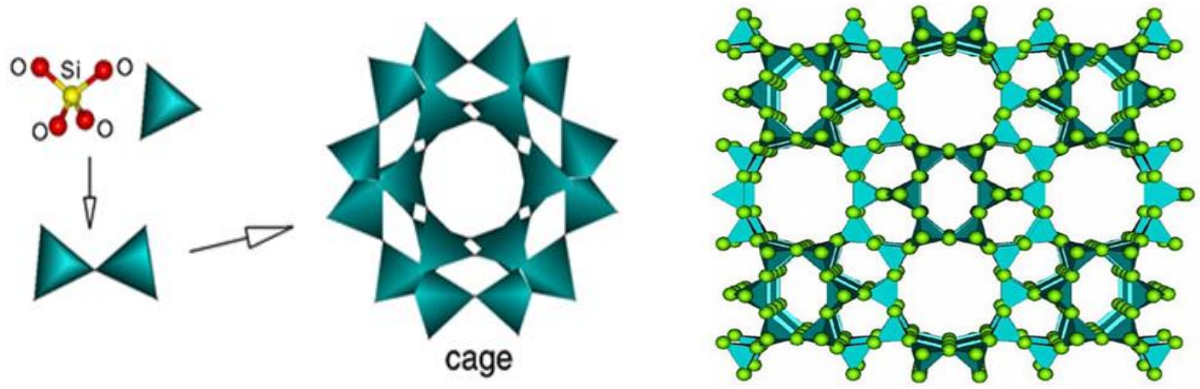


*Figure 2.4: A Combination of $(SiO_4)^{4+}$ PBUs to form SBUs and Crystal structure of zeolite [80]*

Zeolites have much scientific and industrial significance because of their good ion exchange properties, high surface area, nontoxicity, low cost, abundance, and hydrophilic characteristics. Zeolites are mostly applicable in the cause of water treatment due to their satisfactory potential for the removal of dyes from waste water [28, 81]. Zeolite can be classified as natural zeolite and synthetic zeolite based on the source in which they occur in nature and synthesized zeolites both are used for different applications [49]. They are used as solid catalysts, biomass conversion, fuel cells, thermal energy storage, $CO_2$ capture and conversion, air-pollution remediation, and water purification, etc. [82].

The application of natural zeolites is limited because of impurities that are triggered inside the pores while synthetic zeolites have interesting properties such as greater thermal stability, good properties as specific catalysts, and uniformity due to the purity of synthetic zeolite [49]. The idea of Zeolite synthesis was originated by Richard Barrer and Robert Milton in the 1940s and after that time more than one hundred different types of zeolite are synthesis up to now [83]. There are two groups to synthesize crystalline materials which are solid-state reaction and liquid phase reaction. In the cause of the solid-state reaction, the temperature used is above 300°C to overcome difficulties in the transportation of molecules. While in the cause of liquid phase reaction the transportation of a molecule is easier due to the presence of solvents so the synthesis process is done at low temperature.

There are three methods for Zeolite syntheses in the liquid phase are Hydrothermal method, Solvothermal method, and Ionothermal methods all synthesis mrthods are performed in an autoclave however, in hydrothermal method the solution is aqueous while in solvothermal method the solution is non-aues and in ionothermal mehod the solution is ionique liquid [84]. So, both solid-state and liquid phase synthesis methods need a sealed reaction for the crystallization process which needs autoclave.

Zeolites have much scientific and industrial significance because of their good ion exchange properties, high surface area, nontoxicity, low cost, abundance, and hydrophilic characteristics. Due to those characteristics zeolites are applicable in many areas like drying, purification, water softening, environmental treatment, radioactive waste storage, catalytic activities, and so on. Zeolites are mostly applicable in the case of water treatment due to their satisfactory potential for removal of metal ions from solution [57, 85, 86].

### A. Natural Zeolite

Natural zeolite is a naturally occurring zeolite that was first discovered by Swedish mineralogist Freiherr Axel Fredrick Cronsted, during the collection of minerals in a copper mine. The new mineral is called zeolite because of its characteristic observed during blowpipe tests on the new crystals he invents. However major geological discoveries have revealed the widespread occurrence of natural zeolites after 1950. Since the beginning of the last century natural zeolites whose origin is sedimentary were used for different applications in different areas of environmental protection. These applications are due to important properties exhibited in these materials, such as cation exchange, alkali metals reactivity, physical adsorption and expansion tendency, thermal insulation, compressive strength, and durability [88-91].

Nowadays the application of natural zeolites is limited due to more interesting properties of synthetic zeolite such as greater thermal stability as well as good properties as specific catalysts. Synthetic zeolite gets more interest than natural zeolites due to the purification method as variable phases and chemical impurities. Contrarily at a time where uniformity and purity are not useful natural zeolite may get favor due to its cheapness [49].

## B. Synthetic Zeolite

The idea of Zeolite synthesis was originated by Richard Barrer and Robert Milton in 1940 [92]. Synthetic zeolites are also called molecular sieves which are crystalline aluminosilicates manufactured by heat. Zeolites identify as minerals of natural origin however recently more than one hundred different types of zeolite are synthesis [93]. Zeolite was formed when a reaction occurs between volcanic ash and water of basic lakes by taking several thousands of years. However, in laboratory conditions, it takes a short time and can be made by hydrothermal processes from natural materials or synthetic silicates [93, 94]. Many sources such as coal ash, SCBA, and rice husk ash were used to prepare synthesized zeolites [92, 93, 95, 96]. Many researchers have been involved in synthesizing different types of zeolites [97] So far, more than 20 different zeolite types have been prepared as molecular sieve membranes on porous supports for gas or liquid separation [98]. Among these molecular sieve membranes, the zeolite LTA and Sodalite octahydrate zeolite membrane were synthesized and studied in our work due there special interest because those types of zeolites have strong hydrophilicity, and thus shows excellent performance in hydrophilic separations [98]. The combination of the strong hydrophilicity and implying uniformity regarding the size of their pores they used as extremely effective for the adsorption process [99, 100]. In this work, we have synthesized the two types of zeolite and studied their performance on the removal efficiency of methylene blue. Even if there are various zeolites investigated and studied, still their use was limited due to the challenge in the area, and here most issues are solved in our work.

- Using nanomaterials is choosing over bulk materials because of certain reasons. The properties of Nanostructured Materials differ from those of bulk materials with the same average chemical composition. This difference results from the reduced size and dimensionality of the Nano-sized materials. Nanomaterials are always in Nano size but they may have different dimensions as shown in Fig 2.5. Nanomaterial's properties make them deviate from the bulk materials, including high surface energy, a large fraction of surface atoms, reduced imperfections, and spatial confinement [101].

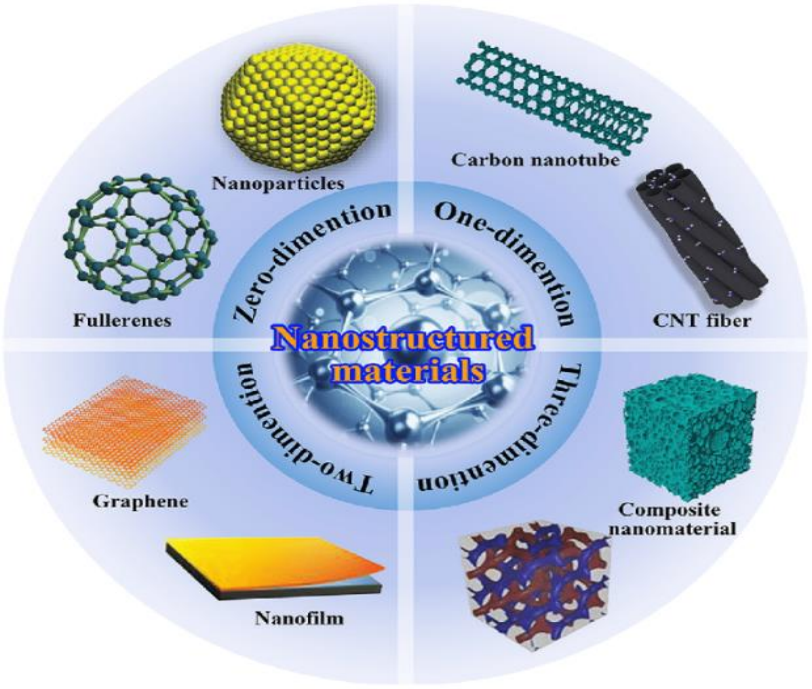


*Figure 2.5: Solid-nanostructured-materials-with-different-dimensions [102]*

## 2.3 Nanostructured materials

Nanostructured Materials are materials with a microstructure whose structural elements, clusters, crystallites, or molecules have dimensions of 1 to 100 nm range. Their fundamental electrical, optical, and magnetic properties lead to a great interest in both academic and industrial levels over the past decade [103]. Conventional materials have limitations of adsorption capacity and do not provide the desired removal efficiency for most treatments of dyes due to the reason scientists perform research's to develop novel adsorbents with the best characteristic [104]. Nanomaterials are adsorbents that efficiently remove dyes from wastewater due to their enhanced active sites, high surface area, and the functional groups on their surface [105].

There are few naturally formed nanomaterials and many are man-made nanomaterials [106]. There are different classes of Nanoparticles due to morphology, size, physical properties, and chemical properties [101], while our work mainly concerns metal oxide nanoparticles. Due to their small size and high density of edge surfaces metal oxide nanoparticles have a unique physical and chemical property [107]. The interesting and promising uses of the materials are due to their high selectivity and capacity to remove dyes from wastewater besides this property their size also helps them to penetrate contamination zone where bulk materials cannot [108].

Opposing the whole advantages of metal oxide nanoparticles there is a problem reported due to the size reduction of metal oxides. The decrease in the size of metal oxide leads to poor stability because of the increase in surface energy [108]. The poor stability of particles leads to agglomeration so the surface area would decrease and leads to a decrease in the removal efficiency of the material [109]. Scientists are working on it and suggest using those materials by emerging with other porous materials as a stabilizer or supporter to form nanocomposite adsorbent this overcome the limitations on the application of metal oxide nanoparticles [108].

A material that is made up of two or more constituent materials with different chemical and physical properties is then combined to make a single material that is varying from the individual material in the property. The use of metal oxide nanoparticles in water treatment was improved by the combined use of porous support materials as a matrix [110].

Various matrixes are used as a supporter for metal oxide nanomaterials but among those matrixes, zeolite is considered the best host and stabilizer because of its large surface area, hydrophilic, high ion exchange capacity, high thermal stability, tunable chemical properties, pores with 1.3 nm diameter, eco-friendly nature, and inexpensive nature But still, researchers are looking for a less costly method to produce zeolite [108, 111]. Despite the whole good properties of zeolite in the adsorption process, the difficulty of separation limits the broad applications of zeolite.

Hence, there was no report on the synthesis of zeolite by using wastes for both aluminum oxide and silica sources and there was no report on the synthesis of magnetic Zeolite/ZnO ternary composite for degradation of organic dyes. And, no work incorporated those metal oxides with zeolite material with zeolite produces without using hydrothermal. This study is reported to overcome the limitations that are discussed above by the synthesis of a new magnetic zeolite/ $Fe_3O_4$ ternary composite. Zeolite is produced from the waste product of SCBA and food packaging aluminum foil. The resulting adsorbents were characterized by using different characterizing instruments. The adsorption capacities of the adsorbents were also examined on the removal of Methylene blue dye within a given time. Consequently, the reusability of zeolite and ternary composite were studied for three consecutive rounds.

# CHAPTER THREE

## 3. Materials and Methods

### 3.1. Materials

In this work, all reagents were analytical grade. Zinc acetate dihydrates (Loba Chem, 98%,), Hydrochloric acid (35% HCl), Ferric chloride ($FeCl_3.6H_2O$) (Alpha Chem), ferrous sulfate ($Fe_2SO_4.7H_2O$) (Alpha Chem,). Sodium hydroxide (NaOH) and Methylene Blue (MB), were purchased from Loba Chemical Reagent Company. Sugar cane bagasse ash for this experiment was collected from the Wonji sugar factory. The aqueous solutions were prepared using distilled water and in some cases by using DI water.

### 3.2 Methods

#### 3.2.1 Collection and preparation of sugar cane bagasse ash

Sugar cane bagasse ash for this experiment was collected from the Wonji sugar factory, which is 13 Km far from 'Adama' town. Then, the collected bagasse ash was washed repeatedly with distilled water to remove different impurities, especially salt and organic compounds, and Sun-dried for 2 days in the laboratory and sieve with 200 μm sieves and stored at room temperature for the next experiment as shows in Fig 3.1.

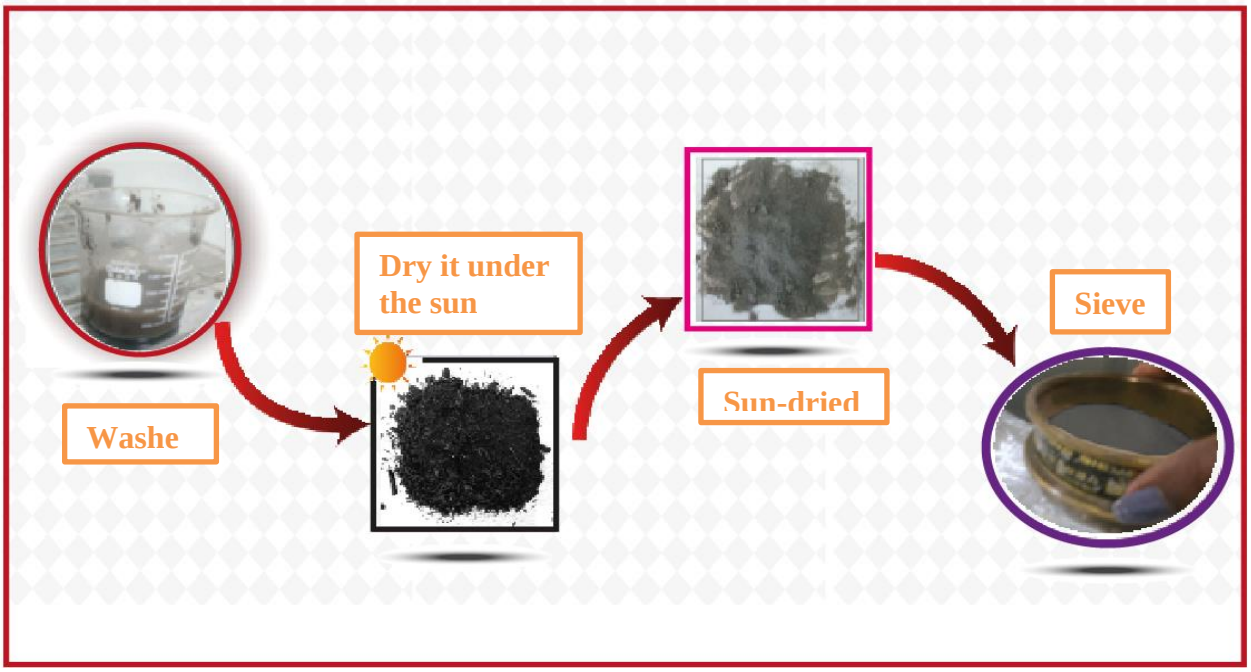


*Figure 3.1: Schematics for preparation of sugar cane bagasse ash.*

### 3.2.2 Preparation of Sodium silicate solution

To obtain pure Sodium silicate solution, Sugar cane bagasse ash was used as a silica source which is a waste product of sugar-factory burned in Furnace for 3hour at 600ºC. Calcination can be used to adjust its chemical composition, particularly by reducing its carbon content [102].

Then SCBA was mixed with sodium hydroxide in a ratio of 1:1.3 respectively and followed to burn at600ºC for 1hours. After the cooldown of the mixture, it was mixed with 200ml of distilled water and stirred for 10 hours. Then the solution was filtered by using filter paper to obtain sodium silicate solution. Figure 3.2 shows an illustration of the overall sodium silicate preparation process.

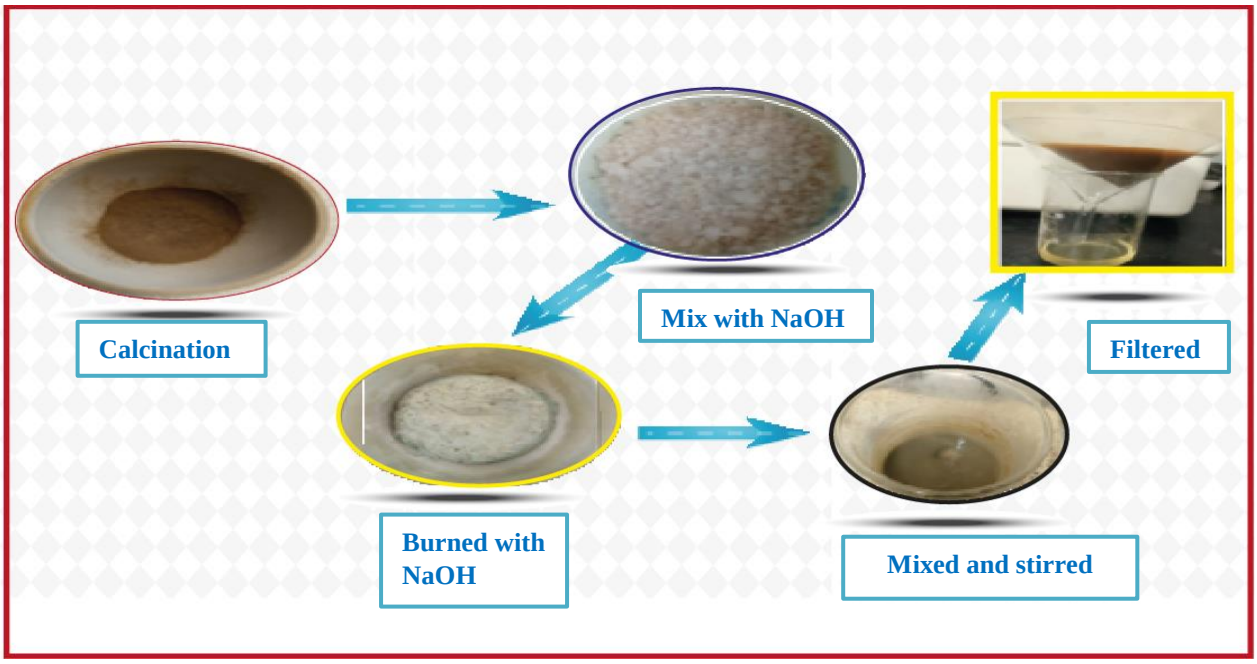


*Figure 3.2: Schematics for preparation of Sodium silicate solution from SCBA.*

### 3.2.3 Extraction of sodium aluminate

A waste food packaging Al foil was washed and cut into small pieces. 27g of the powder were dissolved in 250 ml distilled water with 1M NaOH. Then, the solution was stirred continuously at 60ºC with a magnetic stirrer until a homogeneous solution was obtained [112]. The process is shown in Fig 3.3 below.

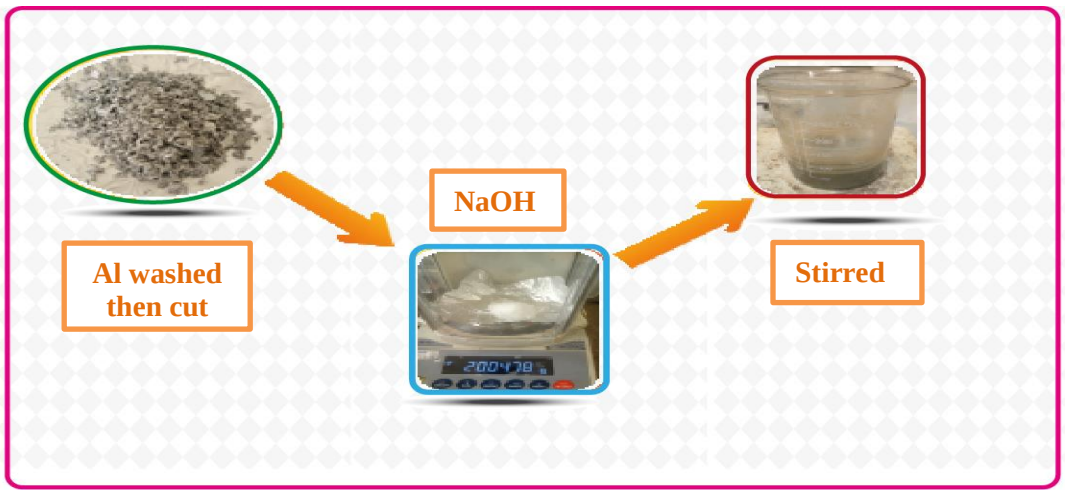


*Figure 3.3: Schematics for Extraction of sodium aluminate.*

### 3.2.4 Synthesis of Zeolite

The prepared sodium aluminate solution and prepared sodium silicate solution were mixed under fast stirring for 10 hours and then left at room temperature to allow the transformation of the mixture from sol into a gel [51]. The mixture is divided into two parts the 1st solution puts in an autoclave and the 2nd solution is in a beaker and abbreviated as Z-A and Z-B respectively. The gels were transferred to an oven at 100ºC for 24 hours. Then; Dry solids were washed repeatedly by distilled water to drop the pH, and were dried in the oven. Finally, dried solids were ground into a powder and subsequently calcined at 550°C for 6 hours.


*Figure 3.4: Schematics for the Synthesis of Zeolites by using different synthesis methods*

### 3.2.5 Synthesis of $Fe_3O_4$ nanoparticle

The $Fe_3O_4$ magnetite nanoparticles were synthesized by the conventional co-precipitation method according to the procedure done at [104]. First 2.794 g $Fe_2SO_4.7H_2O$, 3.11 g $FeCl_3$, and 0.85 ml HCl dissolved in 25 ml deionized water to obtain a homogenous solution. The obtained solution was then syringed to a 250 ml solution of 1.5mol NaOH under vigorous stirring at 80 °C. This reaction was continuing until nanoparticle crystals were observed. Finally, the suspension was gathered by applying a magnetic field, washed with deionized water several times to remove any unwanted impurities, and placed in an oven to get dried as shown in Fig 3.4.

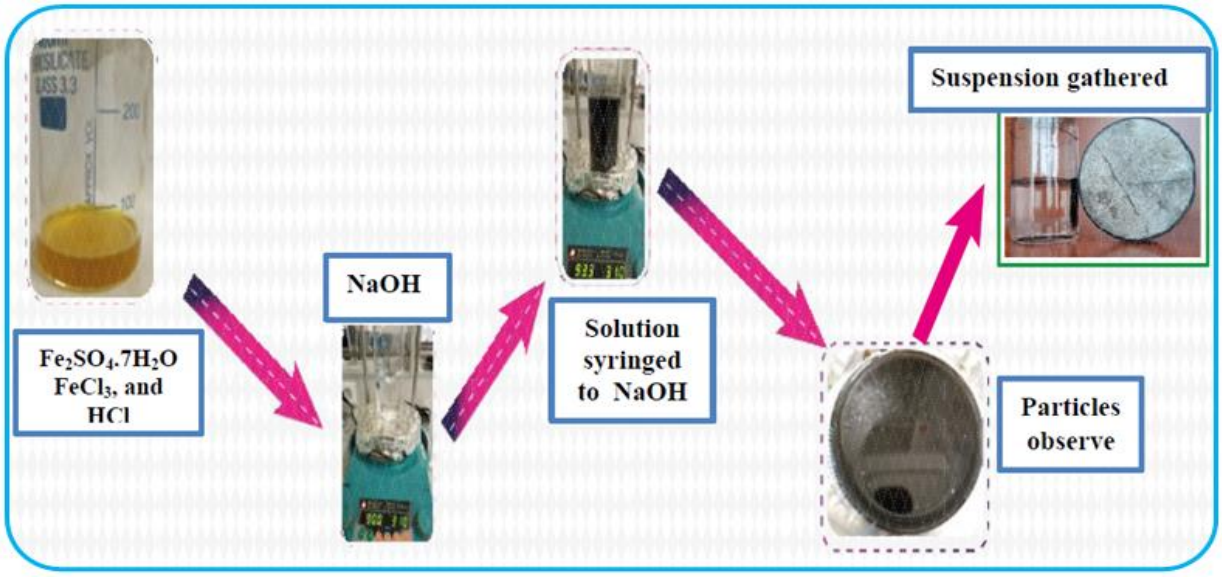


*Figure 3.5: Schematics for the Synthesis of $Fe_3O_4$ nanoparticle*

### 3.2.6 Synthesis of Magnetic Zeolite/ZnO composite

5 g of zeolite was dispersed into 100 ml deionized water and $Zn(Ac)_2$-$2H_2O$ was added to the corresponding wt% of ZnO (3, 5, and 7 wt % of ZnO). The samples are abbreviated as Z-A/Z3, Z-A/Z5, Z-A/Z7, Z-B/Z3, Z-B/Z5, and Z-B/Z7 when Z-A is zeolite made by autoclave and Z-B is zeolite made in a beaker. Z3, Z5, and Z7 stand for 3 wt%, 5 wt%, and 7wt% of Zinc oxide respectively. Then the slurry was stirred under 80ºC for 5 h for ion exchange. After that 0.1 M of NaOH was added to the suspensions until reaches pH11 according to [108]. Thus before going to further step test of absorption performance was done for the three samples Z3, Z5, and Z7 (3, 5, and 7wt% of ZnO) then as shown in Fig 3.5 the sample with 5wt% of ZnO shows the higher removal efficiency so the further synthesis of composite (addition of magnetic particle) was done on this sample (Z5).

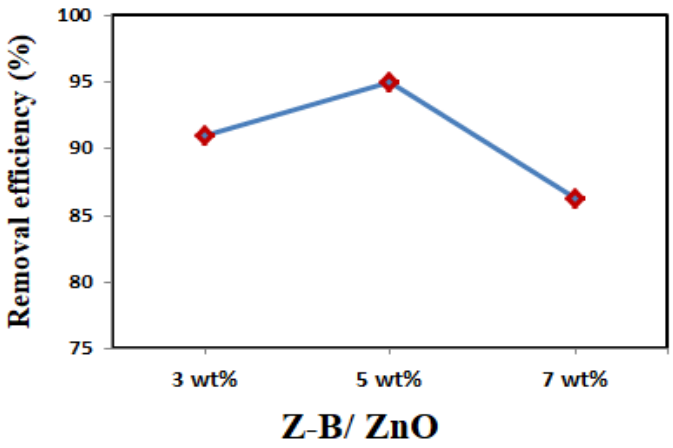


*Figure 3.6: Flow diagram synthesis of ZnO composite at different wt. % om Z-B/ZnO*

Zeolite/ZnO samples and 5%$Fe_3O_4$ solution were dispersed under the ultrasonic bath in 20 ml DI water for 3 hours separately. The obtained dispersed solution of $Fe_3O_4$ was added to zeolite/ZnO solutions on (Z-A/Z5 and Z-B/Z5) because those samples show higher performance. After the homogenization is completed each adsorbent was separated by applying an external magnet and placed in an oven to become dry [113]. The samples after the addition magnetic compound are abbreviated as MZ-A/Z5 and MZ-B/Z5 when M stands for magnetic substance. Figure 3.6: shows a schematic procedure for the synthesis of Magnetic Zeolite/ZnO composite.

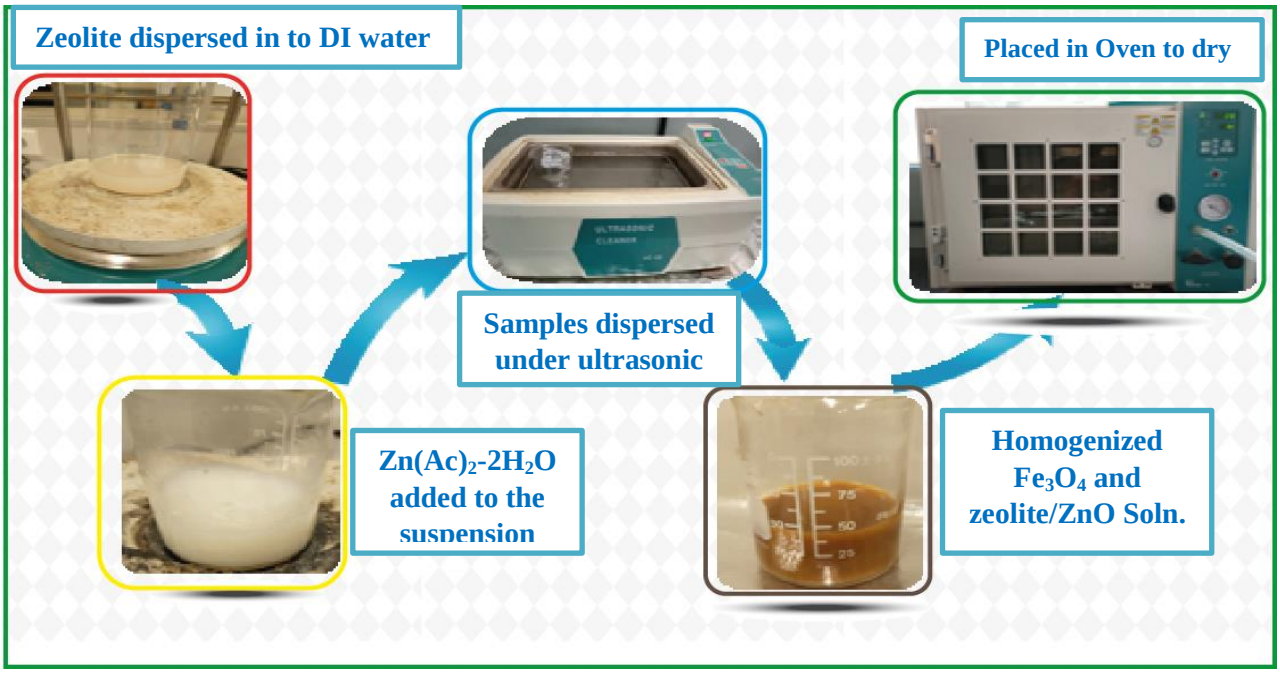


*Figure 3.7: flow diagram Magnetic Zeolite/ZnO composite*

### 3.2.7 Characterizations

Determination of the crystal structure of phases purity of each sample was characterized by us using X-ray powder diffraction at copper Kα radiation ( λCuKa = 1.5418 Å), a scan speed of 3.0000 (deg/min), voltage (40 kV), current (30 mA), and scanning range (10-80 °). The surface morphology was analyzed by Scanning electron microscopy (SEM) as well the chemical bonds and functional groups of the synthesized zeolite from and other samples were determined by using FTIR instrument (Ft/IR-6600 type A) with a wavenumber range of 200-4000 $cm^{-1}$, and finally, Thermogravimetric analysis coupled with its differential analysis (DTG-60H, Shimadzu) was used to study the thermal stability of the samples from 20 to 800°C under an inert atmosphere maintained by injecting $N_2$ at a flow rate of 50 mL/min.

### 3.3. Adsorption Experiment

Methylene blue stock solution was prepared in distilled water by using a standard concentration of Methylene blue. Then, a series of adsorption tests were carried out at typical equilibrium conditions for the optimization of adsorbents. The mixture was stirred using a magnetic stirrer during all of the experiments and finally, samples were analyzed by using UV–Visible spectrophotometer (UV-vis-3600plus Shimadzu).

Removal efficiency and adsorption capacity of the adsorbents were calculated using equations 2.1 and 2.2 as follows:

$$qe = \frac{V(Co-Ce)}{m} \quad \text{..... (2.1)}$$

$$\eta(\%) = \frac{(Co-Ct)}{Co} \times 100 \quad \text{..... (2.2)}$$

Where qe (mg/g) is the equilibrium adsorption capacity, Co is the initial concentration of Methylene blue, Ce (mg/L) is the concentration of Methylene blue at equilibrium time, Ct is the concentration of Methylene blue at a given time, V is the volume of solution, m is mass of the adsorbent, η (removal efficiency).

# CHAPTER FOUR

## 4. Results and Discussions

### 4.1. XRD Analysis

Figure 4.1 shows the XRD results of Z-A and Z-B. In Z-A the diffraction peaks at angles of 2θ=13.99º, 19.8º, 24.3º, 31.5º, 34.6º, 37.4º, 42.7º, 58.09º correspond to the (100), (200), (211), (310), (222), (321), (411), (440) crystallographic plane, indicating sodalite octahydrate zeolite. These results are aligned with the results reported in Reference [105]. In addition to this, the crystal structure of Z-A was compared with the standard zeolite material and found that they have similar structures. The XRD pattern of Z-B was also indicated in Fig.4.1. Then, diffraction peaks of Z-B were observed at angles of 2θ = 7.3º, 10.3º, 12.6º, 16.2º, 21.7º, 24.1º, 27.2º, 30º, 34.2º correspond to the (100), (001) (101), (110), (101), (101), (210), (001), (220) crystallographic plane. These data revealed that Z-B is Zeolite LTA by comparing with the XRD pattern of the standard of zeolite materials. We can conclude that the synthesis of zeolite by using different techniques may give different types of zeolite. On the other hand, no considerable amount of amorphous materials was detected in both synthesis techniques. Synthesize of the zeolite without utilizing expensive autoclaves was good in terms of economic and safety cases [106].

The crystallite size of Z-A and Z-B particles was calculated to be around 23.14 nm and 49.73nm respectively using the Scherer equation by assuming the crystallites were cubic and monodisperse in size [114]. The difference in the crystalline size is due to the different synthesis methods those are hydrothermal and sol-gel methods. The crystalline size was calculated according to equation (3.1) below and it's known that as particle size decreases the surface area of the material increases and the possible active sites parallel increasing which may promote high adsorption processes.

$$D = \frac{K\lambda}{\beta\cos\theta} \quad \text{..... (3.1)}$$

Where, $\lambda$ = 0.15406nm (wavelength of X-ray),

K = 0.9 (Scherer constant),

D = crystalline size (nm) and =FWHM.

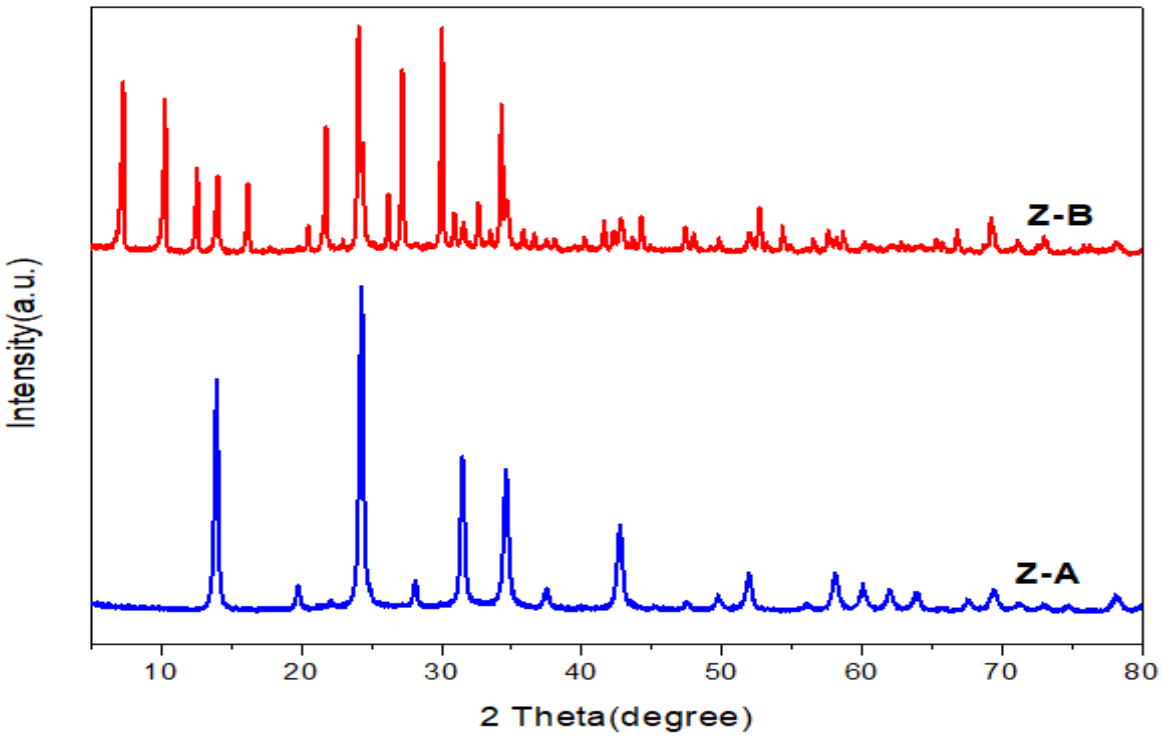


*Figure 4.1: XRD patterns of Z-A and Z-B*

The peaks patterns of zinc oxide doped composites are mostly similar to zeolite peaks before the addition of zinc oxide. Peaks that represent ZnO were not observed on the XRD pattern of both Z-A/Z and Z-B/Z as shown in Fig 4.2 this is due to the small quantity of ZnO and also meaning that ZnO particles are confined (intercalate) inside zeolite pores as studied before [108]. Even though the peak of the ZnO did not appear, it was observed the relative shift of peaks intensity and small shift to the higher diffraction angles which belong to the formation of ZnO without changing the structure of zeolite material.

Table 4.1: Represents the values for the average crystallite size of each sample

| No | Zeolite/ZnO Composite | crystallite size(nm) |
|---|---|---|
| **1** | Z-A/Z5 | 23.0944 |
| **2** | Z-BZ3 | 49.42086 |
| **3** | Z-B/Z5 | 47.85245 |
| **4** | Z-B/Z7 | 46.2791 |

Table 4.1 shows the relative crystalline size of the ZnO loaded on the Zeolite material. The results indicate that as the amount of loaded ZnO on the zeolite increase, the crystalline size showed small compression of the zeolite crystalline structure. The crystalline size for all composite is less than 50 nm. Moreover, there are no other diffracting peaks appeared in the product except the diffraction peaks of ZnO NPs, which means the prepared product is pure [108].

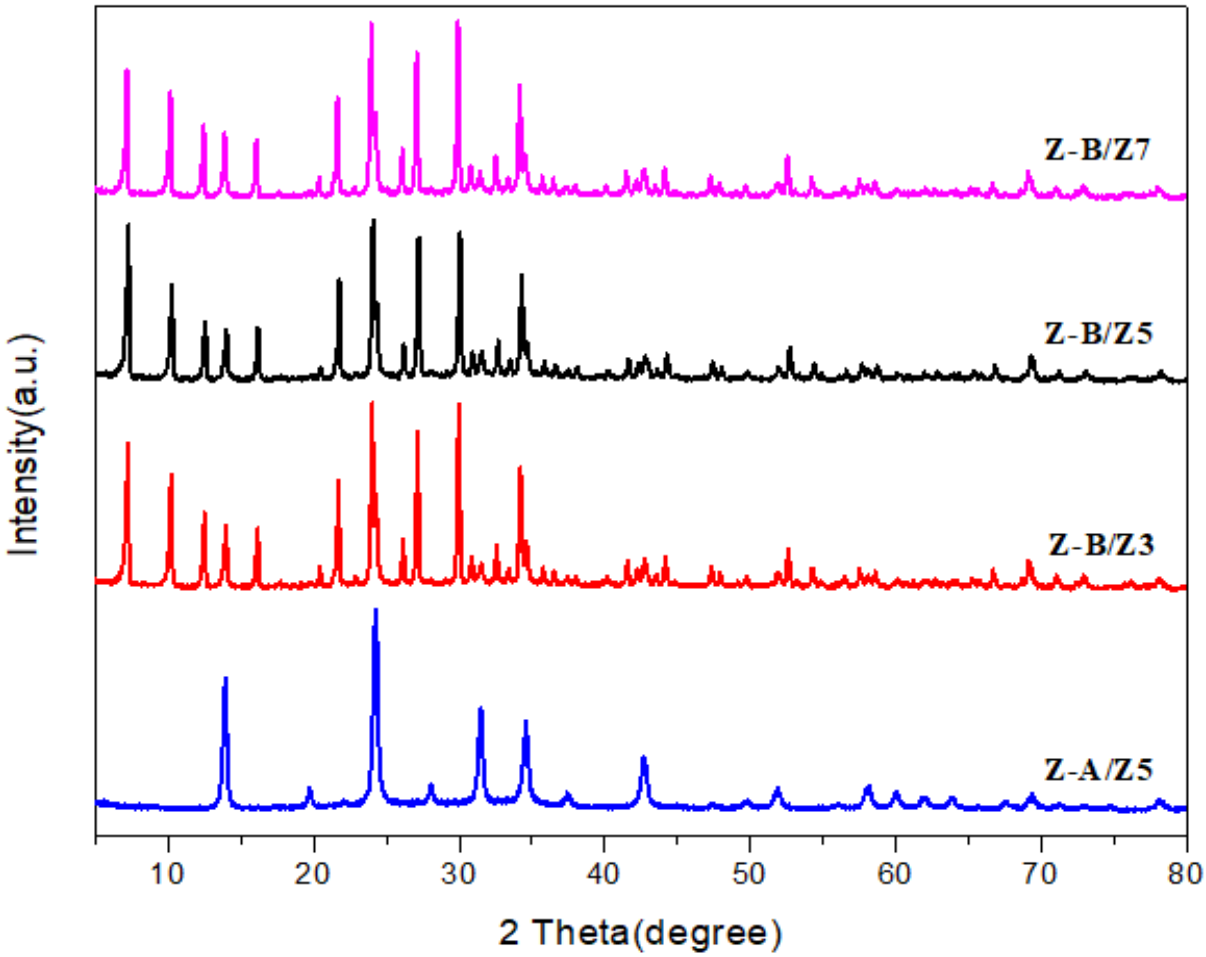


*Figure 4.2: XRD patterns of Z-A/Z5, Z-BZ3, Z-BZ5and Z-BZ7*

Figure 4.3 shows the XRD pattern for iron oxide ($Fe_3O_4$). The prominent peaks at 30.27°, 35.6°, 43.3°, 57.2°, and 62.9° (2θ) are attributed to (220), (311), (400), (422), and (440) planes. The XRD peaks show that the synthesis of pure iron oxide and the crystalline size estimated from the Scherer equation was17.45nm which is small particle size.

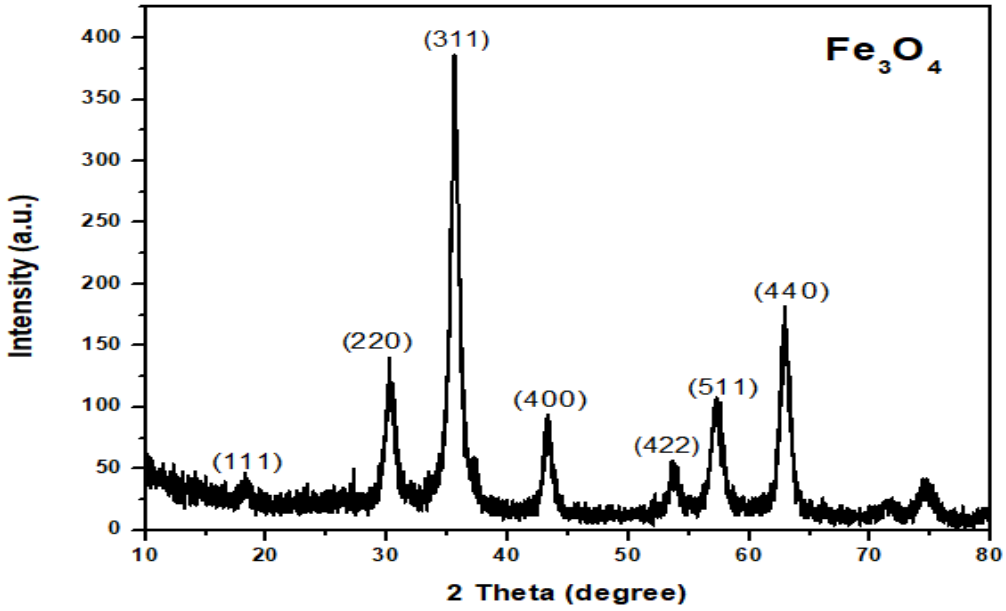


*Figure 4.3: XRD patterns Iron oxide ($Fe_3O_4$)*

Figure 4.4 Shows the XRD pattern for MZ-A/Z5 and MZ-B/Z5. Several relatively discernible diffraction peaks are observed in the 2θ range from 5 to 80°. The prominent peaks in both MZ-A/Z5 and MZ-B/Z5 at 12°, 35°, 41°, 50°, 63.5°, 67.74°, and 74° (2θ) which attributed to (111), (220), (311), (400), (422), (511), and (440) planes, respectively are the characteristic peaks of magnetic $Fe_3O_4$ particles.

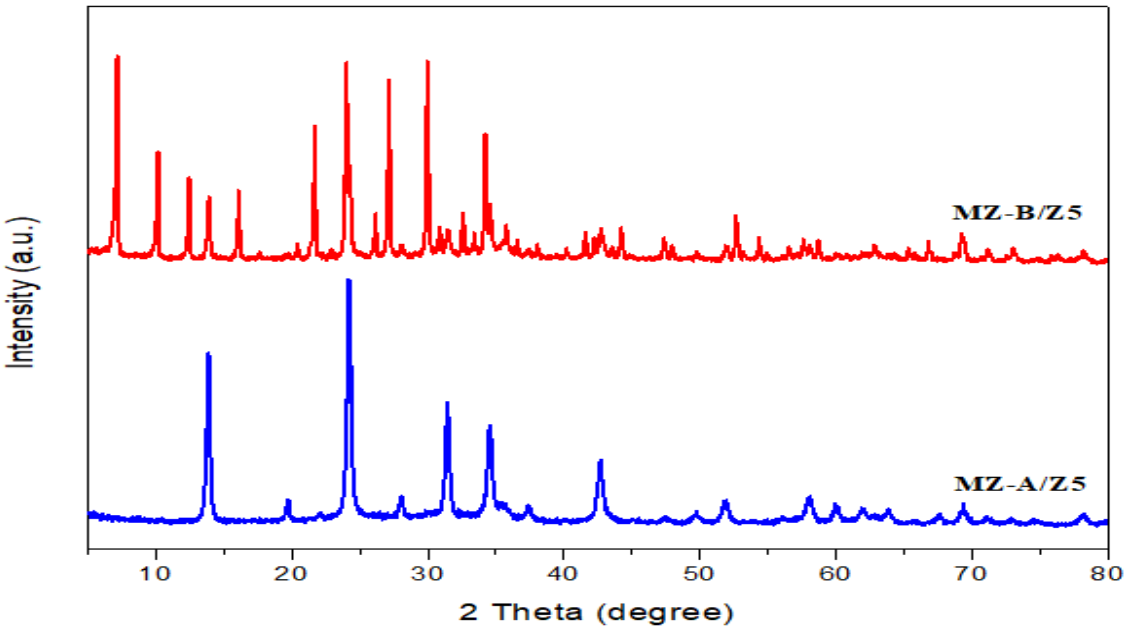


*Figure 4.4: XRD patterns of MZ-A/Z5 and MZ-B/Z5*

Table 4.2: Shows the values for the average crystallite size of each sample

| No | Zeolite/ZnO Composite | the crystallite size (nm) |
|---|---|---|
| **1** | MZ-A/Z5 | 23.91224 |
| **2** | MZ-B/Z5 | 56.64052 |

Table 4.2 shows that as the addition of $Fe_3O_4$ leads to an increase in the crystalline size this may be attributed to the formation of more defects and deformed lattice structure [115]. The $Fe_3O_4$ XRD peaks did not appear due to the small amount of $Fe_3O_4$ and intercalation as discussed above. When we compare MZ-A/Z5 and MZ-B/Z5 crystalline size the size of MZ-A/Z5 is less than the size of MZ-BZ5 as calculated by the sheerer equation but generally both samples have a small crystalline size which allows having larger surface area.

### 4.2. SEM Analysis of Z-A and Z-B

The surface morphology of Z-A and Z-B is shown in Fig 4.5. a) is for Z-A which is an interconnected porous structure with small particle size and b) is for Z-B with similar morphology as Z-A with a larger average particle size as calculated from XRD by using the sheerer equation. The SEM image of Z-A and Z-B samples clearly shows the existence of porous material, being porous is one of the important characteristics of adsorbent. The image produced at low magnification (1000 x) indicated the presence of clusters while taking a Closer look at the cluster by increasing the magnification shows that the presence of grains with different sizes and shapes, spread over the surface. The sample synthesis by using the hydrothermal method and non- hydrothermal method gives different types of zeolite so it's expected to have different shapes of particles [116, 117]. Zeolite synthesized by using an autoclave (hydrothermal) is Sodalite octahydrate zeolite type which has spherical shape this is clearly shown on the SEM images on Fig 4.5(a), and the one synthesized by ignoring autoclave (non- hydrothermal) gives as Zeolite type LTA that have cubic shape and these kinds of crystal shapes are more evidently display at highest magnification and resolution SEM image that's why they didn't observe in Fig 4.5 (b) however few of them are observed in the second picture of Fig 4.6 so we can conclude that both types of zeolite were successfully synthesized. According to Figure 4.5 c,) and d) ZnO and $Fe_3O_4$ particles were not observed at this magnification level. Therefore, the utilization of

Zeolite as a matrix for the synthesis of composite material was effective. Meanwhile, the morphology of the material did not change due to the addition of ZnO and $Fe_3O_4$ these obtained from the XRD result.

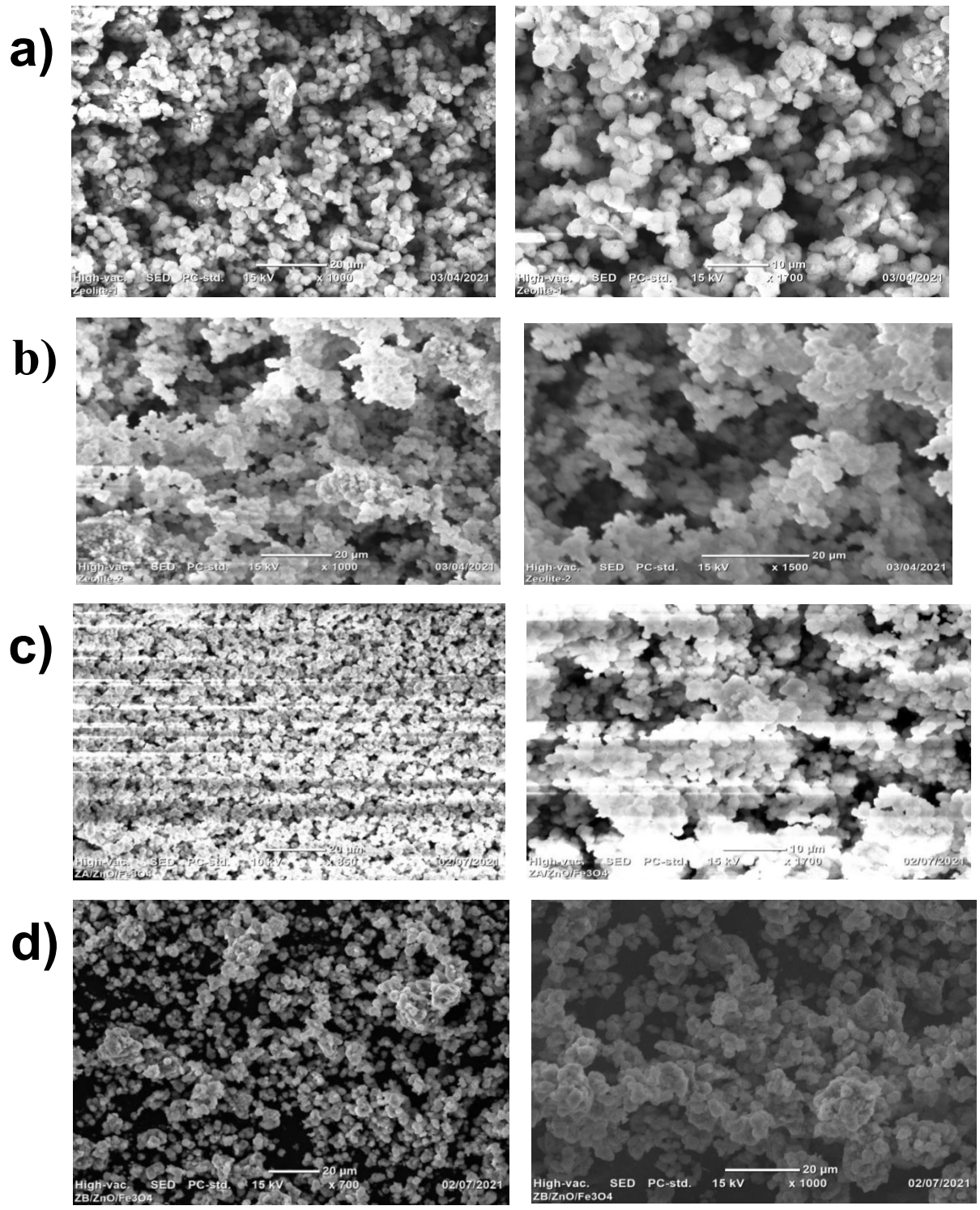


*Figure 4.5: SEM image of a) Z-A, b) Z-B, c) MZ-A and d) MZ-B*

### 4.3. FTIR Analysis

FTIR spectral analysis was used to obtain detail information about the chemical bonding within the material. Accordingly, the FTIR spectrum of Z-A, Z-B, MZ-A/Z5, and MZ-B/Z5 are shown in Fig 4.6 shows an almost similar spectrum of peaks with different intensities. In the fingerprint region, the spectrum shows a broad and intense band around 1000 $cm^{-1}$, shows that the characteristic of anti-symmetric stretching vibration of the Si-O-Si and a less intense band around 789$cm^{-1}$ is due to Si-O-Si symmetric stretching vibrations, this has the same stretching as [40]

The synthesized Zeolite and the prepared magnetic Zeolite/ZnO composite show peaks around 3500 $cm^{-1}$ which corresponds to the stretching of the hydroxyl groups (OH-) from adsorbed water molecules This may be due to atmospheric moisture or moisture absorbed on the surface of the material. The sharpness of the peaks could determine the amount of water ($H_2O$) molecule adsorbed on the surface of the samples, which in turn can be used to estimate the amount of the hydroxyl functional groups present in the sample as indicated in other research's [118]. The decrease in peak intensity on the sample MZ-A/Z5, and MZ-B/Z5 is due to the heat treatment aafter the aaddition of ZnO and $Fe_3O_4$ particles.

Other functional groups that exist in the samples are Si-O-Si, indicated by the absorption band at 1020 $cm^{-1}$, Al-O indicated by the peak at 770 $cm^{-1}$, and Si-O-Al is indicated by the presence of an absorption band at the region between 420 and 494 $cm^{-1}$. Concerning the existence of functional groups Si, O, and Al observed in the spectrum, it was then concluded that the formation of the zeolite framework was confirmed by the FTIR results as reference [51].

In general, comparing the FT-IR spectrum of the sample containing zinc oxide and iron oxide particles with pure zeolite spectrum were not observed because metal oxides have shown on FTIR spectrum below the wave number of 500 $cm^{-1}$ also the amount of ZnO and $Fe_3O_4$ particles were very small comparing to zeolite material (matrix) however we can see that; small decrease in the peaks intensity, broadening, and shift in the positions of the peak at 357 $cm^{-1}$ to 353 $^{-1}$cm which are evident for the presence of ZnO and $Fe_3O_4$ particles as indicated in other researches [41, 42, 45].

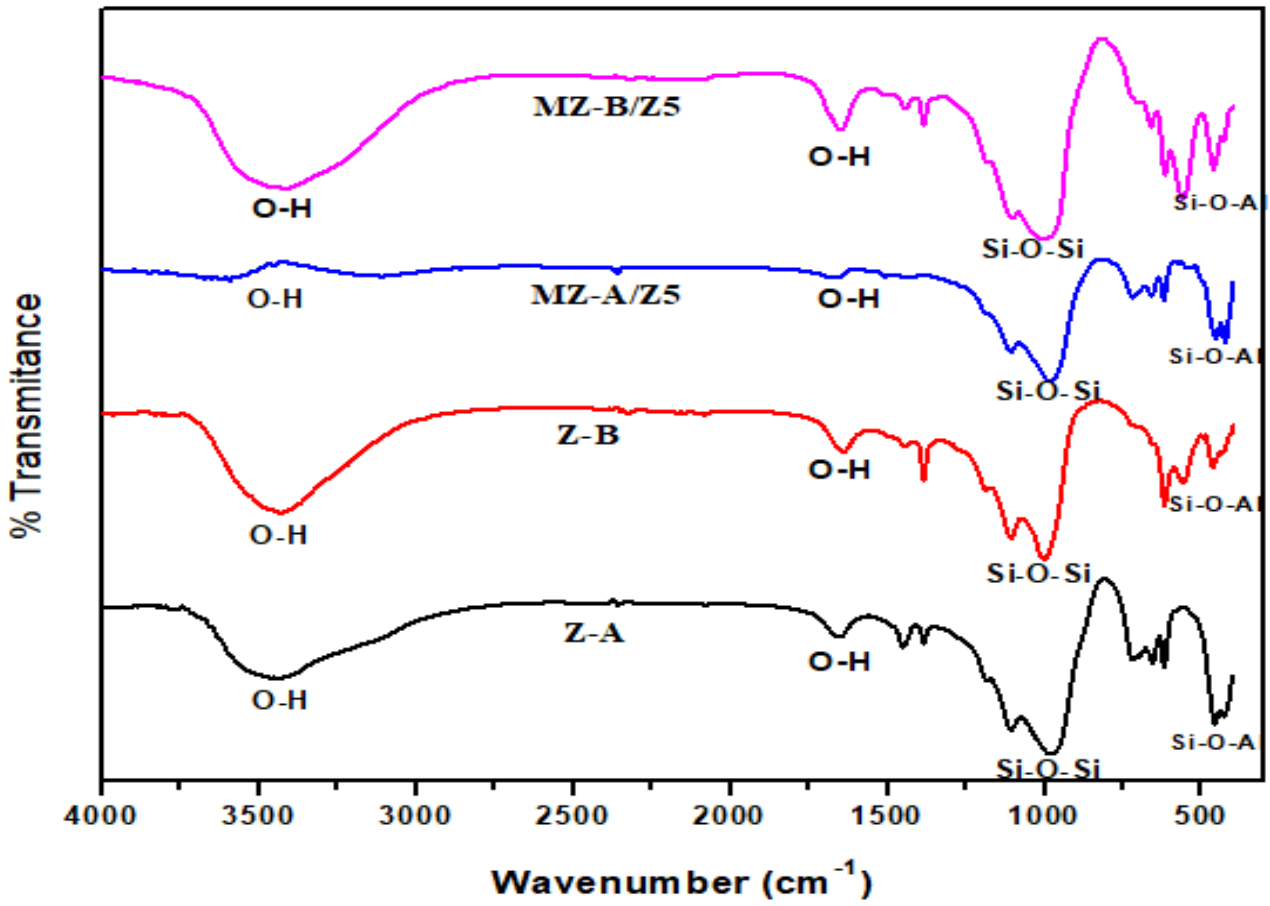


*Figure 4.6: FTIR spectra of Z-A, Z-B, MZ-A/Z5 and MZ-B/Z5.*

## 4.4. Thermal Property Analysis

The thermal stability of Z-A, Z-B, M Z-A/Z5, and M Z-B/Z5 were assessed from the TGA and DTA curves as shown in Fig 4.7 (a-d) respectively. Moisture loss for all samples started from room temperature and continued up to approximately 250℃. Comparison of the percentage weight loss of Z-A (11.932%) with that of Z-B (16.776%) revealed a difference and this noticeable weight loss could be associated with loss of free and physically adsorbed water inside the zeolite pores. The relatively large difference between moisture losses for different zeolite types observed could be because of the hierarchical nature of zeolite [119]. Hence, the difference observed due to relative moisture loss was lower for Sodalite octahydrate zeolite than that of Zeolite LTA because of the hierarchical nature of zeolite.

Researchers suggested that the negligible mass loss occurring up to 250℃ could be because of dehydroxylation. Dehydroxylation proceeds by the destruction of hydroxyl bonds formed when exchangeable cations polarize water molecules; this then leads to the expulsion of more water from the zeolite cavities. The zeolite water content has been reported to be dependent on the nature, type, and size of the exchangeable cation [120]. The mass loss obtained from the TGA thermographs presented in this study for both zeolite types and its composite were in good agreement with observations as studied before by other researchers [121].

DTA curves obtained from both zeolites trends similar to those apparent from TGA thermographs were noted of particular from the TGA–DTA analysis, it can be concluded that both zeolite types and their composite were stable up to 800 ℃ similar to synthesized zeolite materials before. The total amount of weight loss of the samples follows M Z-A/Z5 (11.399%) and M Z-B/Z5 (16.637%) shows a slight weight loss than the corresponding zeolite samples Z-A (11.932%) and Z-B (16.776%). This shows that the composites have slightly higher thermal stability than pure zeolites. The presence of zeolite matrix in all samples could attribute to the higher thermal stability Moreover, the presence of iron oxide in the composite of M Z-A/Z5 and M Z-B/Z5 improved its thermal stability due to iron oxide have high thermal stability [122].

Generally, all samples were found to retain their structural integrity (crystallinity) and no phase transitions occurred even after being heated; so the synthesized zeolite and its composites can be used in applications that require high-temperature environments as the materials can withstand harsh conditions without collapsing to a denser phase or even turning into an amorphous compound.

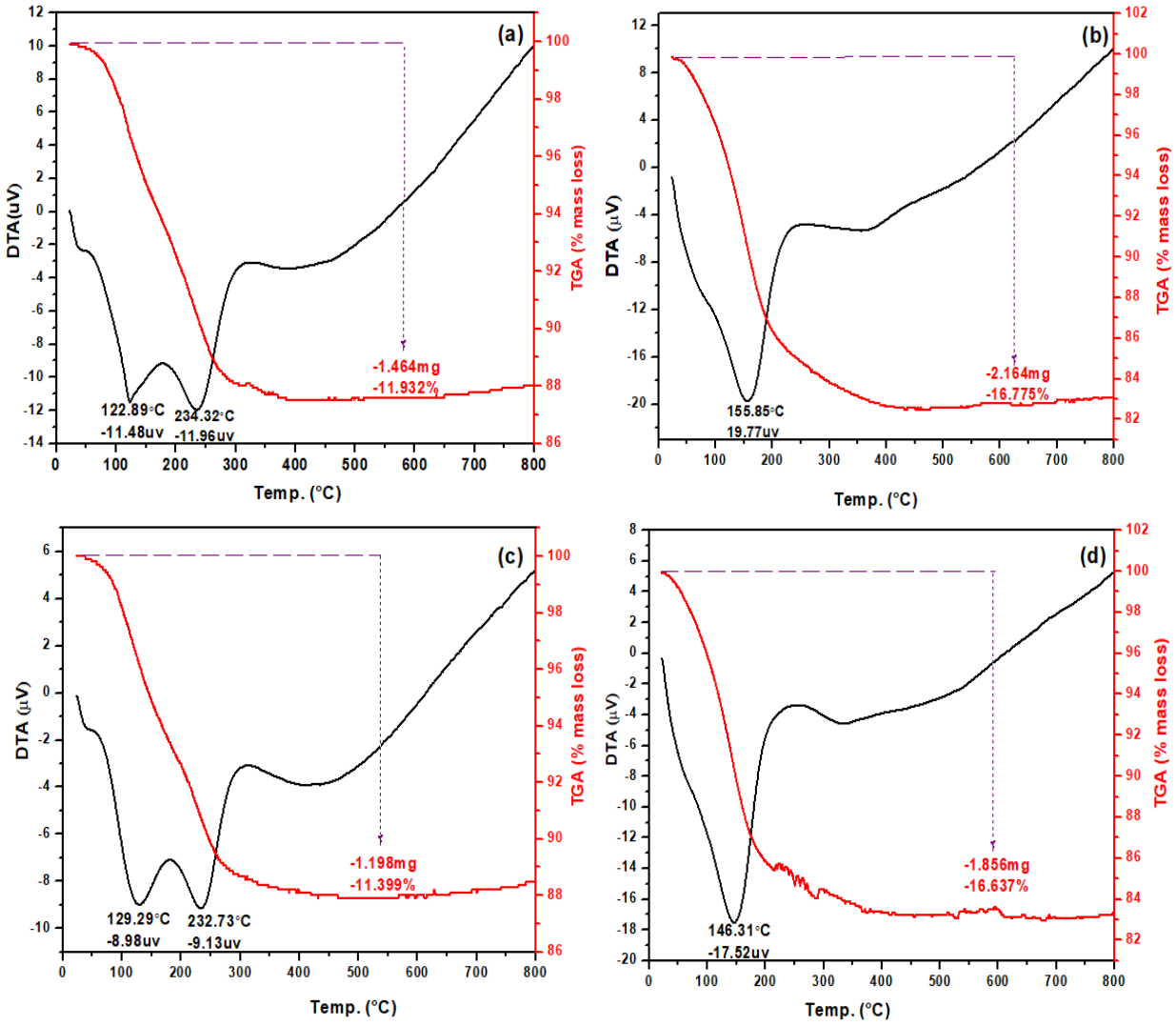


*Figure 4.7: TGA-DTG analysis of (a) Z-A, (b) Z-B, (c) MZ-A/Z5, and (d) MZ-B/Z5.*

## 4.5. Adsorption performance analysis

The efficiency of adsorbents in water purification is affected by many factors such as contact time, initial concentration of impurity, adsorbent dose, and pH. In this section, the adsorbent performance is studied concerning those parameters [108, 113]**.**

### 4.5.1. Adsorption performance on the effect of Contact Time

The adsorption of Methylene blue by Z-A and Z-B at room temperature by initial Methylene blue concentration of 10 ppm and adsorbent dosage (Z-A and Z-B) of 3g/L were used to study the effect of contact time for 150 minutes to study the removal efficiency of adsorbents. The adsorption of Methylene blue was slow for both Z-A and Z-B at concerning time because of the low capacity of adsorbents to adsorb.

However, adsorption of MB increases as time increases this is due to the occupation of available vacant active sites on the surface of the adsorbents. The maximum removal efficiency of Z-A is 66.77% and 57.9% for Z-B in 150 minutes this phenomenon is shown below in Fig 4.8 and 4.9.

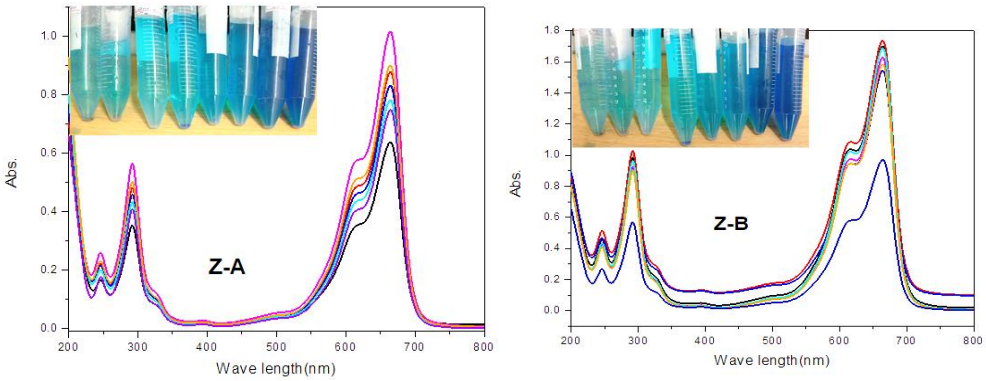


*Figure 4.8: Effect of contact time on UV result of Z-A and Z-B*

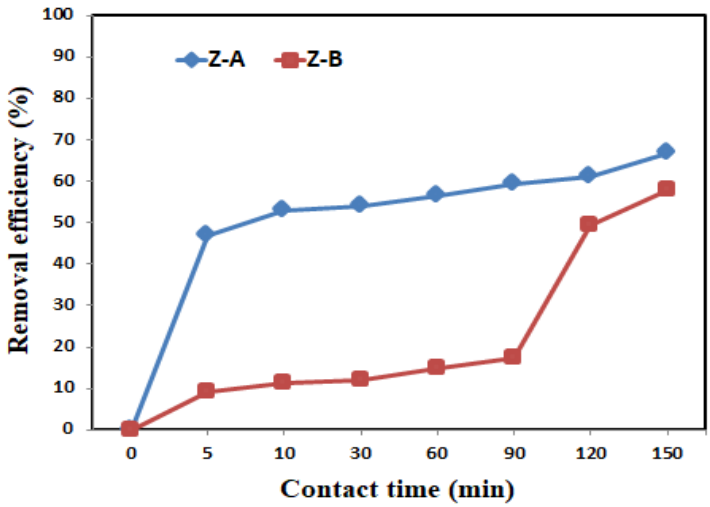


*Figure 4.9: Effect of contact time on removal efficiency of Z-A and Z-B,*

The adsorption of Methylene blue for Z-A/Z5, Z-B/Z5, MZ-A/Z5, and MZ-B/Z5 samples were very fast at first, due to the presence of a large number of active sites on the surface of the adsorbent. Then sample shows only a slight increase and eventually reached equilibrium at 30 min, as shown in Fig.4.10. Then samples show a slight decrease for Z-A/Z5 and Z-B/Z5 after 30 min this is due to desorption of MB from the occupied sites, this phenomenon was also observed by other researchers [50, 113]. The maximum removal efficiency was 95.3%, 95.04%, 94.57& and 92.117% for Z-A/Z5, Z-B/Z5, MZ-A/Z5, and MZ-B/Z5 composites respectively at a time of 30 min.

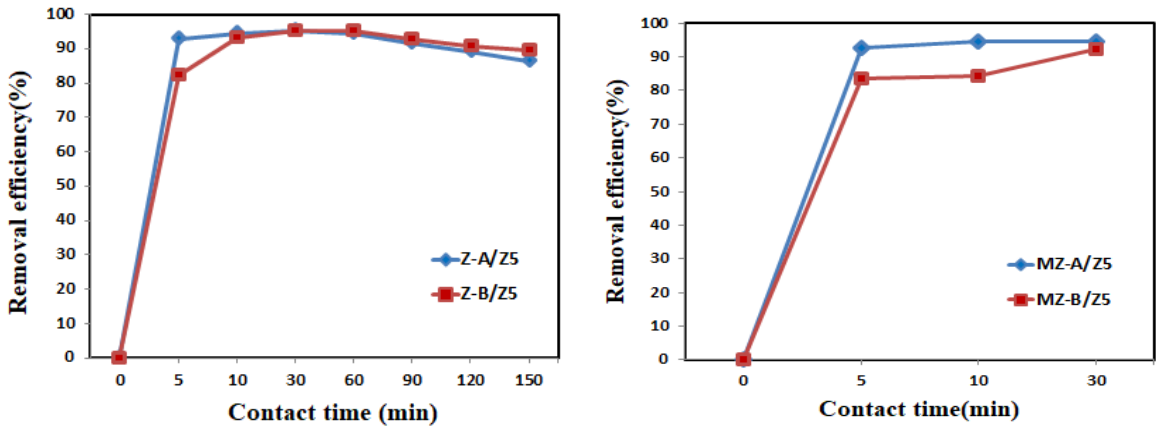


*Figure 4.10: Effect of contact time on removal efficiency of Z-A/Z5, Z-B/Z5 and MZ-A/Z5, MZ-B/Z5*

### 4.5.2. Effect of Initial Concentrations

The removal efficiency of methylene blue decreases from 66.77% to 52.94% for Z-A and from 57.9% to 48.27% for Z-B as the concentrations of methylene blue increase from 10ppm-40ppm. This is because, at a low initial concentration of methylene blue, many adsorption sites are relatively high compared to the amount of adsorbate while at high initial concentration, the total available adsorption sites of the adsorbents meet saturation of adsorption site which causes a decrease in the adsorption efficiency. On the other hand, when the initial concentration of methylene blue increased from 10ppm-40ppm the adsorption capacity is increases from 1.68mg/g to 4.02mg/g for Z-A and from 1.46mg/g to 3.67mg/g for Z-B this is because the active sites of Z-A and Z-B adsorbent were enclosed by much more methylene blue thus adsorbed MB is increased due to the formation of gradient concentration between aqueous solution and adsorbent surface. This was shown below in Fig .11 and referred from other research conducted on this area [113, 123-125].

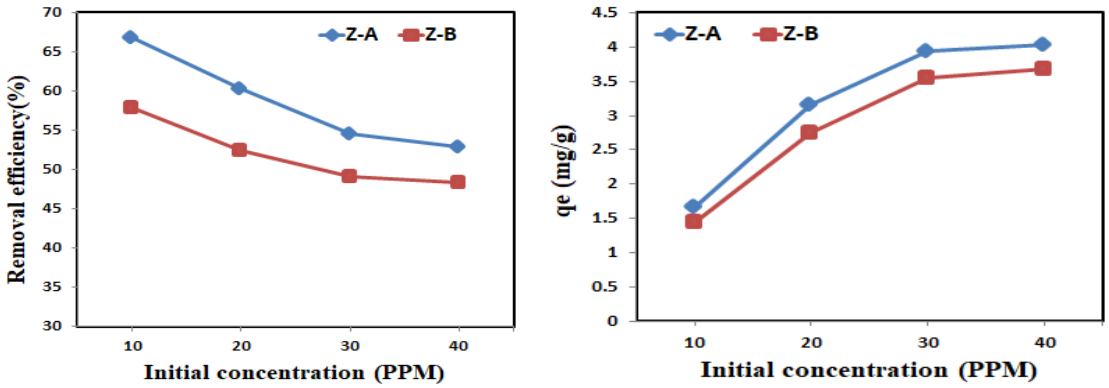


*Figure 4.11: Effect of dye concentration on removal efficiency and adsorption capacity of Z-A and Z-B*

### 4.5.3 Effect of mass of adsorbent

The amount of methylene blue adsorbed by varying the amount of adsorbent Z-A, Z-B, MZ-A/Z5, and MZ-B/Z5 is shown in Fig.4.12. Adsorbents dosage was increased from 1g/L to 5g/L which leads to an increase in removal efficiency from 35.62% to 80.59% for Z-A and from 16.32% to76.42% for Z-B. This is due to the more adsorbent dosage leads to more adsorption sites that introduced to the solution by increasing the number of adsorbent particles which tends to more methylene blue attached as the adsorbent weight increasing as indicated [126, 127].

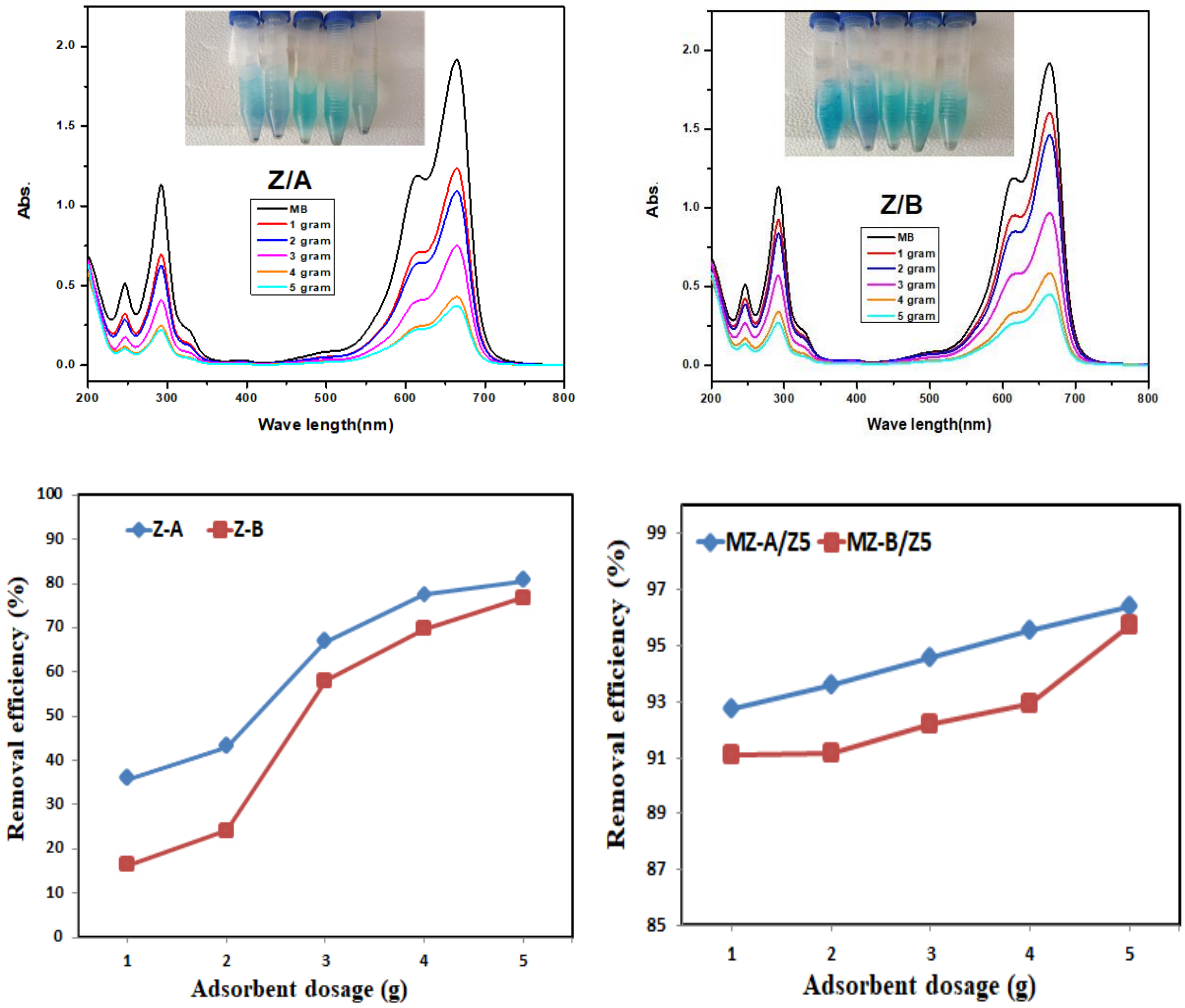


*Figure 4.12: Effect of adsorbent dosage on removal efficiency of Z-A, Z-B, MZ-A/Z5, and MZ-B/Z5*

### 4.5.4 pH value

High removal efficiency and adsorption capacity of Z-A and Z-B were shown at neutral pH value as shown in Fig.4.13. At low pH Value adsorbents show less removal efficiency and adsorption capacity due to highly acidic hydrogen ions competes with MB ions to occupy the sites of the adsorbent [128]. At a higher pH value which is a high alkali region, there is the generation of more hydroxyl sites which also decreases the removal efficiency and adsorption capacity of the material not only the removal efficiency but also the adsorption capacity shows the same result [129]. So the optimum pH value was obtained to be pH 7.

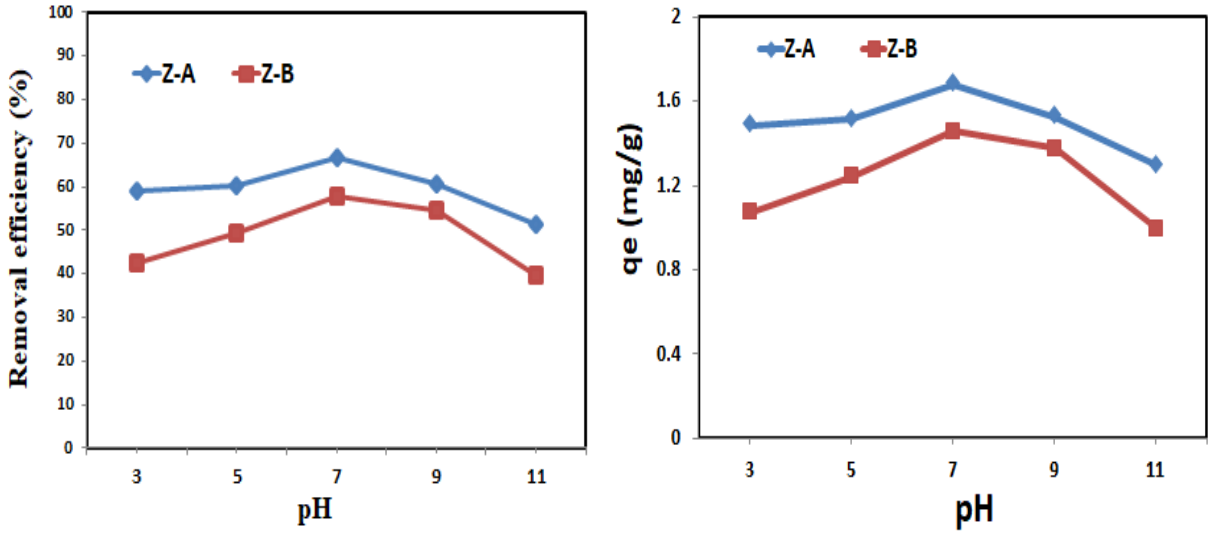


*Figure 4.13: The Effect of PH on removal efficiency and adsorption capacity of Z-A/Z5 and Z-B/Z5*

### 4.6 Recyclability study

Recyclability of adsorbents is a very important issue in the study of adsorption due to high economic factors. In this work, the reusability of Z-A, Z-B, MZ-A/Z5, and MZ-B/Z5 adsorbents were done three times and the result is shown in Fig.4.14. The results showed that the amount of MB adsorbed onto Z-A, Z-B, MZ-A/Z5, and MZ-B/Z5 for the three cycles, by using different regeneration techniques [130, 131]. The first method was done by washing the adsorbents using distilled water several times, then centrifuged, and finally, oven-dried. In the cause of using this method, it was difficult to regenerate the samples because of the MB ion triggered inside the pores of the adsorbent.

The other method of reusability done on this work was using strong acid (0.005mol of HCl) to wash the adsorbent, centrifuge, and dry. The result indicated that the prepared adsorbent can be easily regenerated by using acid rather than water so acid-treated samples have good reusability than those were washed by water.

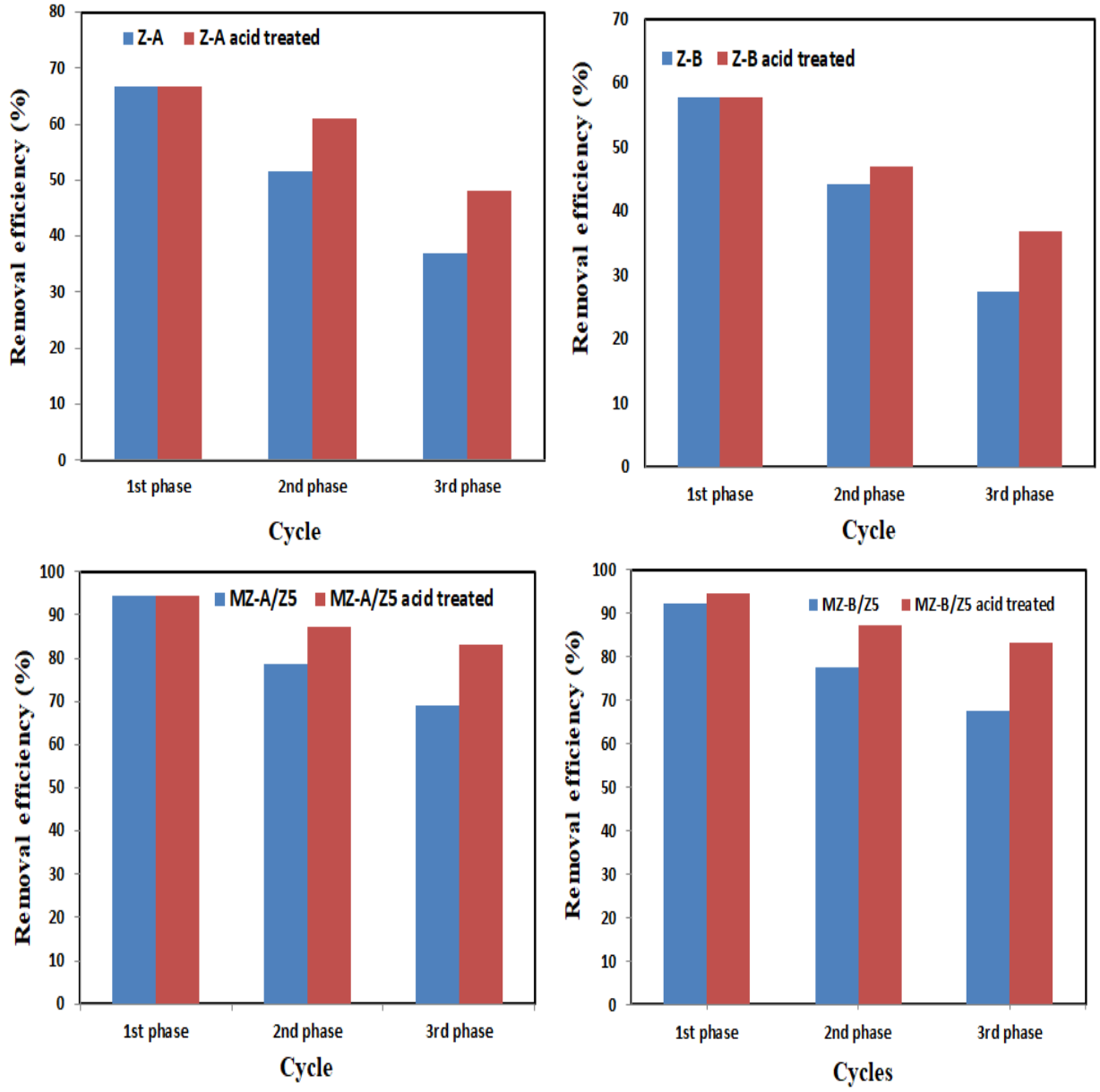


*Figure 4.14: Shows the recyclability of Z-A, Z-B, MZ-A/Z5 and MZ-B/Z5*

### 4.7 Adsorption isotherm analysis

The equilibrium model used to characterize equilibrium behavior by describing the amount of adsorbate adsorbed as a function of a gas or liquid concentration at a constant temperature is called an isotherm[132]. The basis of the study of the adsorption process is the adsorption isotherm model. The adsorption isotherm is the main source for measuring the adsorption of substances [132].

Several equilibrium models have been used to explain the adsorption process, such as Langmuir, Freundlich, Temkin, Hill, Radke-Prausnitz, and Flory-Huggins isotherms. Langmuir and Freundlich's adsorption isotherms are the most commonly used models [133]. The Langmuir model assumes that the surface of the adsorbent for removing adsorbate is uniform and flat, and the adsorbed molecules or ions have no interaction. On the other hand, the Freundlich model assumes that adsorption occurs on an uneven surface, each local adsorption site has its binding energy, and the strongest binding site is established before the end of the adsorption process [133, 134].

Table 4.3. Equations for Langmuir and Freundlich isotherm models

| Isotherm model | Non-linear equation | Linear equation | plot | reference |
|---|---|---|---|---|
| **Langmuir** | $q_e = \frac{q_{max}\, bC_e}{(1 + bC_e)}$ | $\frac{c_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}}$ | $C_e/q_e$ vs $C_e$ | [135] |
| **Freundlich** | $q_e = K_F C_e^{1/n}$ | $\ln q_e = \frac{1}{n}\ln C_e + \ln K_F$ | $\ln q_e$ vs $\ln C_e$ | [136] |

Among them, qe (mg/g) is the equilibrium adsorption capacity, qmax (mg/g) is the maximum adsorption capacity that the adsorbent can achieve, b (l/mg) is the Langmuir adsorption constant, and Ce (mg/l) is the equilibrium Concentration, $K_F$ is the Freund's constant [(mg/g)(l/g)1/n], which represents the binding energy of the adsorbent, and n is the adsorption intensity.

### 4.7.1 Langmuir Isotherm model

Langmuir isotherm assumes on solid surfaces assumes that adsorption is homogeneous or monolayer adsorption [137]. The Langmuir isotherm model can be described according to the equation in Table 4.3 to determine adsorption isotherm.

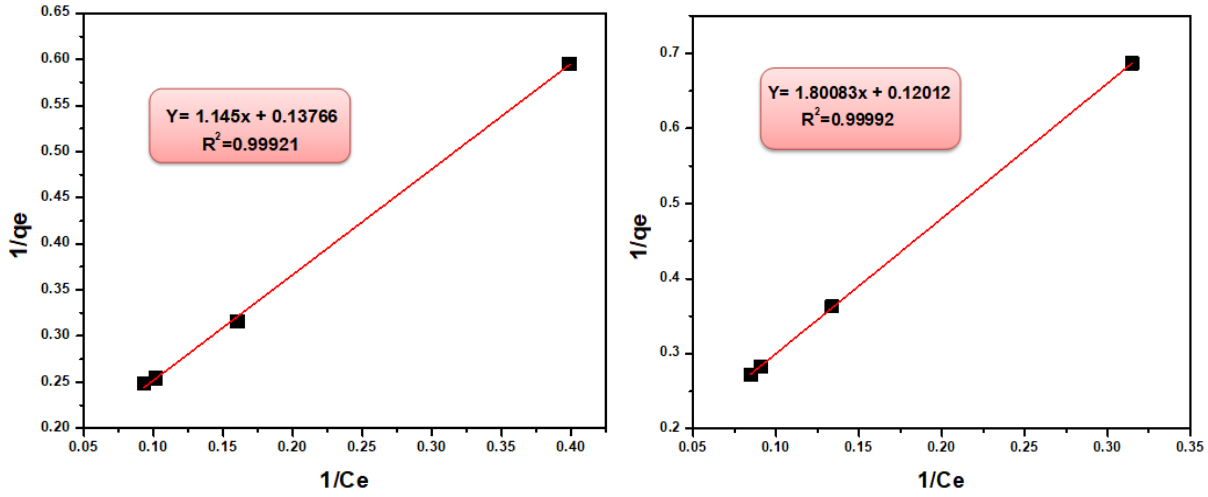


*Figure 4.15: Langmuir isotherm a plot of 1/qe against 1/Ce for sample Z-A and Z-B*

### 4.7.2 Freundlich Isotherm model

Freundlich Isotherm is an empirical relation between the concentrations of a solute on the surface of an adsorbent to the concentration of the solute present in the liquid [138]. Freundlich Isotherm equation is described in Table 4.3.

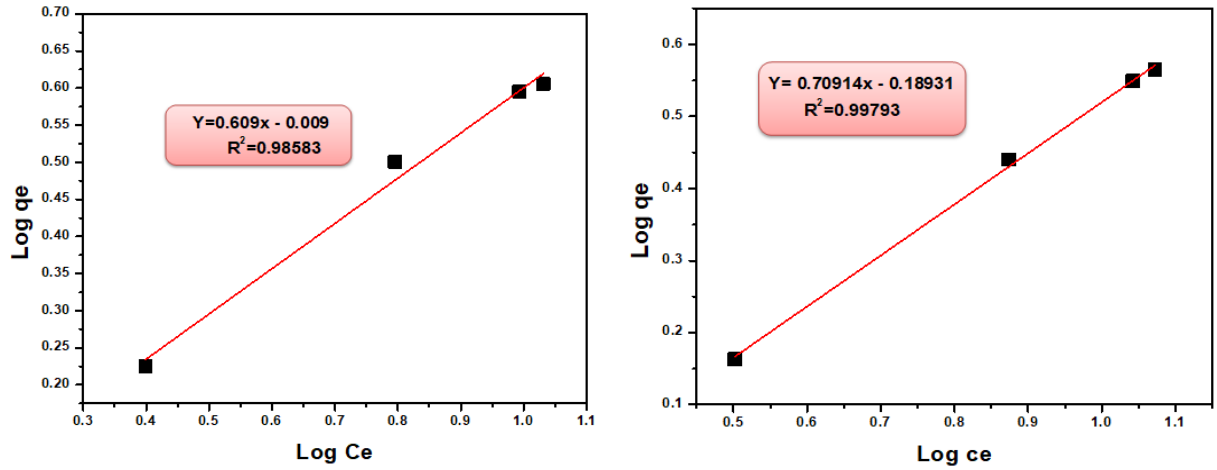


*Figure 4.16: A plot of lnqe against lnCe which shows Freundlich isotherm for Z-A amd Z-B*

Table 4.4. Langmuir and Freundlich's parameters extracted from isotherm models

| Samples | Langmuir parameters | | | Freundlich parameters | | |
|---|---|---|---|---|---|---|
| | q max | $b$ | $R^2$ | $1/n$ | Kf | $R^2$ |
| **Z-A** | 4.0299 mg/g | 1.145 | 0.99921 | 0.609 | 0.97949 | 0.98583 |
| **Z-B** | 3.678 mg/g | 1.80083 | 0.99992 | 0.70914 | 0.647 | 0.99793 |

Therefore, based on the result obtained from the experiment as listed in Table 4.4, the adsorption data conformed to both the Langmuir and Freundlich isotherm with a correlation coefficient ($R^2$) greater than 98, while Langmuir isotherm is the best-fitted model with R-value greater than 0.99 for both Z-A and Z-B zeolite types. Langmuir model is associated with monolayer adsorption, while Freundlich one is related to multilayer adsorption, according to the previous studies, the Langmuir isotherm reveals chemisorption, while the Freundlich equation gives to inform about physisorption [138]. Meanwhile, as the best-fitted model for our experimental work is the Langmuir isotherm the adsorption process reveals to chemisorption process which is Chemical adsorption due to the formation of a chemical bond between adsorbate molecules and the adsorbent. The maximum adsorption capacity of Z-A towards methylene blue was 4.0299 mg/g and 3.678mg/g was for Z-B samples.

Furthermore, the dimensionless Freundlich constant n >1, (n = 0.609 for Z-A) and (n= 0.70914 for Z-B) which implies adsorption was favorable on the heterogeneous surface. Generally, the value 1/n < 0.5 implies easy adsorption, and 1/n >2 implies difficult adsorption [139]. In this work, the adsorption intensity (1/n) = 0.609 and 0.70914 for Z-A and Z-B samples respectively, and this implied that the adsorption of methylene blue on the surface of zeolite was favorable as the isotherm [140]. This can be also related to the result of adsorption performance of the materials that were studied by using UV–Visible spectrophotometer, and that were also shown favorable adsorption capacity as discus above.

### 4.8 Adsorption Kinetics

The study of adsorption kinetics is very important for wastewater purification because it provides important information about process characteristics, reaction forms, and adsorption reaction mechanisms. The adsorption process is mainly described by pseudo-first-order and pseudo-second-order kinetic models based on chemical reaction kinetics[141].

Table 4.5 Equations for pseudo-first-order and pseudo-second-order kinetic models

| Isotherm model | Equation | Plot | Reference |
|---|---|---|---|
| **Pseudo-First Order** | $\log(qe - qt) = \log qe - \frac{K_1}{2.303t}$ | $\log(qe - qt)\ vs\ time$ | [142] |
| **Pseudo-second Order** | $\frac{t}{qt} = \frac{1}{k_2 qe^2} + \frac{t}{qe}$ | $\frac{t}{qt}$ vs time | [143] |

### 4.8.1 Pseudo-First Order

Lagergren's pseudo-first-order model is based on the assumption that the rate of change of solute absorption over time is proportional to the difference in saturation concentration and the amount of solid absorbed over time, which is usually applied in the early stages of kinetics. When adsorption occurs through interface diffusion, this pseudo-first-order large particle rate equation is usually observed [140]. The pseudo-first-order Lagergren model can be described by the equation shown in Table 4.3.

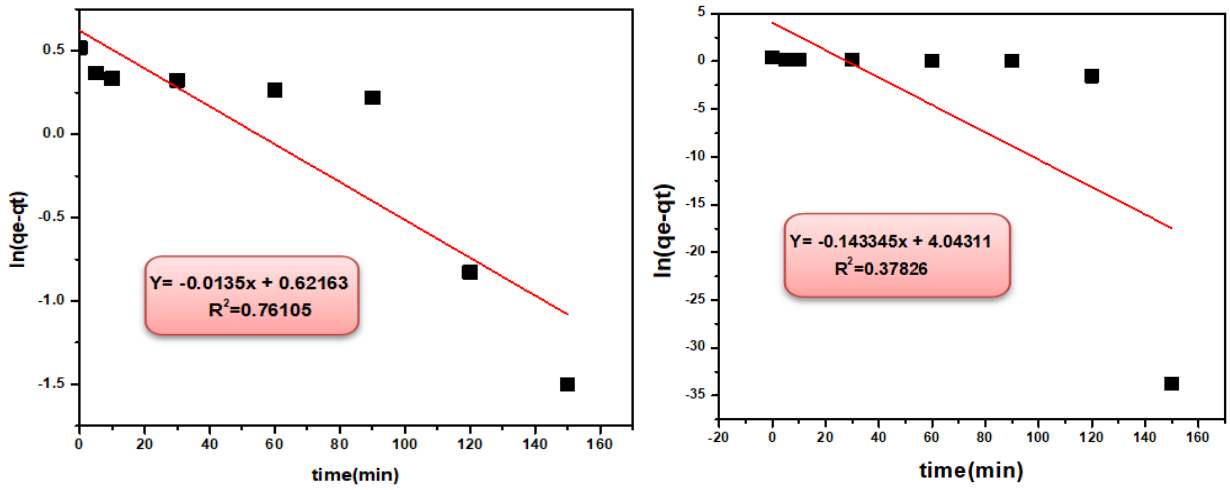


*Figure 4.17: Pseudo-first-order for sample Z-A and Z-B*

According to pseudo-first-order dynamics, if the adsorption process follows the true first-order kinetics, the intersection of log (qe-qt) and t is equal to the logarithm of qe, which is determined by experiment or corrected to match the experimental value. In this case, the pseudo-first-order Lagergren equation does not fit the entire adsorption time range as shown in Fig 4.17.

### 4.8.2 Pseudo-second Order

The pseudo-second-order kinetic model is based on the assumption that the rate-limiting step is chemical adsorption or chemisorption and predicts the behavior over the entire adsorption range. In this state, the adsorption rate depends on the adsorption capacity, not on the concentration. An important advantage of this model over first-order storage quantities is that the equilibrium adsorption capacity can be calculated from the model; therefore, there is theoretically no need to evaluate the equilibrium adsorption capacity from the experiment [140].

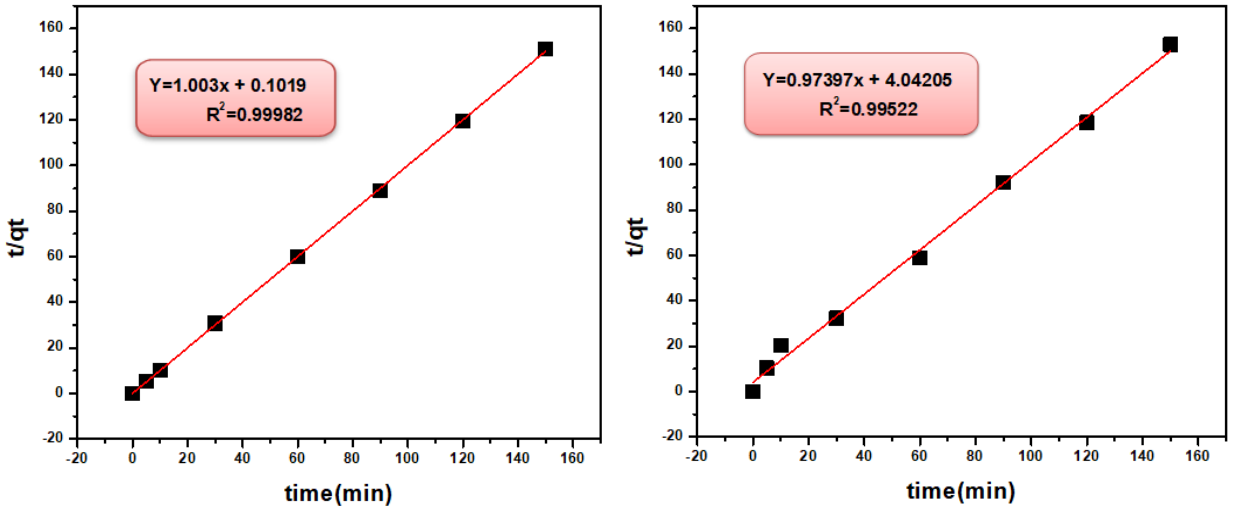


*Figure 4.18: Pseudo-second-order for sample Z-A and Z-B*

In pseudo-second-order kinetics the adsorption process follows true second-order kinetics, then the intercept of t/qe versus t plots had been adjusted to fit the experimental value so pseudo-second-order kinetics was fitted well for the whole range of adsorption time as shown in Fig 4.18.

In pseudo-first-order kinetic models, there is a big difference in qe,exp, and qe, cal which indicates that the adsorption of methylene blue by Z-A and Z-B adsorbent which doesn't obey pseudo-first-order kinetics in the other hand the value of qe,exp, and qe, cal obtained in pseudo-second-order model is very closer. In addition to this, the correlation coefficient ($R^2$ ) =0.76105 and 0.37826 respectively for Z-A and Z-B in pseudo-first-order kinetics while pseudo-second-order kinetics model showed a higher correlation coefficient ($R^2$ ) = 0.99982 and 0.99522 for Z-A and Z-B respectively so we can confirm that pseudo-second-order is the best-fitted model for the adsorbent which indicated chemisorption.

# 5. CONCLUSIONS

In this study, Sodalite octahydrate zeolite and Zeolite LTA were successfully synthesized by using different techniques (hydrothermal and non-hydrothermal) those zeolites were produced from SCBA and food packaging aluminum foil. The synthesized zeolites were characterized by using XRD, SEM, FTIR, TGA-DTA, and UV-Vis Spectroscopy, The XRD's results confirmed that the synthesis of Sodalite octahydrate zeolite (Z-A) and Zeolite LTA (Z-B) while the addition of ZnO and $Fe_3O_4$ did not appear on the XRD pattern due to their small quantities and intercalation. The SEM results showed the porous nature of the material. Si, O, and Al functional groups observed in the FTIR spectrum revealed the formation of the zeolite, and also the formation of the composite was confirmed by FTIR's peak shift from 357 $cm^{-1}$ to 353 $cm^{-1}$. TGA–DTA analysis indicates all samples were found to retain their structural integrity while heated to 800◦C. Z-A and Z-B were optimized over the adsorption of Methylene blue and they were shown 66.7% and 57.9% removal efficiency within 150 min respectively. Both Langmuir isotherm and pseudo-second-order kinetic model indicated the adsorption process was chemisorption. Furthermore, the addition of ZnO leads to an increase in the adsorption site so it shows the highest removal efficiency of Methylene blue dye 95.3% for Z-A and 95.04% for Z-B/Z5 within 30 min. Moreover, Iron oxide was added to the Composite to gain magnetic property for easy separation way. Therefore, the Magnetic composite was founded to be the best adsorbent of this work with a removal efficiency of 94.57% for M Z-A/Z5 and M Z-B/Z5 92.17% in addition to that adsorbents recyclability test were done three times and obtain outstanding performance. In summary, the experimental results suggest that M Z-B/Z5 which is outstanding, cost-effective, safe, and environmentally friendly, could be a potential adsorbent of MB from wastewater.

# 6. RECOMMENDATIONS

Due to time and economic reasons, the scope of this work is limited a bit. Based on the current research, some suggestions can be made for future work. We recommend that at the time of zeolite synthesis the operating conditions i.e., aging period, crystallization period, and temperature ought to study because they have a great influence on the final formation of the desired zeolite structure. In other respect, the course of this study was canvassed the adsorption potential of the Magnetic zeolite/ZnO compound to remove methylene blue dye from wastewater because dyes pay special attention to environmental and social health. As well, we recommend studying the eliminating potential of those ternary composites towards different types of dyes, organic compounds, and heavy metals which might be poisonous and carcinogenic to human health.

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