Sudan University Of Science and Technology

College Of Graduate Studies

Removal of Heavy Metals from wastewater by Zeolite and Silver nanoparticals doped Zeolite

ازالة العناصر الثقيلة من المياه الملوثه بواسطة الزيولايت والزيوليت المطعم بجسيمات الفضة النانوية

A Thesis Submitted in Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Chemistry

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استهلال

قال تعالى :

(يَرْفَعِ اللَّهُ الَّذِينَ آمَنُوا مِنكُمْ وَالَّذِينَ أُوتُوا الْعِلْمَ دَرَجَاتٍ)

صدق الله العظيم

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Dedication

To my family

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My sincere thanks and respectful gratitude to my supervisors Prof: Mohammed Adam Abbo.
for his extreme assistance, and comprehensive advices throughout my study.
Finally, my deep appreciation goes to anyone who supported me in this research until it reached its final steps.

Abstract

Zeolite have been used for removal of heavy metals in many application in different fields such as agriculture, industry and medicine

The present work aimed to test the efficiency of natural zeolite collected from Gadaref State as adsorbents for treating heavy metals in wastewater and also to study aimed to compare the efficiency of natural zeolite with that of silver nanoparticals doped zeolite for removal heavy metals, beside modeling of adsorption data by Langmuir and Freundlich models.

The possibility of using natural Sudanese zeolite have been investigated for removal of lead and cadmium as one of the toxic heavy metals .Batch processes using aqueous solutions under different conditions and parameters have been considered, such as the concentration of ions, pH and tempreture Physicochemical characterization of zeolite was carried out using different analytical techniques such as XRD which indicate that the main composition of zeolite sample was silica and natrolite, the XRF analysis revealed that it contains Si_2 O_4(),Al_2 O_3(),and other metal oxide () .The TGA results show that the natural zeolite was stable up 900 ^{0}C. The main functional groups zeolite were hydroxyl and Si-O-Si as obtained from FTIR study. The silver nanoparticals were confirmed using UV\VIS spectrum which show absorbance at 430 nm.

The results of removal efficiency indicated that maximum removal were 97.50 and 97.10% for Lead and Cadmium respectively.

Comparing the two types of zeolites , showed that nano silver doped has been found to be more officinal than normal zeolite, its removal capacity has been found to be 98.50 % .

المستخلص

ان الهدف من هذا البحث هو دراسة كفاءة الزيولايت الطبيعي واستخدامه كمادة لمعالجة التلوث بالمعادن الثقيلة وقد تم الوصول لتحقيق الهدف بدراسة عدة من المتغيرات الاتية: مقارنة كفاءة الزيولايت الطبيعي مع المعدل النانوي و النمذجة الرياضية لعملية الامتزاز.

درس تاثير بعض المتغيرات مثل درجة الحموضة(pH), تاثير تركيز المعادن الثقيلة وتاثير درجة الحرارة .

حددت مواصفات الزيولات بواسطة بعض الطرائق التحليلية مثل XRF, XRD, TGA, FTIR

اظهرت نتائج ال(XRD) ان الزيولايت يحتوي علي نسبة عالية من السليكا والنترولايت, وان نتائج (XRF) ايدت ذلك بان نسبة السليكا كانت (70.24)% وان نسبة اوكسيد الالمونيوم Al_2 O_3 كانت (13.51)%. نتائج (TGA) اظهرت ثباتا حراريا حتي درجة 900^0C .بينت دراسة (FT–IR) أن ابرز المجموعات الوظيفة هي مجموعة الهيدروكسيل بجانب Si-O-Si

وجد ان نتائج المعالجة الاستاتيكية تتوافق مع نموذج لانغمير(Langmuir) بدرجة اكبر من نموذج (Freundlich).

واظهرت النتائج ان الحد الاقصي لازاله التلوث كان 97.50 % و97.10 % للرصاص والكادميوم علي الترتيب بالنسبه للزيولايت الطبيعي.

وبمقارنة الزيولايت الطبيعي مع المطعم بنانو الفضة اتضح ان الزيولايت المطعم بنانو الفضة لدية سعة تبادلية اكبر من الزيولايت الطبيعي وكانت نسبة الازالة تساوي %98.50 .

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EDS	Energy Dispersive Spectroscopy
FT-IR	Fourier Transform Infrared Spectroscopy
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
XRD	X-Ray Diffraction analysis
XRF	X-Ray Fluorescence analysis
ICDD	International Centre for Diffraction Data

Chapter One

Introduction and Literature Review

Chapter One

Introduction and Literature Review

1.1 Industrial Wastewater Effluents.

Natural resources has been damaged by the various anthropogenic sources over the past several decades, and such sources include but are not limited to municipal wastewater treatment plants .agricultural cultivation and fertilization activities, as well as mining and industrial wastewater effluents (Asubiojo and ajelabi, 2009, Barakat, 2011, Fu and Wang, 2011). Surface water, ground water, as well as municipal and industrial wastewater contain many different types of organics and inorganics pollutants, causing toxic effects on our ecosystem (Wang and Peng, 2010). Natural water systems are comprised of chemical and physical processes that affect both the distribution and circulation of pollutants. The hydrologic cycle has climatic and seasonal variations, which influences geo-chemical processes and many cause dissolution and chemical reaction with soils, liquids and gases. Anthropogenic interferences associated with industrial processing effluents may cause slight variations in these natural waters, directly causing an influx of pollutants, such heavy metal, which adsorb onto particulates and deposit onto sediments affect the overall balance of metals in the aquatic system (yabe and de Oliveira. 2003).

Heavy metals are an environmental priority as they deteriorate water quality, and are a detriment threat to our ecosystem (Alvarez- Ayuso *et al.*, 2003, Fu and Wang, 2011). Because of their high solubility in the aquatic environment, heavy metals can impact living organisms (Kocasoy and sahin, 2007, Barakat, 2011). And once entered and transferred through the food chain, they trigger various diseases and disorders (Erdem *et al.,* 2004, Akcil and Koldas, 2006). The effects of heavy metals in effluents wastewater not only impact the environment, but are detrimental to humans also, the toxic impact can be (acute, chronic,), neurotoxic, carcinogenic(Akpor *et al.,* 2014).

Being part of a very complex and dynamic system, there are many anthropogenic sources and sinks of heavy metals, which can be transported in their dissolved from in water or part of suspended sediments, volatilized to the atmosphere or stored in sediments (Curenature 2018). The most common source of pollution is through the discharge of wastewater as a by-product of industrial processing. The increased demand for the production of commodities produced by various industries has triggered an accumulation of pollutant. These pollutant put the entire ecosystem at risk, and therefore it is imperative to remove them prior to their discharge into wastewater. (Barakat. 2011)

Various treatment technologies for the removal of heavy metals from industrial wastewater have focused on physic- chemical removal processes (Barakat, 2011) Among these, sorption (adsorption- ion exchange) (Inglezakis and poulopoulos, 2006) . The removal efficiency of metal ions by natural zeolite from various sources of wastewater and shown that sorption is superior compared to standard physico- chemico techniques (Wang *et al.,* 2009).

Adsorption is an effective and economic method leads to the potential the sorbent material (Fu and Wang, 2011). Natural zeolite have garnered particular research interest due to their co- existing molecular sieve action,

ion –exchange and catalytic properties(Wang *et al*., 2009, Nezamzadeh-Ejhieh and Shiradi, 2014), and are applied worldwide in various industries, which include agriculture, soil remediation and energy (Wang, 2010), as well as the wastewater treatment industry.

In 1756 Swedish mining scientist, Axel Fredrik Kronstadt, collected some well-formed crystals and named it “Zeolite” from the Greek ζέω (zéō), meaning "to boil" and λίθος (líthos), meaning "stone".

Fredrik reported that when pure Zeolite heated rapidly, large amount of adsorbed vapour emits, accordingly, he named this substance (Zeolite).

This compound also named (Phillipsite) as appreciation to British scientist William Phillips (1773-1828) who contributed much to geological and mining researches.

The Volcanic tuff is a type of igneous rocks formed from material ejected during an explosive volcanic eruption and it is the most suitable substance to contain natural zeolite due to its easy chemical reaction (Aldwiry *et al.*, 2014).

Zeolite is defined as any of a group of hydrated silicates of aluminum with alkali metals, commonly occurring as secondary minerals in cavities in basic volcanic rocks, with a structure characterized by open-framework structures of linked tetrahedra, each consisting of four oxygen atoms surrounding a silicon or aluminum cation represented by the symbol $TO_{4,}$ where T can be Al or Si, and consequently a negative charge formed on zeolite structure which in turn can be compensated by alkali cations, which can be exchanged with other ions giving Zeolite the characteristic feature of Cation Exchange Capacity (CEC).

Zeolite can be obtained from natural precipitations or through industry.

In 1948, Union Carbide synthesized the first zeolite as a result of the efforts exerted by two scientists; R. M. Milton and D. W. Breck, and commercial production of this substance commenced in 1950 (Ocelli and Robson, 1988).

About 150 types of zeolite have been synthesized till this day, and six highly- pure natural types, these are; Clinoptilolite, Chabazite, mordenite, erionite, ferrite, and Phillipsite.

Numbering and nomenclature of Zeolite is the responsibility of International Zeolite Association (IZA, 2014). The most famous synthetic zeolites are: Zeolite A and Zeolite X.

Generally, Zeolite have high thermal stability and resistant to acidic environment.

1.2 Characteristic features of Zeolite:

Zeolite characterized by two main features:

1/ Molecular Sieving: A term stated by Scientist Macben in an attempt to define solid porous substances acting as sieves at molecular level. These molecular sieves characterized by the following features (Breck, 1974):

a/ Selective adsorption: due to regular size of pores in zeolite structure, measuring 3-10 angstrom where cations and water molecules are contained inside. Space made by pores represents 50% of crystalline size and water particles contribute to 10-20%.

b/ high adsorption capacity for water and polar substances.

2/ Cation Exchange Capacity (CEC):

Zeolites contain cations like Sodium (Na^+), potassium (K^+), Calcium (Ca^{2+}), and Magnesium (Mg^{2+}). These ions are responsible of other ions exchange which are present in the solution. This ions exchange is known as Cations Exchange Capacity (CEC) and measured by number of moles of cations capable of exchange in each 100 grams of Zeolite.

Zeolite has been increasingly used in different areas and fields like industry, agriculture, environment protection, and even in medicine, although there are no certified records for its actual total reserves in the world, but many countries like Cuba, USA, Russia, Japan, South Africa, Hungary, Bulg…. have big reserves of this substance.

Based on 2001 records the total Zeolite consumption was 3.5 million ton, 18% out of it was the contribution of natural Zeolite (NRA 2011).

More than 50 types of natural Zeolite have been identified but famous ones are: Clinoptilolite, Erionite, Chabazite, Mordenate, Sodalite, Phillipsite.

Zeolite is used as plant growth- promoter when added to soil in order to enhance fertilizer efficiency to keep nitrogen and can be used as molecular sieve or filtration media.

1.2.1 General uses of Zeolite:

General uses of Zeolite can be summarized as follows:

1/ Industrial catalyst.

2/ Adsorption.

3/ Ions exchange and separation.

4/ soap and chemical detergents: Sodium zeolite A is used as hardness softener in detergents industry.

5/ water treatment.

6/ agriculture and soil improvement.

7/ nuclear applications like Cesium (129) eradication.

8/ petrochemical industries.

9/ peptone and cement industry.

Heavy minerals are defined as those having molecular weight greater than 5,000; kgm/m3 (Sharma, 2001), with low concentration in underground water but high concentrations in industrial water.

1.2.2 Heavy Minerals

Heavy minerals can be found separately or combined to other minerals like: iron, Manganese, Chrome, Nickel, lead, Cadmium, Zinc, and Arsenic, and it can be natural or synthetic .

Rock transformation and erosion contribute to presence of heavy mineral in the soil and become available for plants and bacteria. Heavy mineral can reach to water sources through industrial wastes, sewage water, and natural rocks transformations.

Heavy minerals are normally removed from natural and waste waters by different ways and means, important ones are: Electric analysis, precipitation by sulphate or carbonate, extraction, reverse osmosis, fine filtration, adsorption and cation exchange. But there are challenges for each of these means, and recently the modeling mean have been used to determine underground areas polluted by heavy minerals in order to treat it (Awad *et al.*, 2013).

Cation exchange process appeared to be more attractive than other means, due to the fact that substance use like zeolite are economic and available in big reserves in countries plan to use it.

Waters with high concentrations of heavy mineral are prohibited for human and animal use because it accumulate in living tissue causing negative effects on human health.

Concerning cadmium, worth mentioning that it is used in steel and plastic and batteries industry. The presence of cadmium to the surroundings can be attributed to waste water, Phosphate fertilizers and air pollution.

Human daily food is considered as the main source of cadmium in living tissues through plants which he feeds on. Human body receives daily an amount of 10-35 microgram orally, also smoking is an additional source of cadmium in human living tissues (WHO, 2008).

Cadmium absorption depends on solubility of compounds containing, and its half-life (symbol $t_{1/2}$) is relatively long (10-35 years). Half-life stands for the time required for a quantity to reduce to half its initial value. The term is commonly used in nuclear physics to describe how quickly unstable atoms undergo radioactive decay or how long stable atoms survive.

There are evidence that Cadmium is cancerous when inhaled through respiratory system.

The indicative value of Cadmium in drinking water is about 0.003 mg/l. In other hand nano technology is growing field in which control of matter in the nanometer scale is used to develop new solutions. Nanotechnology has been explored for creating lighter and stronger materials, for remediating contaminated groundwater (morose2010).

1.3 wastewater treatment

For the purpose of the removal of contaminants from wastewater, a variety of techniques were developed such as adsorption, chromatography, ion exchange, electro dialysis and membrane technologies (Macingova and Luptakova, 2012). As suggested by many researchers, adsorption processes are assumed to be an effective technique to purify wastewater and the success of the technique primary depends on the improvement of an efficient adsorbent. Activated carbon (Pollard *et al.*, 1992), zeolites (Babel and Kurniawan, 2003) clay minerals (Crini, 2006), biomaterials (Crini, 2005) and some industrial solid wastes (Wang, et al., 2008; Wang and Wu, 2006) have been widely used as adsorbents for the adsorption of ions in wastewater treatment. Different methods and techniques have been utilized for the purpose of removing heavy metal ions from wastewater. Some of these processes are relatively cheap in operational costs, abundant in supply, ease of use and flexibility to quickly switch to different applications such as adsorption and ion exchange technique. Other techniques, are expensive in operational costs and incur the problem of residual disposal (Ramalho, 1997). Therefore, many companies have experienced economic pressures due to the costs of operation and remediation (Popuri *et al.*, 2008). Previous studies established the findings of the successful modification of zeolitie and the good achievement while using zeolites as adsorbents for the purpose of removing heavy metal ions from wastewater. Zeolites have advantages over other adsorbents due to their spetioal characterises as mentioned (Gottardi and Galli, 1985 Inglezakis *et al.,* Misaelides *et al.*, 1994; 2004; Erdem *et al.*, 2004; Peric *et al.*, 2004; Gedik and Imamoglu, 2008).

Literature Review

Zeolites materials were investigated in previous research due to their distinctive characteristics. Zeolite is not a recent substance as it was studied more than two and a half centuries ago. Since, after the discovery of Stilbite and Natrolite in 1750 AD, several researches were conducted during the past twenty years on using natural and industrial Zeolite: A, X, Y, Z .

It was confirmed that the characteristics of Zeolite depend on its source due to changes in natural formation process during formation. Townsed and Iazidou (1984), Mondale *et al.,* (1995) reported that structural deformations, diversity of Cations and the occurrence of clay can lead to clogging openings and internal channels and consequently slow rate of transfer of Electrolytes during processing.

It is important to know that the concentration of raw Zeolite depends on volcanic deposits from which the Zeolite is extracted. Mondale *et al.,* (1995) used samples containing 80-100% of Zeolite with other substances such as volcanic glass, Quartz and Feldspar.

Similarly, Curkovic *et al.,* (1997) used the Clinoptilolite of 40-50%,

Rivera-Garze et al (2000) conducted a study to add silver to the Mexican Zeolite in order to be used as an anti-bacterial substance. They found that Zeolite with a higher concentration of silver removed the pathogenic microbes such as (*E.coli*) and (*S.Facalis*) from water.

Targo and Petric (2003) investigated removing zinc from water. The removal in acidic conditions was due to ion exchange and partially to adsorption. In alkaline conditions, the removal was due to the formation of a zinc compound with hydroxyl ions causing precipitation, and due to attacking hydroxide ions for Zeolite construction, which caused a decrease in the value of pH.

Doula and Ioannou (2003) studied the adsorption of copper and some exchangeable Cations from the surface of Zeolite. They used FTIR and X-ray to identify the appropriate mechanism for the removal process. The results of this study showed that the adsorption copper adsorption increases with increasing the pH and decreases electrolyte concentration.

Doula and Ioannou (2002) conducted another study, investigating the adsorption and demineralization of copper. Three salts were used, namely; potassium chloride, potassium nitrate and potassium sulfate, it was observed that the Zeolite surface was able to hold the chloride and nitrate ions by the mechanism of forming surface compounds and this process contributed to adsorption due to the surface negative charge.

Ponizoudky and Tsadilas (2003) verified how Lead retained by soil and Clinoptilolite at different pH values. They found that Zeolite took Lead from soil 20-30 times more based on ion exchanges between solution and Zeolite. It was considered that ion exchange mechanism was the mechanism used to remove Lead.

In another study, Castellar et al (1988), used the Zeolite to produce Ethanol, they observed that production was improved and concentrations of ethanol increased at pH 4

Turkmen (2001) used the natural Zeolite as an ion exchanger to remove the heavy metals: (Pb, Cu, and Zn) from acidic industrial water containing high concentrations of heavy metals. The presence of the natural Zeolite was effective in removing these minerals.

Inglezakis and Loizidou (2007) conducted a recent study using the natural Zeolite compared with polarized organic solvents to remove the heavy metals Cu^{2+}, Cr^{3+}, Fe^{3+} , the researchers found that the factors affecting the removal of heavy metals are: the nature of solvent, the formation of sediments, Cations and the diameter of internal channel openings of the Zeolite.

On the other hand, Yuan *et al.,* (1999) studied the ion exchange capacity and the removal efficiency of mardenite and Clinoptilolite in removing (Pb^{2+}, Cd^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}) whereas the fixed treatment (batch) was used in conducting experiments.

The results of the study showed that both types are able to remove these minerals and Lead is distributed inside the Zeolite while Cadmium is accumulated on the surface of the grains.

Brigitte et al (1999) verified the ability of natural substances with delicate pores such as volcanic tuff (Chabazite and Phillipsite) to remove ions of the minerals (Pb^{2+}, Cd^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}) from industrial water. According to this study, zeolite showed a high selectivity of Lead and, in contrast, the efficiency of Lead adsorption by activated Carbon is less than that of the volcanic tuff.

Many scientists reported that the natural Zeolite, which contains several Cations, needs to be pre-treated in order to remove all Cations and replace them with one Cation, which is called according to Turkmen (2001), (homionic). Therefore, pre-treatment aims to remove specific ions from the basic structure and to add ions easy removable and moveable.

This mono-charge or semi mono-charge product can improve the exchanging capacity of Zeolite. Most of the research conducted on adsorption of heavy metals by natural Zeolite has focused not only on the selectivity of different Zeolites but also on the effect of pre-treatment on the efficiency of ion exchange.

Inglezkis *et al*., (2001) clarified that the simplest type of Preliminary treatment or pre-treatment is the washing of Zeolite samples, as this method is effective in increasing the exchange capacity of Zeolite. They studied the washing of the accumulated dust on the surface of Zeolite and according to their study results, they concluded that the dust closes part of the openings and internal channels in the Zeolite building, which leads to a slow ion exchange.

According to Helfferich (1995), ion exchange, - theoretically - indicates the higher level of exchange and the effective amplitude indicates the true value of the exchanged Cations. While Gradvec *et al* .,(1988) stated that, the difference between these two capacities is due to the fact that some cathodes on the surface of Zeolite cannot be removed easily due to slow motion and strong bonds within the structure.

Preliminary treatment can be performed under static (batch) or dynamic (column) conditions. In the first case, mono-cationic Zeolites (for example, sodium) is prepared using sodium chloride solution (0.5-2) m, the ratio of solid to liquid substance (0.1-0.025) gm/mL Zeolite at temperature ranging from (60-90) degrees Celsius and for a period of time ranging from 2-7 days, the saline solution periodically changed .

Pretreatment is performed in dynamic conditions (column) through washing the substance packed into the column by modification solutions containing salts under specific operating conditions (flow, solution volume, temperature).

According to Semmens (1988) and Kileve (1980), Sodium chloride is the most commonly used substance in tests, several flows from (1BV/h) to (21BV/h) are used, where BV means (Bed Volume) i.e. size of filling the unit that is usually used in dynamic studies which means the volume of liquid equivalent to the size of filling.

Koon and Kaufman (1975) reported that increase in flow over the efficacy of column was not observed when water direction was from bottom to top while it was observed when water direction was from top to bottom.

Carland and Alpan (1995) stated that the concentrations of solutions used in the Preliminary treatment can change from (2- 0.2) mol/L.

Guangsheng *et al.*, (1988) reported that it was proved that the high concentrations of sodium chloride solution caused higher removal of ions to be treated.

Quki and Kavvangh (1999) reported that wastewater contaminated with heavy metals was treated by natural Zeolite. Two types of natural Zeolite namely the Clinoptilolite and Chapazite, they were used in order to assess their efficiency and selectivity in treating wastewater containing the elements (Pb, Cd, Cu, Zn, Cr, Ni, Co). Chemical treatment transformations, which were; concentration, pH, and presence of competitive ions were investigated. The study found that the efficiency of the Chapazite was higher than that of Clinoptilolite that was because Aluminum considerably replaced Silicon. Also the modification of Chapazite and Clinoptilolite by Sodium chloride improved the exchange capacity.

Kurkovic *et al.*, (1997) conducted a study through which Cadmium was removed from normal water by means of raw and treated Zeolite in a static process (batch), the process was conducted at a temperature of 22 and 70°C. The Zeolite was changed into the Sodium form and proved that the treatment improves efficiency which increases with increasing temperature.

Olivera (2007) implemented the modification and activation of natural Zeolite using each of Sodium, Barium and Copper. The result showed that new produced forms could be an alternative in the field of adsorption.

Polatoglu (2005) carried out a study in which natural raw Clinoptilolite was treated by Sodium carbonate concentration of (0.5M) with 2:1 solid-to-liquid ratio for an hour. The treatment was conducted at a temperature of 100°C and at atmospheric pressure.

Sun *et al.*, (2010) compared Ammonia adsorption by raw and modified Zeolite by Sodium chloride salt using static and dynamic experiments. The results indicated that Ammonia adsorption on modified Zeolite was better than that on raw one in terms of capacity.

Ames (1967) reported that Zeolite can be used to treat radioactive substances in wastewater because of its ability to resist disintegration done by radiation.

Blanchard *et al.*, (1984) stated that Clenobletolite has proven to be a good selectivity for Ammonia ion and heavy metals as follows:

$Pb^{2+}> NH_4>Cd> Cu> Sr^{2+} >Zn^{2+}>Co^{2+}$

Collela (1999) found that the selectivity of the Feldspite is as follows:

Cs > pb >NH4 > Na > Sr > Cd > Zn

Pansini (1991) investigated removing Chromium from wastewater by ion exchange using Zeolites. Two samples from yellow tuff were taken. The first sample contains 59% Feldspite and +15% Chabazite, while the second sample contains 30% of both. Fixed and dynamic treatment was adopted. The effectiveness was compared with the sodium-treated tuff, the exchange capacity (CEC) was 3.6 mEq/gm for the modified Zeolite 3.4 mEq/gm for raw Zeolite. Chromium can be removed but water should be low-salinity.

Alanbar (2008) investigated the possibility of removing triple iron by the Jordanian natural Zeolite. The following variables were studied: equilibrium time, Zeolite weight, and initial iron concentration. The researcher found that the equilibrium time was 150 minutes and Langmuir model was appropriate for equilibrium process.

Serbian natural Zeolite was investigated by Rajic *et al.,* (2010) to remove Nickel from water. Granular volume was (0.1-0.063)mm and acidic medium was (pH 6). 1 gm was taken and treated by (100) ml of M(2) from Sodium chloride. The researchers concluded that Serbian Zeolites was of moderate effectiveness in removing Nickel.

Zamzow (1990) studied removing heavy metals and some other cations from wastewater using the static and dynamic mechanisms. He found that modifying Zeolites improves capacity and selectivity was as follows:

Pb > Cd > Cu > Co > Cr > Zn > Ni > Hg

Semmens and Martin (1988) investigated removing Lead, Silver, and Cadmium by Clenobletolite in the presence of competing ions such as Calcium, Magnesium, and Sodium. Based on this study, they found that the efficiency of Zeolite significantly depended on the concentration of competing ions. The following selectivity was obtained:

Pb > Ag > cd

In addition to the effect of competitive ions, the effect of modification by acid and alkali was studied and it was found that the modification by acid was less effective in improving selectivity and the chemically treated tuff was better.

Mier *et al.*, (2001) investigated the ongoing internal reactions among Lead, Cadmium and Chromium in Clenobletolite as well as the competition of these ions with others for the active locations. This was done through static treatment and at pH acidic conditions, it was found that removing Lead and Cadmium after 18 hours was more than 95%.

Al-Bishtawi and Al-Haj Ali (1997) studied the change in the capacity of Jordanian tuff (rich in Feldspite) in removing Lead and Nickel from aqueous solutions with a change in; granular volume, preliminary acidic pH, initial metals concentration, Zeolite quantity and temperature. Experiments were carried out using modified Zeolite (Sodium Feldspite) it had a granular volume of (45-710) µm, initial pH was 2.5-4.5, the amount of zeolite was from 1.5-8 gm/ L, and temperature ranged between 20-35 ° C.

Langmuir and Friedlich adsorption models were applied to obtain adsorption curves. It was observed that the two models fit with both elements. Al-Haj Ali and Al-Bishtawi found that the Jordanian Feldspite is an effective ion exchanger in removing Lead and Nickel from aqueous solutions. They also found that Lead was removed more effectively than Nickel, regardless of operating conditions. When the granular volume becomes more smooth, the exchange coefficient of both elements increases, in addition to that, they found that the higher ratio of removal occurs at the values of pH 4.

Taffarel and Rubio (2009), in another study conducted to remove Manganese in which samples of Zeolite containing mainly Clenobletolite and Mordenite. The two researchers found that the surface area of the zeolite used was 118m2/gm (nitrogen method), and the exchange capacity was 1.09 mEq Ammonia per each gram.

Researchers found that the acidic medium significantly affects the adsorption capacity. Best results were obtained at 6.0-6.8 pH, fit the adsorption of activated Zeolite with a binary reaction rate. Chabazite activation gave the highest rate of reaction.

Balance results reported that there was a fit with the Langmuir adsorption model. Chabazite was modified by multiple salts, capacity of which was: Sodium chloride (0.77mEq/Mn^{2+}/gm), Sodium hydroxide (0.76), Sodium carbonate (0.72), and Ammonium chloride (.67). It was noted that this capacity increased compared to raw Chabazite capacity which was (0.26 mEq Mn/gm).

There are researches conducted in order to apply types of Zeolite (Clenobletolite and Chabazite) to remove the radioactive elements (Cr, Co, Cs) and well-known pollutants from the heavy elements (Cu, Cd, Zn) that can be found in water-waste of nuclear plants. The experiments were conducted according to the static process (batch) and Clenobletolite selectivity found as follows:

Cs > Cu > Cr > Zn > Co

and Chabazite selectivity as:

Cs > Sr > Cu > Zn > Co

Several studies indicated the effectiveness of natural Zeolite in removing heavy metals and other substances that may be in water. According to Nguyen (1988), the efficiency of natural Zeolite was verified in many countries such as: New Zealand, Australia, Turkey, Hungary, Chile, Croatia and China. It is believed that the characteristics of structure of the different types of natural Zeolite (Mordenite, Clenobletolite, Ironite Chabazite, and Feldspite) affect efficiently as well as the natural Zeolite.

Widiastuti (2008) reported the possible applications of natural Zeolite in removing Ammonium, heavy metals and bacteria coli, and in treating wastewater.

Bosso and Enzwiler (2002) reported Zeolite (Cellulite) as a new substance to remove heavy metals from aqueous solutions which were; (Pb^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Cd^{2+}). Experiments were conducted using (0.5) gm. of the sample containing the appropriate metal and then stirred for (24) hours under room temperature.

Adsorption of elements from solutions depends on several variables: initial concentration (5-60) mg/L, (pH4 to 6), ratio of liquid/solid (200, 1000, 2000).

Experiments proved the effectiveness of Zeolite in removing Copper at 130mEq/gm, pH 6 , an initial concentration 30 mg/L, a liquid-to-solid ratio equal to 200. Under the same conditions, the maximum suitable capacity for other ions was 64 mEq/gm Zinc, $(Pb)^{56}$, $(Ni^{2+})^{31}$, $(Co)^{7.8}$, $(Cd)^{3.2}$

The process of removing heavy metals by (Soliczite) occurs through ion exchange and adsorption inside inner caves of Zeolites. The results indicated that (Soliczite) was a available and good alternative to remove the heavy metals (Cu, Pb, Zn) and to less extent the heavy metals (Ni, Co, Cd). In order to increase the effectiveness of removing the last group of metals, Soliczite can be mixed with other types of Zeolite (such as Chabazite), which are considered very effective in removing these metals.

Sun et al (2011) investigated the Zeolite stiblite, a natural high-crystalline Zeolite with open inner channels. It was treated with iron chloride solution ($FeCl_3$) in order to remove fluoride from drinking water.

Raw and modified Zeolites were described using techniques XPS, FTIR, SEM. Also, several parameters such as contact time, Zeolite concentration, preliminary concentration, pH, and existing competitive ions. It was concluded that fluoride concentration could be reduced to less than (1) mg/L upon the following conditions:

Solid/liquid ratio 1: 100, contact time 2 hours, pH (6.94), when the preliminary concentration of fluoride is (10) mg /L. It was found that Langmuir model describes the adsorption process well, and the maximum adsorption capacity equal to (2.31) mg/gm. Dynamic studies indicated that Fluoride adsorption follows the "first-order reaction" model.

Doula (2009) conducted an experiment to load the surface of Clenbetololite with iron oxide and concluded that there was significant improvement observed in treating heavy metals of drinking water, and the modified Zeolite was able to adsorb high amount of heavy elements compared to unmodified Zeolite. There was also a decrease in water hardness observed. The researcher came up with a conclusion that treated by this method water can be used for human consumption or in agriculture.

Kurkovic (1997) conducted a study to evaluate the effect of chemical treatment on the exchange capacity and selectivity of Zeolite (Clenbetololite) for the elements (Pb, Cd, Zn, Mn).

The results showed that the samples of the natural and transformed to sodium-form Zeolite possess the highest capacity.

There are only few researches conducted on fresh water which treated with Zeolite, compared to wastewater and industrial water.

Bagdanov *et al.,* (2009), investigated the Iranian natural Zeolite ability to remove Arsenic from drinking water using Zeolite type (Clenbetololite).

Badalian *et al.,* (2010) also studied the Iranian natural activated Zeolite (Natrolite) to remove the following hardness and heavy metals:

(Ag, Ni, Zn, Cu, Pb, Fe, Cr, Al, Cd, Mn, Ca, Mg), from groundwater, they pointed out that; Natrolite can remove some heavy metals from drinking water, the higher hardness helps removing, the removal effectiveness was improved by surface modification.

Camacho *et al.*, (2011) verified the adsorption of Arsenic (As^{2+}) on the surface of raw and modified by (MnO_2) Clenobletolite to study the feasibility of removing Arsenic from groundwater using natural Zeolite. The quality of raw and modified Zeolite was described by XRD, XRF techniques, and then static treatment (batch) was adopted to investigate the effect of (pH) and initial concentration.

They reported revealed that the removal rate of modified Zeolite was significantly improved and the modified Zeolite was able to remove Arsenic from water within a wide range of (pH) and the removal rate was doubled compared to raw Zeolite, and therefore, the modified Zeolite is a promising option to use as an adsorption exchanger in removing Arsenic, even if only in a few proportions, in drinking water.

In addition, the possibility of removing Arsenic from drinking water was investigated by Paskan and Pala (2011).They adopted the adsorption on the well-known Zeolites (Clenobletolite), they studied the modified and unmodified type by (SEM), (XRO), surface area and structural composition.

The treatment of (Clenobletolite) was conducted using Sodium chloride and Ferric chloride at concentrations (0.1, 0.01)M, the results were as follow; the modified with Codium chloride Zeolite was removed by 92%, while the modified with Ferric chloride Zeolite was removed by 84%.

The time required to reach the equilibrium was (60) minutes. The time of saturation did not depend on the preliminary concentration of Arsenic. The information resulting from the experiments was described as a second degree equation rather than a first degree equation.

Blanchard *et al.*, (1984) examined the use of Clenobletolite as an ion exchanger to remove Ammonia and heavy metals cations from drinking water. The selectivity of this sodium-treated Zeolite was as follows:

$Pb > NH_4 > Cd > Cu > Sr > Zn > Co$

After static treatment experiment, the Zeolite effectiveness of removing heavy metals through dynamic treatment experiment was studied by passing water over the sodium filling of (modified) Clenobletolite occurring in the exchanger, they studied the change in flow rate and the parameters of exchanger activation.

As a result, the best exchange was obtained at the flow 12 volumes of Zeolite / hour (12BV/h). The best results of activation were obtained when Sodium chloride concentration was (20-25gm/L), the saline flow was (40BV/h) at a pH value ranging from 4-4.5 in order to avoid heavy minerals precipitation.

1.4 Existing wastewater treatment technologies for heavy metal removal

It can be observed from prior sections that efforts have been directed towards developing technologies to remove heavy metals and hence there is a need for an economic technology capable of achieving the desired results. It has recently been mentioned that there are various processes and technologies that are available for the purpose of removing heavy metals from wastewaters. These processes include membranes, ultrafiltration precipitation, reverse osmosis, electrodialysis, adsorption and ion exchange

(Rengaraj *et al.*, 2001; Richardson and Harker, 2002; Peric *et al.*, 2004; Hamdaoui, 2009; Macingova and Luptakova, 2012).

Adsorption is effective, available in large quantities and an economic method with great potential for the removal of metals from wastewater, compared to other wastewater treatment techniques that have expensive operational costs

1.4.1 Adsorption

The term adsorption was first used by Heinrich Kayser in the year 1881. Adsorptionisa removalprocessofasubstance(atoms,ions,ormolecules)calledan“adsorbate”fromagas, liquid,ordissolvedsolidphasebyasolidmaterialcalledan“adsorbent”(Bansal and Goya, 2005).

Hence many studies have been carried out on adsorption techniques as important processes in separation technology (Gupta *et al.*, 2009; Erdem *et al.*, 2004; Freitas *et al.*, 2008; Hameed, 2009). Adsorption processes differ from absorption processes; adsorption is a surface-based process in which atoms, ions or molecules from a substance adhere to the surface of the adsorbent as shown in figure (1.1). Absorption is the process which involves the entire volume of the absorbing substance into the solid material body as shown in figure (1.2) (Erdem et al., 2004). The removal efficiency of any adsorption process depends on selectivity and affinity. According to the type of adsorbent and adsorbate bonds formed, adsorption can be classified into:

i. Physical adsorption: occurs when the adsorbate sticks to the surface of the adsorbent only through Van der Waals (weak intermolecular) interactions (Somorjai, 1993). Physical adsorption is usually fast and reversible this is because the physical adsorptions process involves the formation of week bonds between the adsorbate and adsorbent, thus the adsorption bonds are easily formed and broken (Somorjai, 1993).

ii. Chemical adsorption: occurs as a result of a chemical interaction between the adsorbate molecules and the adsorbent surface. A chemisorption process is usually slow and irreversible this is because the chemisorptions process involves the formation of strong bonds between the adsorbate and adsorbent and can change both the surface and adsorbate chemical character (Somorjai, 1993).

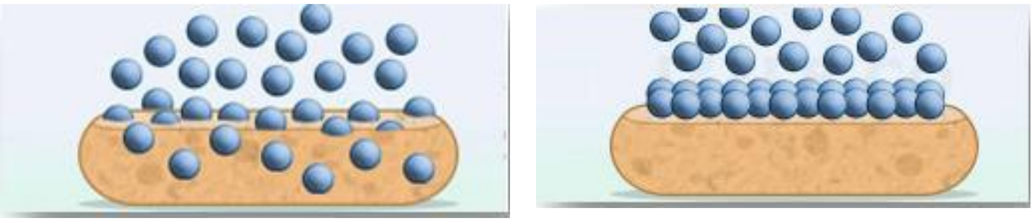


Figure 1.1(A): Shows the adsorption process in which atoms, ions or molecules are adhering to the surface of the adsorbent .Figure 1.2(B): Shows the absorption process, in which atoms, ions or molecules entering the volume of the absorbing substance.

1.4.2 Zeolite framework structure:

The crystal structure of zeolite was analysed for the first time by Taylor in 1930. Since then, their unique physicochemical properties have attracted the attention of many researchers and additional investigations into the framework structures of zeolite have continued. Hey (1930) concluded that natural zeolite is a class of crystalline, porous, hydrated aluminosilicates frameworks with loosely bonded alkaline or alkaline earth metals with important physicochemical characterises, and can be used in many applications as a cation exchange, molecular sieving or catalysis (Dyer, 1988).

In general zeolite can be defined as a microporous crystalline solid substance that is inorganic and contains silicon, aluminium and oxygen in its framework and cations and water molecules within it spores (Mortier, 1982; Dyer, 1988). The general chemical formula of zeolites would be:

M represents the charge-balance cation (Na, K, Li) and/or (Ca, Mg, Ba, Sr), n is the cation charge, x is generally 2, and y is the water contained in the natural zeolite.

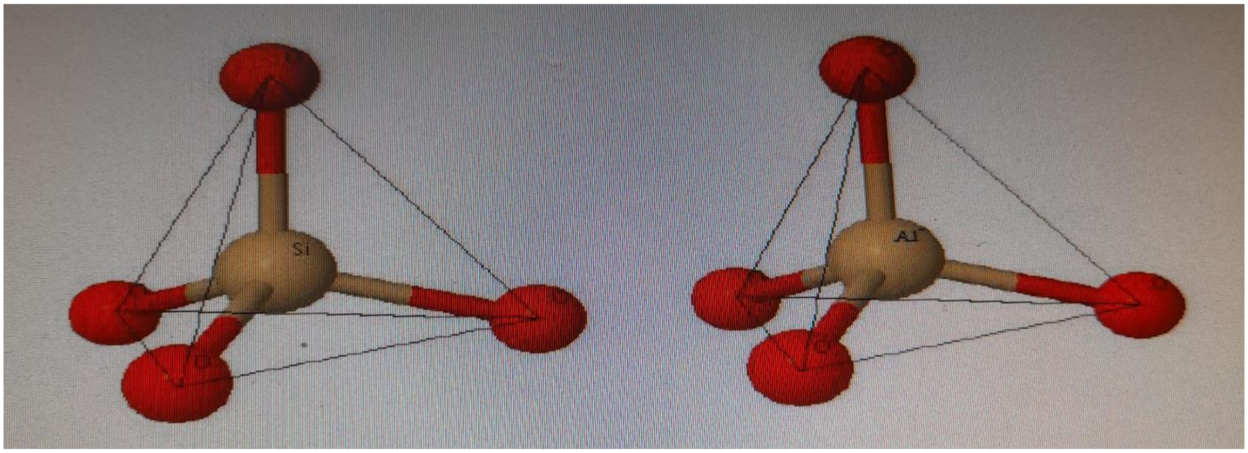


Figure (1.3) Diagrammatic sketch of the zeolite structure and representation of [SiO4]4- or [AlO4]5- tetrahedral (Dyer, 1988).

The above figure shows that the tetrahedron structure unit of the zeolite in which the centre is occupied by a silicon or aluminium atom connected to four oxygen atoms at the corners. The positive charge deficiency caused by the substitution of Al3+ by Si4+ is compensated by cations located together with water molecules in the channels (Mortier, 1982). The framework contains open cavities in the form of channels and cages. Channels and cages are occupied by water molecules and extra-framework cations (Na, K, Li, Ca, Mg, Ba, Sr) that are commonly exchangeable (Gottardi and Galli, 1985; Ribero *et al.,* 1984).

Zeolites can be widely classified in to three schemes. Two of these are based upon specifically defined aspects of the crystal structure, while the third has a more historical basis, placing zeolites with similar properties (e.g., morphology) into the same group. This third method also related to its crystal structure, but not as directly as the first two, which are based upon the crystal structure (Armbruster and Gunter, 2001). In the zeolite structure, three relatively independent components are found: the alumina-silicate framework, exchangeable cations and zeolitic water (Dyer, 1988; Gottardi and Galli 1985).

$M_2/nO:Al_2O_3:xSiO_2:yH_2O$

The alumina-silicate framework is the most conserved and stable component of zeolite. The topology of the framework, and the numbers and distribution of the charges (Al^{3+} sites) are basically formed at the crystal growth stage and they define a series of technologically important properties of zeolites (Galli 1985 and Dyer, 1988;). The water content clearly depends on the distribution of cations because the cations in the channels and cavities are surrounded by both water molecules and oxygen atoms. All water molecules are associated with non-skeletal cations and each hydrogen is bound to a tetrahedral oxygen atom. All of the oxygen in the framework participates in a cation or hydrogen bond. Cations are bound more strongly by water oxygen than by framework oxygen atoms (Breck, 1974 Dyer, Gottardi and Galli, 1985). The water molecules can be present in the voids of large cavities and bonded between framework ions and exchangeable ions via aqueous bridges. The most significant feature of the zeolite structure is the presence of voids and channels, which define the specific properties of these minerals (Gottardi and Galli, 1985). These structural cavities and channels are occupied by alkaline and alkaline-earth cations and water molecules and they constitute 20%-50% of the total volume (Gottardi and Galli, 1985).

As described by Bekkum (1991) both the Si/Al ratio and the cation content determine the properties of most zeolites. Based on the correlation Si/Al ratio zeolites are divided into high, middle, and low silica, which determines their stability at different pH values (Ribero *et al.,* 1984)

1.4.3 Properties of zeolites

As discussed in the previous chapter, the most important attributes for any adsorbent application are: capacity, selectivity, regenerability, kinetics, compatibility and cost. Most researchers have observed that synthesized zeolites have a higher ion exchange capacity than natural zeolites, while the pre-treatment improves the efficiency of natural zeolite in the removal of heavy metals from the industrial wastewater (Inglezakis *et al.,* 2004; Han et al., 2006; Gunay *et al.,* 2007).

1.4.4 Application of zeolites

Zeolite have been utilized for many applications in several fields such as pollution control. The applications of zeolite deeped on three special properties:

Ion exchange: zeolite has high ion exchange ability since they can interact with phases and replace existing ions.

Molecular sieves: zeolite can selectively absorb or release ions and molecules depending on their cavities in their structures.

Catalytic cracking: zeolite can also react with large molecules and break in them down into smaller pieces.

The potential environmental applications of zeolite can be given as:

- Nuclear effluents containing radioactive isotopes in the take-up of Cs and Sr from nuclear waste and fallout (Dyer and Zubair, 1998; Dyer and Zubair, 1998; Faghihian *et al.,* 1999; Abusafa and Yücel, 2002; Gennaro *et al.,* 2003; Um and Papelis, 2004Shahwan *et al.,* 2005).

- Ammonia removal from municipal wastewaters (Langella *et al.,* 2000; Cincotti et *al.,*2001,Watanabe *et al.,*200 Ramos *et al.,* 20043; Sarıoglu,2005;Duff *et al.,* 2005).

- Heavy metal removal from industrial and agricultural effluents for example remediation of acid mine drainage (Ouki and Kavannagh, 1999; Halimoon and Yin 2010; Mier *et al.,* 2001; Langella *et al.,* 2000; Cincotti *et al.,* 2001; Curkovic et *al.,*1997; Blanchard *et al.,*1984; Šiška,2005;Peric *et al.,* 2004).

- The ion exchange property of clinoptilolites is also used in controlling soil pH and nutrient levels (soil conditioning), and also as an animal feed supplement (Alvarez *et al.,* 2003).

- Air pollution control (Axente *et al.*,1983; Khulbe *et al.*,1994 Ackley *et al.*, 2003).

-More recently in several emerging field such
as health and medicine(Payra and Dutta 2003).

1.5 Adsorption isotherms

An adsorption isotherm equation is an expression of the relation between the amount of solute adsorbed and the concentration of the solute in the liquid phase. Adsorption isotherms need to be studied well in order to investigate the characteristic performance of zeolite. Kocaoba *et al*., (2007) have described the use of these models to predict the behaviour of different adsorbates for adsorbents and the theoretical adsorption constants.

There are many factors that affect the equilibrium constant and experimental conditions including: the effect of system temperature; and the effect of the total initial concentration of the solution and the characteristics of the ion exchange system, such as mineral type, solution composition, and pH of the solution (Inglezakis *et al.*, 2002)

Equilibrium experiments were carried out using adsorbent masses of 1g. The adsorbent was mixed with 100 ml solution of the solution. The agitation speed of 150 rpm was used for 120 minutes.Three differentsolution pH were used, as follows: 2, 4 and 6 ± 0.1. This experiment was initially done for $Cd^{2+,}$ Pb^{2+} ions and the concentration range of cations was from 200 to 500 mg/l.

The Langmuir and Freundlich adsorption isotherms were adopted because they are the most widely used for heavy metal solutions and zeolite systems(Altınet al., 1998; Erdem *et al.,* Petrusand Warchoł,2003, Sheta *et al.,* 2003 ,Payne and Abdel-Fattah, 2004;Peric *et al.,* 2004) since they are simple and capable of describing experimental results in a wide range ofconcentrations(Altın *et al.*, 1998).

1.5.1 Langmuir adsorption isotherm

The Langmuir equation (1918) makes the assumption that the maximum adsorption corresponds to a saturated mono-layer of adsorbate molecules into the adsorbent surface. Previous studies have been concerned that the Langmuir adsorption isotherm is based on a number of assumptions, including:

Monolayer coverage of the adsorbent surface. Molecules are adsorbed at stable sites and do not transmigrate over the surface. All adsorption sites are energetically identical and the energy of adsorption is constant (1994, Gunay *et al.,* Richardson *et al.,* 2002 Almaraz *et al.,* 2003; Gunay *et al.,* 2007; Motsi *et al.,* 2009).

The equilibrium data for heavy metal cations over the different concentration range of metal ions have been fitted with the Langmuir Isotherm (for solid – liquid systems) and use the following equation:

$C_e/q_e = 1/Qb + C_e/Q$

Where,

qe is the amount of solute adsorbed per unit mass of adsorbent at equilibrium (mg/g),

Ce is the residual liquid phase concentration at equilibrium (mg/l), Q and b are Langmuir constants related to sorption capacity and sorption energy, respectively. Maximum sorption capacity (Q) represents monolayer coverage of sorbent with sorbate and b represents enthalpy of sorption and should vary with temperature.

Data was used to determine the loading capacity, qe (mg/g) of the different adsorbents, using the following equation:

$qe = (Co - Ce) X V / m$

The percentage removal of metal ions from solution was also determined using the equation below:

Percentage Adsorbed (% removal) $qe = \{(Co - Ce) X 100\} / Co$

Where,

qe is the amount of solute adsorbed per unit mass of adsorbent at equilibrium (mg/g),

Co is the initial concentration of heavy metal ions (mg/l),

Ce is the residual liquid phase concentration at equilibrium (mg/l),

V is the volume of solution from which adsorption occurs (l), and

m is the weight of the zeolite

1.5.2 Freundlich adsorption isotherm

The Freundlich sorption isotherm was developed by Freundlich in 1926. This model is one of the most widely used isotherms. It can be correlated to the experimental data over a wide range of concentration (Motsi *et al.*, 2009). This isotherm gives an expression surrounding the surface heterogeneity and this model assumes that all adsorption sites are energetically unequal and that the energy of adsorption is irregular (Prasad and Saxena, 2008; Gunay *et al.,* 2007). It is a more realistic assumption than the Langmuir isotherm. The Freundlich isotherm describes equilibrium on heterogeneous surfaces that are more often seen in natural systems and can be written as follows:

qe = kCe1/n

Where,

qe is the amount of solute adsorbed per unit mass of adsorbent at equilibrium (mg/g),

Ce is the residual liquid phase concentration at equilibrium (mg/l),

k and n are empirical Freundlich constants that are dependent on experimental conditions.

k is an indicator of adsorption capacity while n is related to the adsorption intensity or binding strength.

The linear form of the Freundlich adsorption isotherm is:

lnqe= lnk+1/n lnCe

As stated by Papageorgiou et al. (2006) values of $1/n < 1$ indicate heterogeneous adsorbents, while values closer to or equal to 1 indicate a material with relatively homogeneous binding sites due to its porosity. Natural zeolite can be classified as a heterogeneous adsorbent (Inglezakis *et al.,* 2002; Alvarez-Ayuso *et al.,* 2003; Gunay *et al.,* 2007).

1.6Objectives

The aim of this investigation is to develop an effective, low cost, flexible, sustainable and environmentally friendly adsorbent as an alternative method for removing heavy metals from industrial wastewaters. The efficiency of zeolite for the removal of two heavy metal ions from a solution was considered; these were $Cd^{2+,}$ $Pb^{2+.}$ These were chosen as abundance pollutants that are contained in industrial wastewaters.

The effectiveness of zeolite as an adsorbent in industrial wastewater treatment was further investigated by studying further characteristics of Al-Gadarff zeolite. The main parameters that influence zeolite'sadsorptionabilities are considered with regard to heavy metals from industrial wastewaters, thus, the main aims of the thesis can be discussed as follows:

- To analyze zeolite in both its natural, by determining whether pre-treating it improves its selectivity properties or adsorption capacity.

- To determine the applicability of both the Langmuir and Freundlich isotherms and estimate the parameters characterizing the performance of the batch process.

-To synthesis silver nano particle doped in zeolite and use it as tool to remove heavy metal and compere the results with natural zeolite.

Chapter Two

Materials and Methods

Chapter Two

Materials and Methods

2.Materlals and Methods

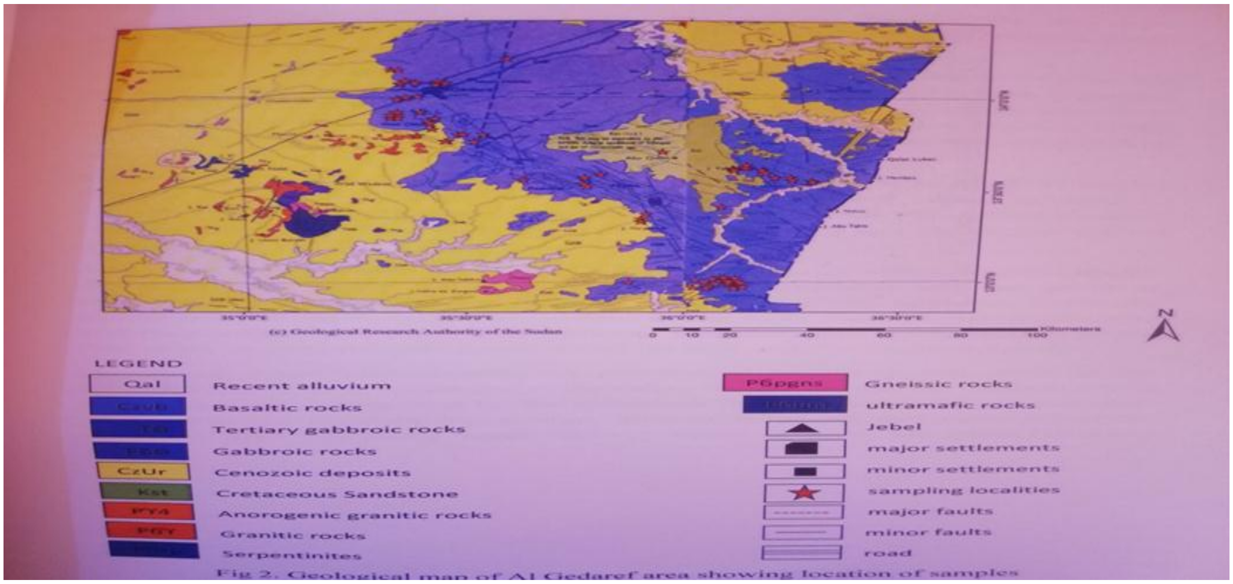
The efficiency of zeolite for the removal of heavy metal ions from the solution was considered; these were $Cd^{2+}$and Pb^{2+}. These two ions were chosen as the most toxic pollutants that may contained in wastewaters. These metals are very common in water and sediment pollutants in harbours surrounded by industrial facilities.

There are some factors that affect the capacity of the adsorption process, including the adsorbent of the initial solution pH and concentration, and the effect of chemical and thermal pre-treatment of the adsorbent. The preparation and analysis of the synthetic solutions used in this research is also discussed.

2.1. Area of the Study

The area of the study covered part of Gedaref state, located at the Eastern Sudan along the

international border with Ethiopian. Generally. It is bounded by the latitudes 120 45-140 53` N



Fig(2.1) Area of the study

2.1.1 Samples Collection

Zeolite samples from AL-Gadarff state .Zeolite samples were digested with 500mL of concentrated HNO_3 and 100 mL of H_2SO_4 until the organic matter has been destroyed(Stylianou *et al.*, 2007). The zeolite was then washed with water, dried over night in an oven at 105^0C.

2.2.2 Chemicals

Stock solutions (1000 mg/L)of Pb and Cd nitrate in nitric acid(0,5 mol/l) Scharlau, Na Cl (99.5%) extra pure

HNO_3(69%) pure, deionised water,distilled water ,Silver nitrate $AgNo_3$ (99%)extra pure, Trisodium citrate $C_6H_5O_7Na_3$ ()

Fig (2.2) natural zeolite from AL-Gadarff state

2.2.3Equipment and Instruments

pH meter209(hanna insturments, hotplate stirrer Jlab Tech, oven(Carbolite,).

AAS(210/211VGP Atomic Absorption Spectrophotometer), Fourier Transform Infrared(FT-IR)300 Spectroscopy(Thermo Nicolet), Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS) Mira-Vega3 (Tescan), X-Ray Diffraction (XRD-GNR Explorer stress analyzer) , X-Ray Fluorescence (XRF, Axions advance, Sequential WD), Thermogravimetric Analysis (TGA, STA Jubeter) ,UV/Visible 7205 Jenway

2.3. Methods

2.3.1. Sample preparation

The natural zeolite samples were used as received without any modification from their natural state, unless stated. The raw and zeolitic material samples were washed with deionized water to remove unwanted dust from their surfaces before use and then dried at room temperature for about 24 hrs.

2.3.2 Synthetic solutions and other chemicals

The experiments have focused on the efficiency of natural zeolite and synthetic nano silver doped zeolite for the removal or reduction of $Cd^{2+,}$ Pb^{2+} ions from synthetic industrial wastewater, to achieve allowable limits.

Synthetic multi-component solutions of Cd^{2+}, Pb^{2+} ions were prepared from analytical.

The initial concentration of the heavy metals in the synthetic industrial wastewater was in the range of 100-500ppm, $Cd^{2+,}$ Pb^{2+} ions respectively. In all the experiment stages deionised water was used, which had almost all of its mineral ions removed. The pH of the starting solution was pH 4 due to get the best adoration rate. The pH values were monitored and adjusted using a pH meter(pH 211HANNA instruments). The pH was adjusted to 2, 4, and 6 ± 0.1 by adding hydrochloric acid (HCl) or bases sodium hydroxide (NaOH).

Samples were ground manually in a porcelain mortar and sieved using laboratory soil sieves. Carbolite . A Memmert model UM200 stainless steel universal oven was used to dry and heat the samples.

Each analysis technique typically investigated only a particular aspect of the material and, therefore, a combination of methods was necessary to obtain a complete description of the raw materials as well as the different zeolitic products. This is very important to use and improve a zeolitic material for a specific application. Generally, the characterization of a zeolite has to provide information on: (1) its structure and morphology; (2) its chemical composition; (3) its ability to sorb and retain molecules; and (4) its ability to chemically convert those molecules.

2.4 Characterization of natural zeolite and raw materials

2.4.1 Scanning Electron Microscopy (SEM)

The surface morphology, topography of the zeolitic materials was investigated using a mira-vega3 scanning electron microscope. The samples were prepared by spreading dried zeolite powder onto 12mm aluminium stubs using double-sided sticky carbon discs and then placing them in a vacuum sample chamber. The samples were coated with gold using an Emscope SC500 sputter coater. Images were taken under high vacuum condition using the secondary electron detector.

2.4.2 Energy Dispersive Spectroscopy (EDS)

The Energy Dispersive Spectroscopy analytical technique was used in this study for the elemental analysis or chemical characterization of the samples. EDS is a chemical microanalysis technique can be used together with SEM. For the EDS analysis the samples were prepared in a similar way to the SEM

2.4.3 X-Ray Diffraction (XRD)

The X-ray diffraction (XRD) was the analytical technique used for phase identification of the natural zeolite sample. The sample was ground to a powder and pressed firmly into the sampler holder before analysis using the X-ray diffract meter with Cu-Ka radiation at 40 mA and 40kVand secondary mono chromation.All data collection data base was present e dinthe2θ range at start position 5 and end Position 50 or 80 degree, with a scanning step of °2 ɵ.

zeolitic products were crushed with an agate mortar and pestle, ground to powder form and mounted in aluminium plate sample holders with a volume of 0.1 cm3. The results of crystalline patterns were compared with the standard line patterns database supplied by the International Centre for Diffraction Data (ICDD) .

2.4.4X – Ray Fluorescence (XRF)

The XRF analysis technique was used in this study to determine the chemical composition of the zeolite. The XRF technique depends on fundamental principles involving interactions between electron beams and X-rays with sample. Mostly, the sample was prepared in a similar way to the XRD sample preparation technique. The sample was prepared by grinding to a powder then pressed firmly into the sampler holder. Sample was analysed a using the XRF spectrometer with 60Kv energy of the X-ray tube.

2.4.5 Thermogravimetric Analysis (TGA)

The thermogravimetric analysis technique was used for the measurement of changes in the physical and chemical properties whilst increasing the temperature constantly. The zeolite was analyzed using thermogravimetry on a TGA thermo balance between 30-1000 °C. The heating rate of 20 °C min-1 was used and the atmosphere in the TGA was nitrogen. The amount 10-15 mg of ground sample was placed directly into the crucible for TGA testing. The TGA crucible was cleaned properly before test and after each run. The results of TGA patterns were analyzed and interpreted at each stage. This analytical technique was very useful in estimating the thermal stability of the thermally treated zeolite and synthetic zeolite products .

2.4.6 Fourier Transform Infrared (FT-IR) Spectroscopy

The FTIR Platinum make single reflection diamond module was used for materials analysis in this study. An infrared spectrumre presents afinger print of the sample.

The sample platform and the stub were cleaned properly before sample analysis and after each run using acetone. The amount 10-15 mg of ground sample was placed onto the diamond ATR crystal surface. Finally, a force was applied to the sample for spectrum collection. OPUS software was used. The sample was then removed from the crystal surface and cleaned again in order to prepare the accessory to collect additional spectrathe .

2.4.7Atomic Absorption Spectrophotometer (AAS)

The heavy metal ion concentrations in the solution were determined using 210/ 211VGP. The standard solutions for metal analysis were prepared from standard metal solutions to determine the amount of Cd^{+2}, Pb^{+2} ion concentrations which present in the solutions.

2.4.8 UV\visible

The UV absorption spectra have been proved to be quite sensitive to the formation of silver nanopartical because it exhibit an intense absorption peak due to the surface plasma (it describes the collective excitation of conduction electrons in metal) excitation.

2.5 Experimental procedure for the removal of ions by the zeolite

2.5.1. Equilibrium studies

Equilibrium studies were carried out when 1g of natural zeolite was mixed with 100 ml of solutions. The level of initial heavy metal concentrations was (141, 335) mg/l of Cd^{+2} Pb^{2+} respectively. Three different pH values of initial solution were preferred 2, 4 and 6 ± 0.1 The mixtures were agitated for 360 minutes at 150 rpm, until equilibrium was achieved then the solution samples were filtered to remove solids and analyzed using the AAS.

2.5.2. Regeneration in batch studies

Regeneration of the natural zeolite was carried out using 0.5M NaCl. After each run, the zeolite sample was agitated in the stripping solution using a magnetic stirrer at 150 rpm for 45 minutes. The samples were rinsed twice in deionised water for 15 minutes and dried at room temperature. They were then re-used for the next experiment run and the regeneration was repeated 4 times in order to observe the adsorption efficiencies with time. The adsorption was performed to determine the reversibility of the reactions and reusability of natural zeolite.

2.5.3 Effect of pH

Three different pH values of initial solution were preferred 2, 4 and 6 ± 0.1 for the solutions. The solution pH was adjusted using sodium hydroxide (NaOH) solution and hydrochloric acid (HCl) solution. Thus 100ml of the solution samples were in contact with 1g of natural zeolite for 360 minutes.

Samples were collected analyzed using the AAS. The agitation speed was 150 rpm at room temperature.

2.5.4 Effect of metal concentration

The effect of the initial metal concentration on the efficiency of natural zeolite in the removal of heavy metals from the solution was determined using solution concentrations in the range of (100, 200.300 and 400) mg/l. Thus 100ml of the solution samples were in contact with 1g of zeolite at an agitation speed of 150 rpm for 120 minutes. The pH of the solution was adjusted to 4 ± 0.1.

2.5.5 Thermal pre-treatment of adsorbent

The thermal pre-treatment process of natural zeolite was performed by heating natural zeolite samples in a furnace for 30 minutes under a slow heating rate of 100, 200 and 300°C to avoid destroy the zeolite structure. Then 4g of the thermally modified natural zeolite samples were in contact with 100 ml of solutions. Agitation was carried out in a beaker using a stirrer at a speed of 150 rpm for 120 minutes at room temperature. The pH of the solution was adjusted to 4 ± 0.1.

2.5.6 Chemical pre-treatment of adsorbent

The chemical pre-treatment of the natural zeolite were carried out by placing natural zeolite sample with 200 ml of 0.5M NaCl. The zeolite sample was agitated in a beaker using a stirrer at a speed of 150 rpm for 24 hours at room temperature. Thereafter the sample was rinsed three times in sample deionized water for a total period of 15 minutes and put in an oven to be dried at 100°C. Then 1g of chemically modified natural zeolite samples were in contact with 100 mLof solutions for 360 minutes. The agitation speed applied was 150 rpm at room temperature. The pH of the solution was adjusted to 4 ± 0.1.

2.5.7 Synthetic of nano-silver doped zeolite

A known mass (1g) of zeolite was dispersed in 30 ml of deionized water and slowly stirred for 10min to obtain a homogeneous mixture .In order to control the oxidation of sliver during the reaction $AgNO_3$was prepared in the dark bottle and 18 ml of the prepared 0.001M $AgNO_3$ was added to the zeolite solution without direct sunlight during the reaction. The mixture was then stirred for a period of 30 min at boiling temperature before introducing 2 ML of trisoduim citrate into it and stirred for another 15 min. The obtained mixture was centrifuged at 600rpm for 30min, washed and dried in an oven for 2 h. It was then allowed to cool in air. The sample obtained was stored in a dark bottle and characterized using UV\VIS and SEM.

Chapter Three

Results and Discussion

Chapter Three

Results and Discussion

3.1Characterisation of Natural Zeolite

Knowledge of the characteristics of natural zeolite, used in synthesis are very important. The technological properties of zeolite products depend on the physical, chemical and mineralogical characteristics of the starting materials; this also controls the overall processing treatment of polluted effluents. Particle characterisation discloses information on the physical, chemical and mineralogical nature of zeolite product particles, which is related to removal efficiency of heavy metals ions from solution. This chapter describes the characterisation of the natural zeolite to provide information on: (a) its structure and morphology; (b) its chemical composition; (c) its ability to sorb and retain molecules; and (d) its ability to chemically convert those molecules.

3.1. 1Analytical techniques

3.1.2. Scanning Electron Microscopy (SEM)

The surface morphology of the natural zeolite sample was determined using SEM under the following analytical conditions: EHT = 10.00 kV and 20.00 kV, Signal A = SE1 and VPSE, WD = 6.0, 6.5, 7.0 and 8.5mm at different magnifications. Scanning Electron Microscopy (SEM) results show that the micrographs clearly the natural zeolite structure contains anumber of different diameter size (macro-pores) and defined crystal of natural zeolite

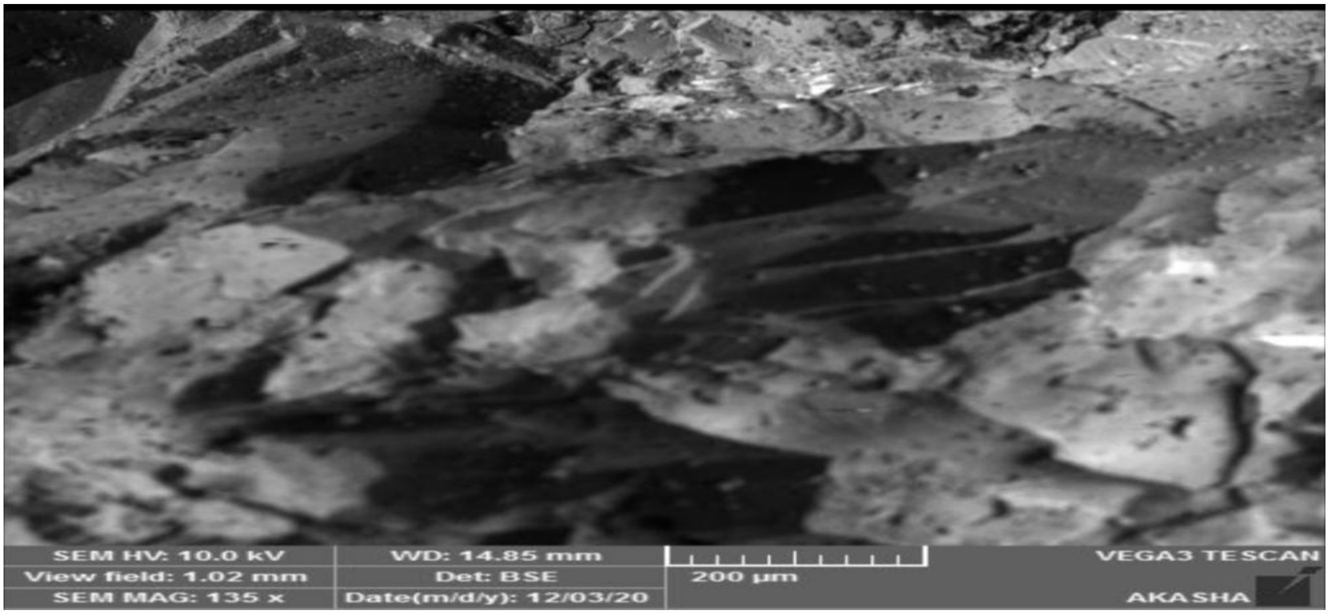


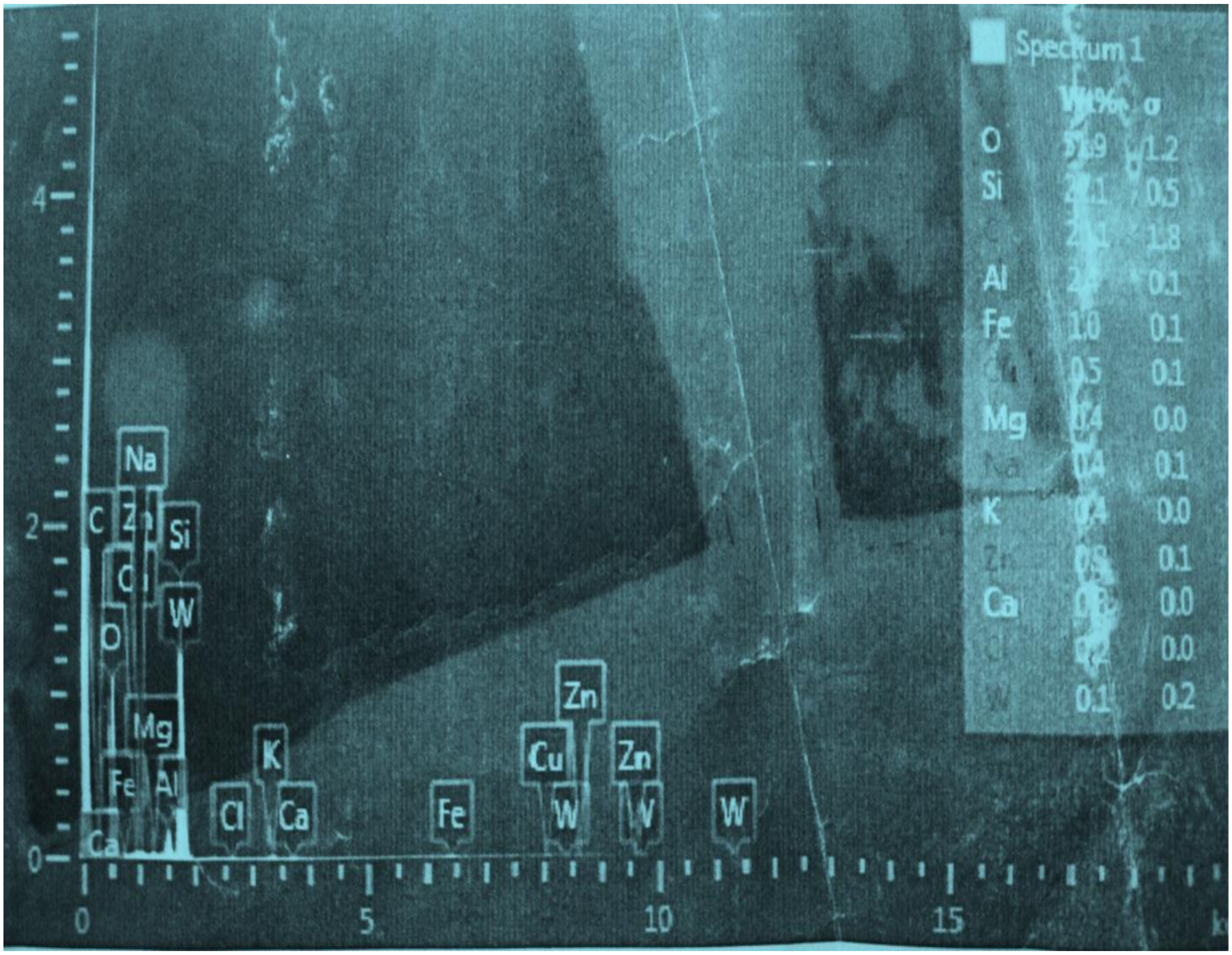
Figure3.1 show the micrographs of the“asreceived”natural zeolite samples.

3.1.2. Energy Dispersive Spectroscopy (EDS)

The EDS is an analytical technique that was used to identify the elemental composition and chemical characterization of different natural zeolite samples as presented below:

Energy dispersive spectroscopy (EDS) results

An electron beam was randomly directed onto different parts of the natural zeolite sample in order to get a more accurate analysis. As shown in figure (3.2) it is noticeable how the different parts of the sample were analysed. In the meantime the elemental composition for natural zeolite sample were indicated rapidly. The main elements were determined by EDS. The localisation of four analysed sites designated by numbers and a typical EDS spectra are shown in fig 3.3



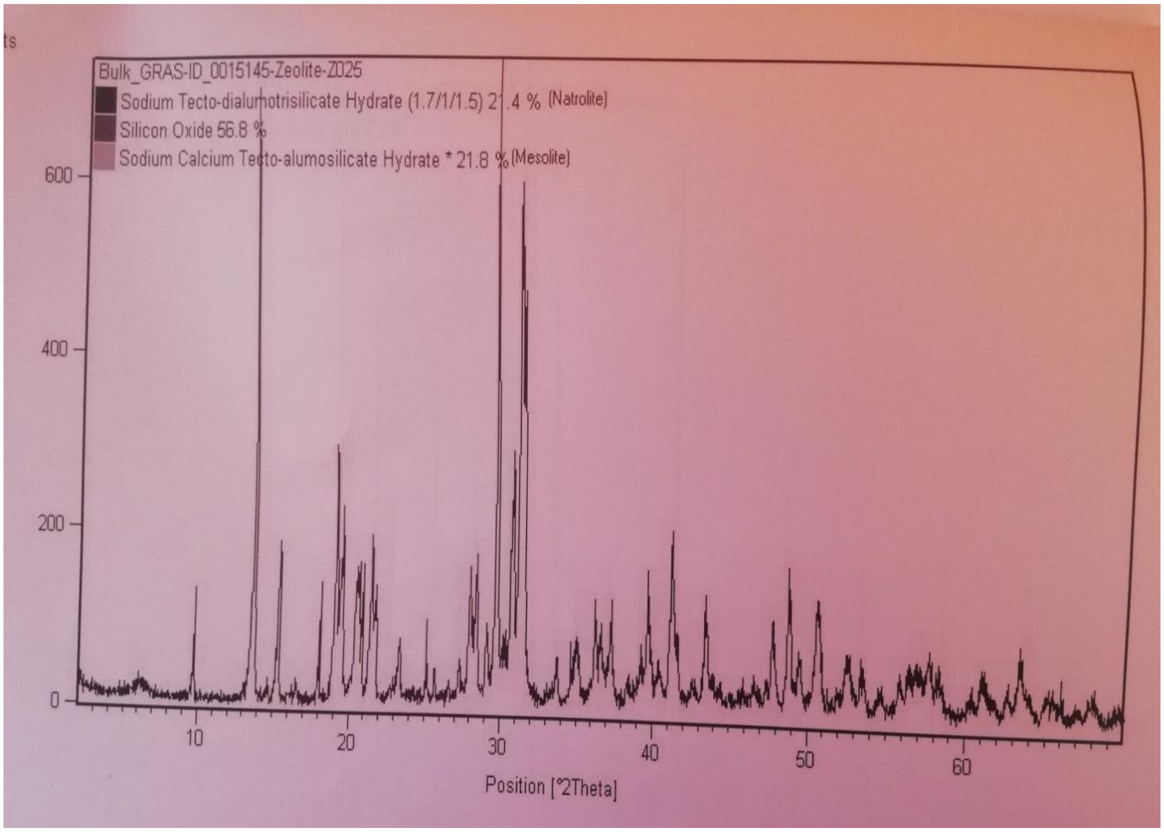
	Wt%	σ
O	[illegible]	1.2
Si	[illegible]	0.5
C	[illegible]	1.8
Al	[illegible]	0.1
Fe	1.0	0.1
Cu	0.5	0.1
Mg	0.4	0.0
Na	0.4	0.1
K	0.4	0.0
Zn	0.5	0.1
Ca	[illegible]	0.0
Cl	0.2	0.0
W	0.1	0.2

Fig(3.2) EDS spectrum of zeolite sample

The results of the EDS analysis also shows that the predominant exchangeable cations in the natural zeolite structure were found to be Na^+, Mg^{2+}, K^+ and Ca^{2+}.

3.1.3.TheX – Ray Diffraction (XRD)

The X-ray diffraction (XRD) analytical technique was used for phase identification of the natural zeolite sample and characterization of the heterogeneous solid mixtures to determine the relative abundance of crystalline compounds and obtain information on the unit cell dimensions.



Figure(3.3): XRD analysis showing the mineralogical analysis of (Natural Zeolite)

X-Ray diffraction analysis shows the pattern of X-ray diffraction carried out on natural zeolite, in which different mineralogical phases are observed

The first peak in range (140-160) due to silicon oxide and natrolite.

The procedure was carried out and data were collected in the range 0-50 degrees, with a scanning step of °2 ө. The crystalline patterns were compared with the standard line patterns from the powder diffraction file database supplied by the International Centre for Diffraction data.

3.1.4.The X – Ray Fluorescence (XRF)

The XRF analytical analysis of the natural zeolite samples was carried out to determine the elemental composition of the samples.

X-Ray Fluorescence (XRF) result

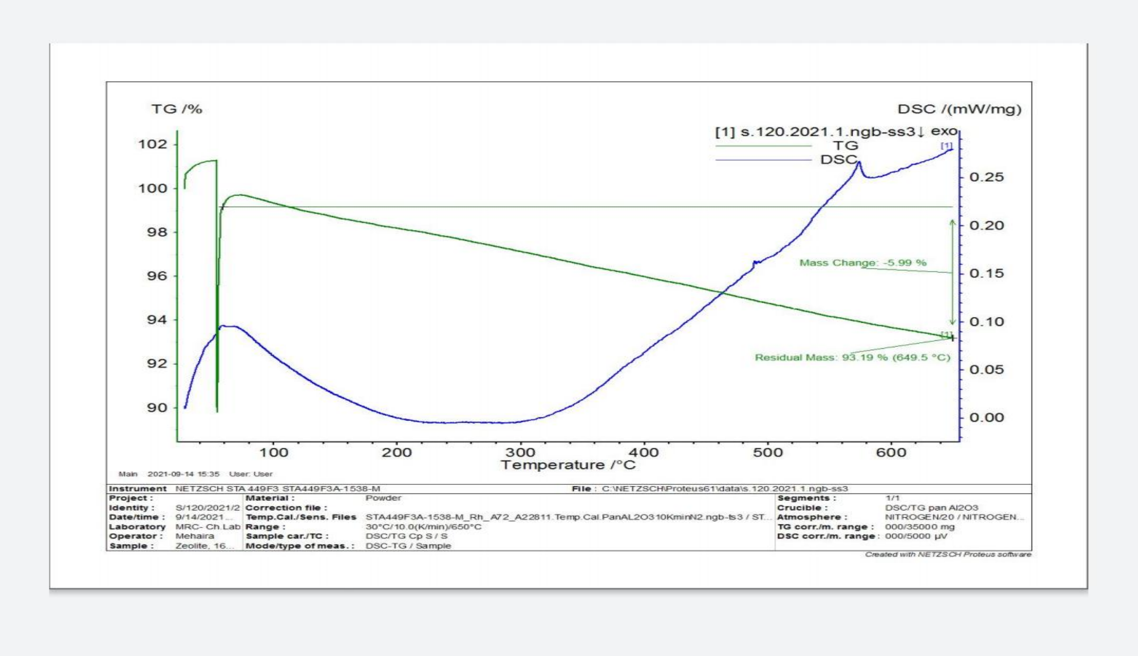
The results of the XRF analysis are presented in Table 3.1 The result shows that SiO_2, Al_2O_3, Na2O and K_2O are main components of natural zeolite with higher rate compared to EDS analysis result. The results of the EDS analysis also showed that the predominant exchangeable cations in the natural zeolite structure were Na^+, $Mg^{2+,}$ K+ and Ca^{+2}. The result of analyzed samples designated by numbers and a typical table are shown in appendix B.

Table 3.1: Chemical composition (wt. %) of the natural zeolite.

SiO_2	Al_2O_3	Fe_2O_3	Mg O	CaO	Na_2O	K_2O	L.O.I
70.24	13.51	2.24	0.58	1.60	1.01	4.89	8.22

3.1.5. Thermo gravimetric Analysis (TGA)

The thermal stability of the zeolite was obtained from thermogravimetric analysis (TGA) this is to measure changes in the physical and chemical properties whilst increasing temperature constantly and to obtain information about the mass loss during the thermal treatment process. Results obtained from TGA show that, zeolite sample was continually losing weight after heating up to 1000 °C (Figure 5.9). The main reasons of this are due to dehydration and dehydroxylation processes. According to Perraki and Orfanoudaki (2004) weight losses at 20–100 °C and 100–200 °C are due to hygroscopic water and loosely bonded water, respectively (Dyer, 1988; Gottardi and Galli, 1985).The results indicated that any loss below 400°C was corresponding to the zeolitic ,materials water. The total loss calculated from the thermo gravimetric analysis was 13 wt. %. Similar values were



Instrument	NETZSCH STA 449F3 STA449F3A-1538-M	**File :**	C:\NETZSCH\Proteus61\data\s.120.2021.1.ngb-ss3		
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Identity :	S/120/2021/2	**Correction file :**		**Crucible :**	DSC/TG pan Al2O3
Date/time :	9/14/2021...	**Temp.Cal./Sens. Files**	STA449F3A-1538-M_Rh_A72_A22811.Temp.Cal.PanAL2O310KminN2.ngb-ts3 / ST...	**Atmosphere :**	NITROGEN/20 / NITROGEN...
Laboratory	MRC- Ch.Lab	**Range :**	30°C/10.0(K/min)/650°C	**TG corr./m. range :**	000/35000 mg
Operator :	Mehaira	**Sample car./TC :**	DSC/TG Cp S / S	**DSC corr./m. range :**	000/5000 µV
Sample :	Zeolite, 16...	**Mode/type of meas. :**	DSC-TG / Sample		

Fig (3.4) Thermogravimetric analysis (TGA) of zeolite (20-900) ^{0}c

obtained by other authors (Korkuna *et al.,* 2006; Al-Dwairi, 2009; Ugal *et al.,* 2010)

3.1.6. Fourier Transform Infrared (FT-IR) Spectroscopy

The FT-IR spectra of the natural zeolite were carried out for materials analysis in this study. FTIR spectroscopy is used to probe the structure of zeolites and monitor reactions in zeolite pores. Initially the data were collected in the range of 4000-400 cm–1

Fourier Transform Infrared (FT-IR) Spectroscopy results

In this study the characterization of zeolites with transmission Fourier transform infrared spectroscopy (FT-IR) is described. Only the 1200-400 cm-1 region was investigated; this is where the all spectra showed remarkable changes. A broad band between 3500 and 3700 cm-1 in all the adsorbents is indicative of the presence of both free and hydrogen bonded OH groups on the adsorbent surface. In the OH stretching region, infrared spectra of zeolites provide a wealth of information on hydroxyl groups attached to zeolite structures (Li, 2005).

The 1015 cm^{-1}band corresponds to asymmetric stretching vibration modes of internal Si-O-Si bonds. The 796and 448 cm^{-1}bands are assigned to the stretching vibration modes of Si-O-Si. These results are similar as those abtained by other authors (Olad and Naseri,2010. Perraki and Orfanoudaki 2004).

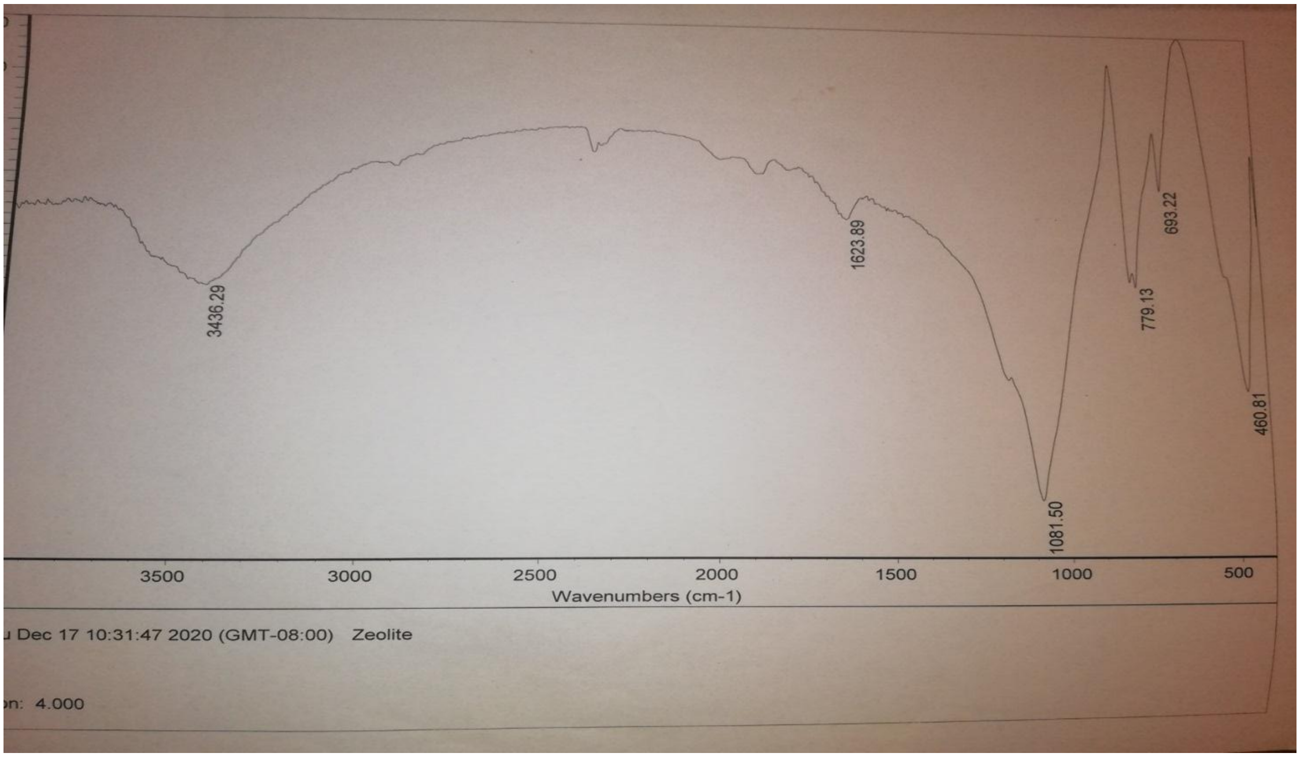
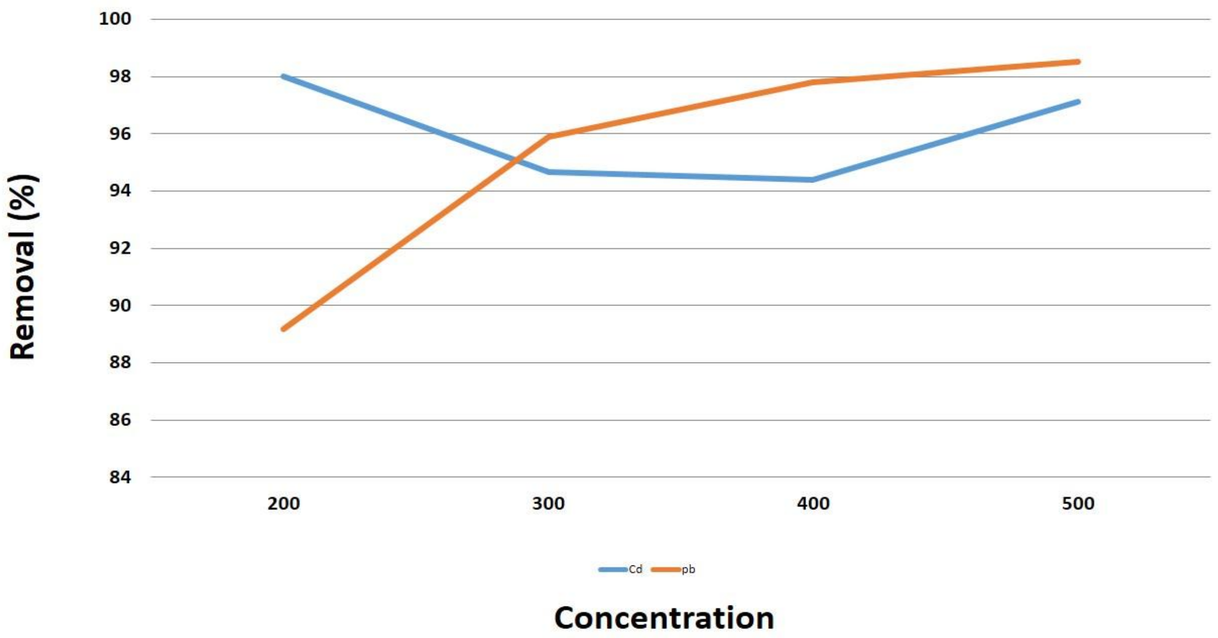


Figure .3.5: Shows the FT- analysis of IR spectra the as received

3.1.7 Atomic Absorption Spectrometer

The heavy metal ion concentrations in the waste water solution were determined using AAS . The standard solutions for metal analysis using the AAS were prepared from standard metal solutions to determine the amount of $Cd^{2+,}$ Pb^{2+} present in the solutions before and after the ion exchange shows the behavior of adsorbents, factors that affect the rate of adsorption and maximum effective capacity of natural zeolite towards $Cd^{2+,}$ Pb^{2+} ions removal. Ion concentration analysis using the AAS. After a mathematic calculation the results were presented



Fig(3.6) Removal of Cd, Pb with different concentrations by zeolite

Table(3.2) removal of Cd $^{2+}$ ion by natural zeolite

pH	Initial conc Ci (mg\L)	Final conc Ce (mg\L)	qe	Removal %
4	200	1.7	18.8	97.00
4	300	16	28.4	94.67
4	400	22.5	37.75	94.38
4	500	3.5	47.55	97.10

Table (3.3) Removal of Pb^{+2} ions by natural zeolite

pH	Initial conc Ci (mg\L)	Final conc Ce (mg\L)	qe	Removal %
4	200	32.5	26.8	89.17
4	300	16.5	38.4	95.88
4	400	11.0	48.9	96.80
4	500	1.8	38.8	97.50

The adsorption equilibrium can be defined as a completed state that takes place when the rates at which both molecules are adsorbed and desorbed onto a surface are equal (Richardson *et al*., 2002).

Table (3.4) provides a summary of several relevant literatures that showcase the various types of influent stock investigated in the removal of heavy metal ions.

Table (3.4) Existing trends in heavy metals

Zeolite	Removal trend	Reference
Sudan	Pb>Cd	This study
American zeolite	Pb>Cu> Cd> Zn> Cr> Co> Ni	Ouki and Kavannagh(1999)
Mexican zeolite	Pb> Cd> Cr	Vaca-Mier et al(2001)
Brazilinan zeolite	Cu>Zn> Pb> Ni>Co>Cd	Bosso and Enzweilier(2002)
Turkish zeolite	Cu> Fe> Zn	Kocasoy and Sahin(2007)

Two famous isotherm equations have been selected in the present investigation, namely; Freundlich and Langmuir (Sprynskyy *et al.,* 2006).

The Langmuir and Freundlich isotherm models are the most well-known. They describe the sorption equilibrium used for environmental studies (Hashem, 2007; Erdem *et al.,* 2004; Inglezakis *et al.,* 2002; Kocaoba *et al.,* 2007).

system, such as mineral type, solution composition, and pH of the solution (Inglezakis *et al.,* 2002)

The experimental data obtained from the equilibrium studies were correlated with the Langmuir adsorption isotherms. A linear plot was obtained when Ce/qe was plotted against Ce over the entire concentration range of metal ions from 50 to 800 mg/l. The values of the Langmuir model parameters for each cation are presented in

Table 3.5Freundlich and Langmuir parameters

Langmuir	Cd	Pb
Q_{max} mg\g	38.9	12
B	0.35	0.1
R^2	0.9419	0.99814
Freundlich		
K	15.4	33.5
N	2.1	7.83
R^2	0.8071	0.8621

Table 3.5 shows that the Langmuir isotherms for the adsorption of Cd^{+2}, Pb^{+2} from solution give a straight line. This means that the linear fits fairly good to the experimental results as revealed by the values of the correlation coefficients, r2, which range from 0.94 to 0.99. The Langmuir isotherm constants and their correlation coefficients r2 are listed in table 3.5

It can be observed from figure 3.2 that in each equilibrium study there is a variation in the equilibrium pH values with respect to the initially adjusted pH values. On the whole the equilibrium pH values are higher than the initially adjusted pH values. This may be due to the increasing initial Cd^{+2}, Pb^{+2} concentration. The highest experimental amount of Cd^{+2}, Pb^{+2} removed was at initial pH 4

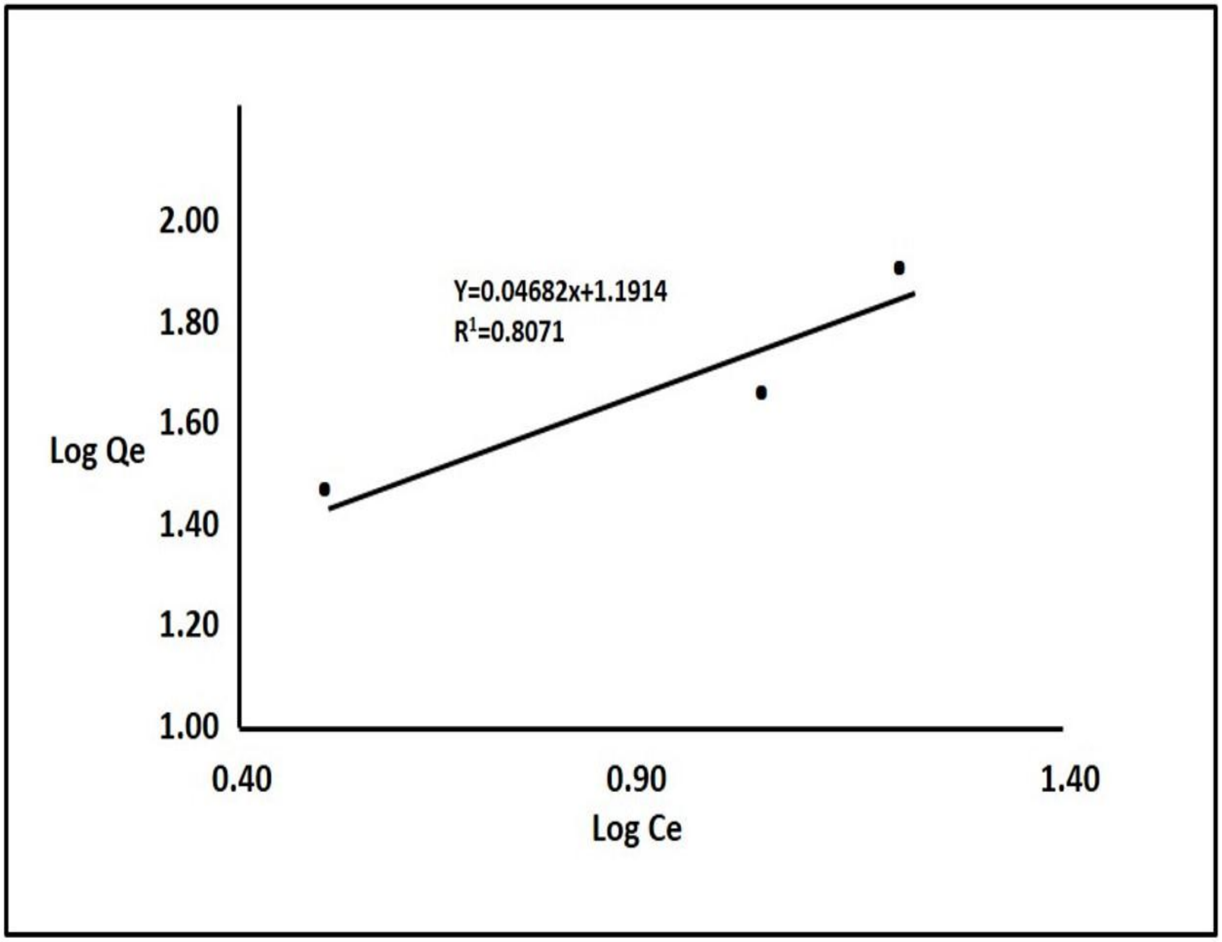


FIG 3.7 Adsorption isotherms of Freundlich which applied Cd by natural zeolite

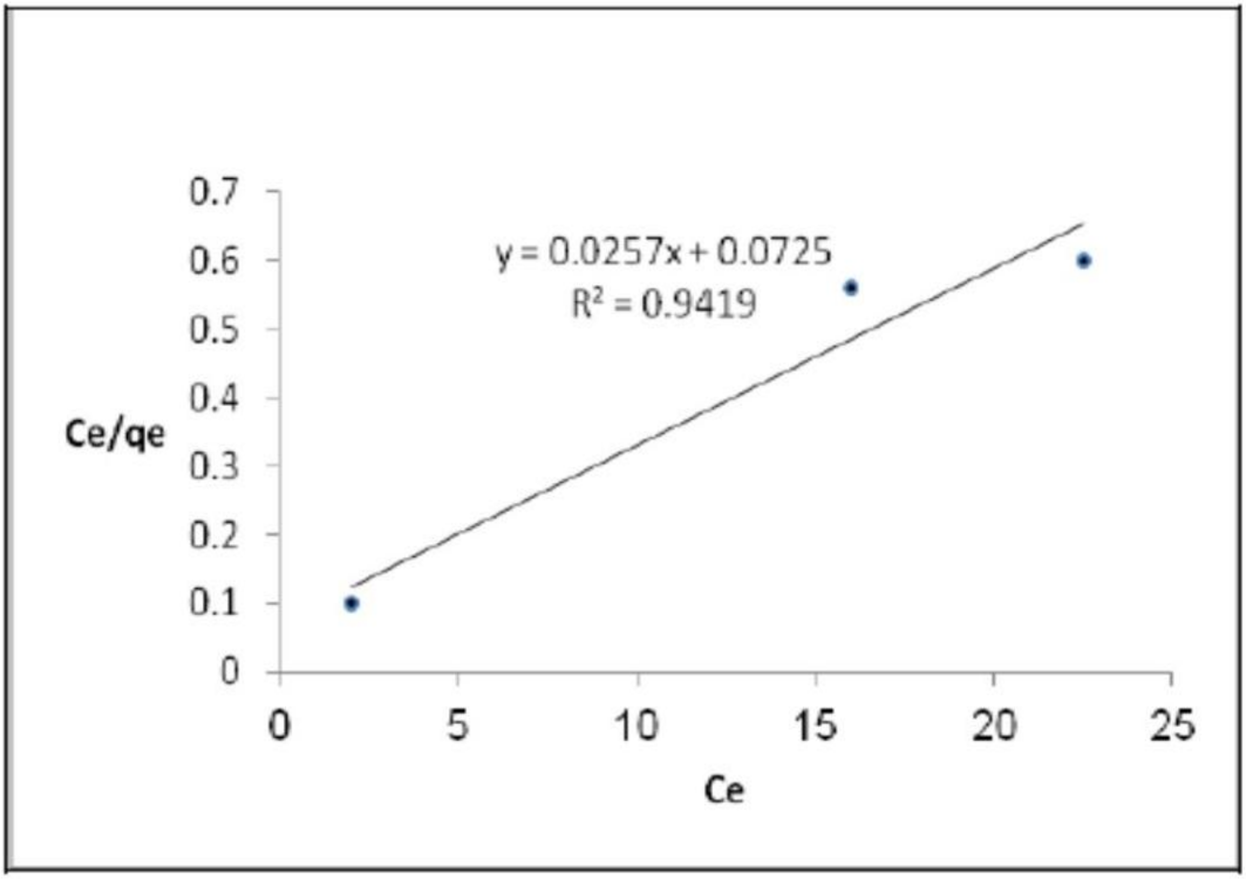


Fig. 3.9 Adsorption isotherms of Langmuir which applied in the Cd by natural zeolite

solution give a straight line. This means that the linear fits fairly good to the experimental results as revealed by the values of the correlation coefficients, r2, which range from 0.85 to 0.99. The Langmuir isotherm constants and their correlation coefficients r2 are listed in table 3.5

While the Freundlich isotherms A linear plot is obtained when lnqe is plotted against ln Ce over the entire concentration range of metal ions investigated and the values of k and n were calculated. The constants k and n were calculated for each cation

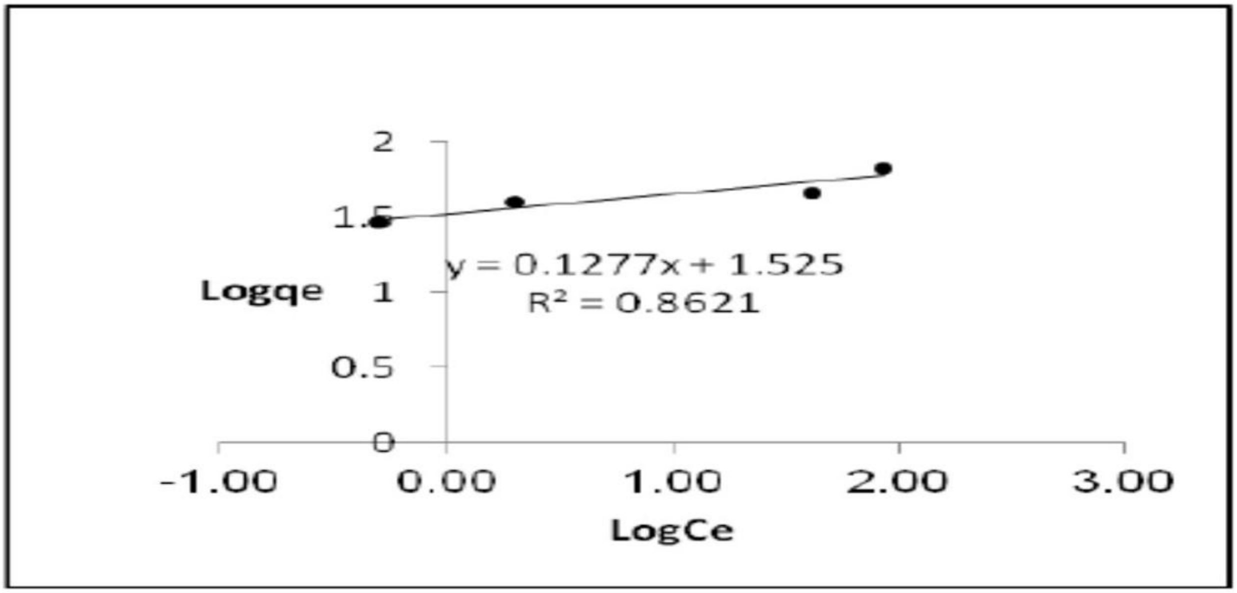


Fig 3.10 Adsorption isotherms of Freundlich which applied in the Pb zeolite

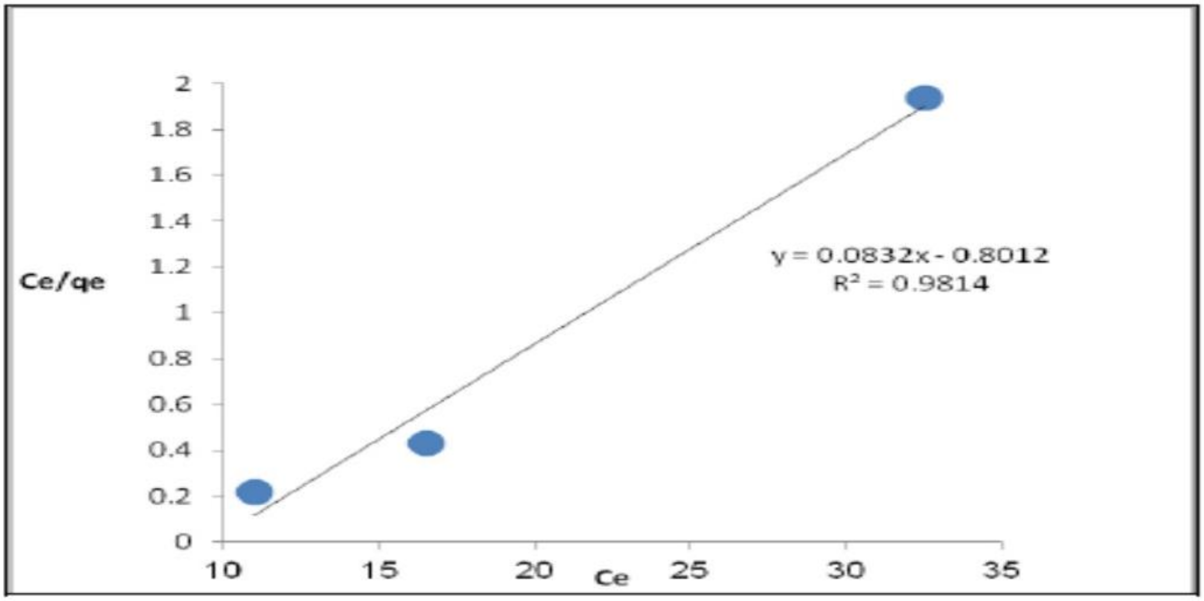


Fig (3.11) Adsorption of Langmuir which applied in Pb by natural zeolite

In this study different analytical techniques were used in order to provide more information on the characteristics of natural zeolite sample. The technological properties of zeolite products depend on the physical, chemical and mineralogical characteristics of the natural zeolite, which also controls the overall processing treatment of polluted effluents.

3.2 Effect of pH

Initial solution pH is a critical parameter for adsorption experiments. This parameter has a significant impact on heavy metal removal processes since it can influence and impact on adsorbent ability to remove metals and is connected with the competition of hydrogen (H+) ions with heavy metal cations for active sites on the adsorbent surface (Dimirkou, 2007; Inglezakis *et al.,* 2003; Hui *et al.,* 2005). An acidic solution can impact on both the character of the exchanging ions and the character of the adsorbent.

Solutions with different pH values were used as follows: 2, 4 and 6 ± 0.1 for the solutions.100 ml of the solution was contacted with 4g of natural zeolite for 360 minutes.The agitation speed was 150 rpm at room temperature. This experiment was initially done using fixed metal concentrations of $Cd^{2+,}$ $Pb+^{2}$cations. The results obtained are presented in Figure (3.12).

The results show that as the solution pH increases, the heavy metal removal efficiency also increases. This is due to the competition between the hydrogen ions and heavy metal cations for the same exchange sites (Inglezakis *et al.,* 2001; Wingenfelder *et al.,* 2005; AlvarezAyuso *et al.,* 2003) and electrostatic repulsion between the heavy metal cations in solution; as more hydrogen ions are adsorbed, the number of protonated zeolite surfaces increases (Cabrera *et al.,* 2005 The results show that the ion exchange process increases with an increase in pH up to a maximum value and the best heavy metal removal efficiency value was obtained between pH values of 4 and 6, while pH values below pH4 or above pH6 decreased the heavy metal removal efficiency, as shown in figure (3.12).

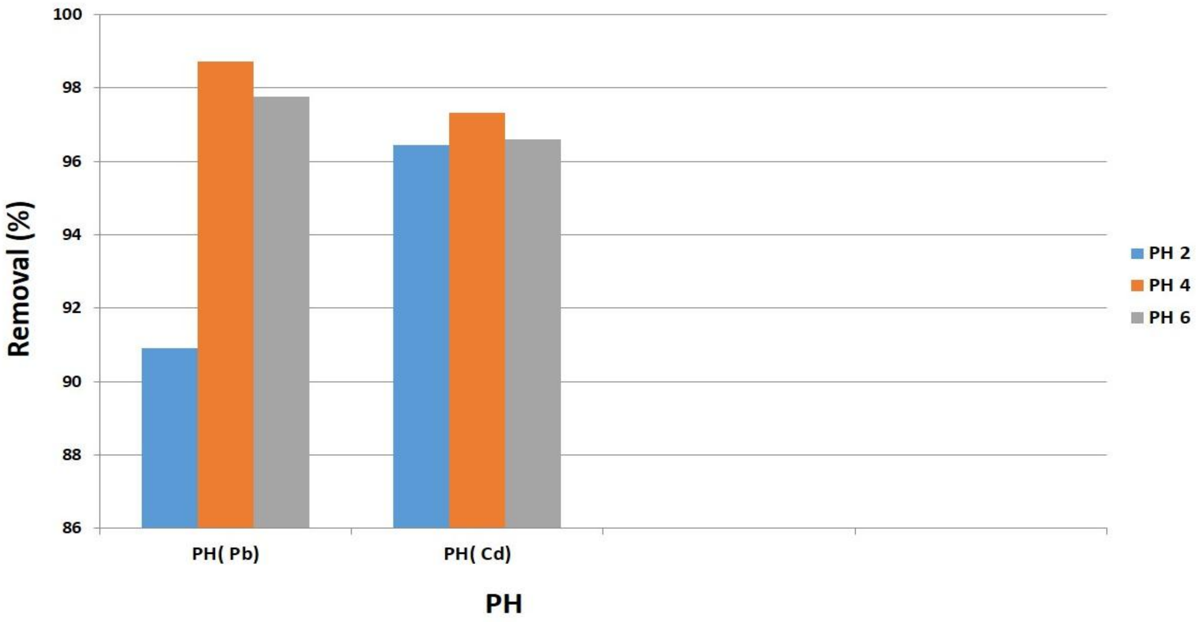


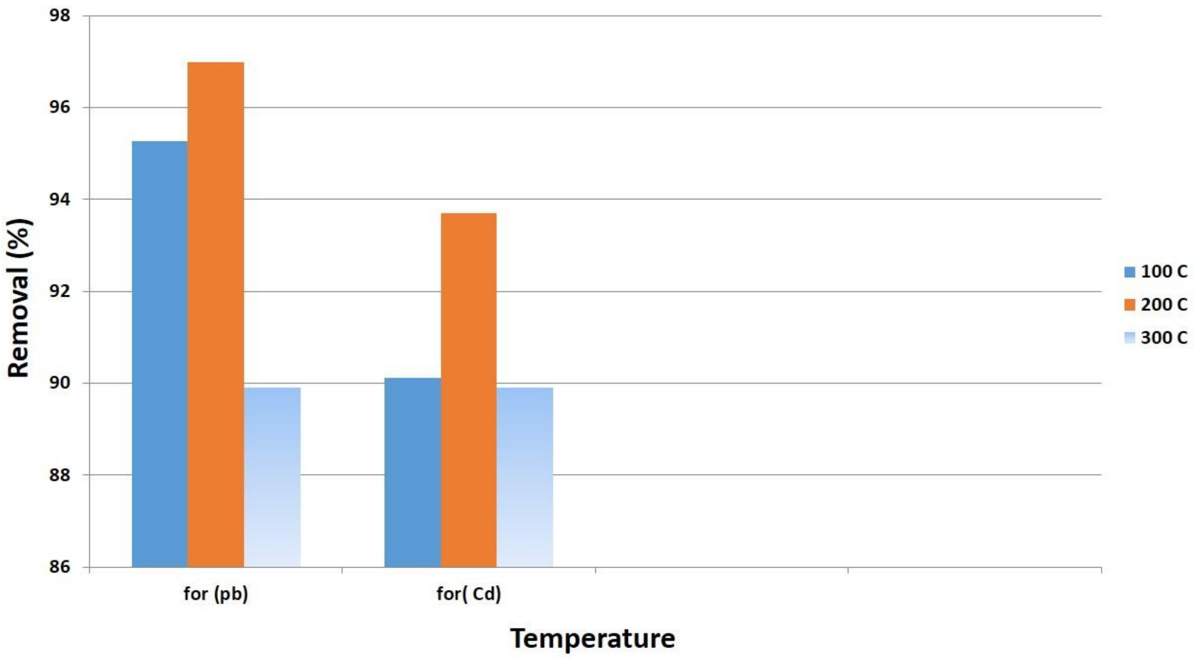
Fig.(3.12) Removal of Cd and Pb in different values of pH.

3.3 Thermal treatment of natural zeolite

The thermal treatment process of natural zeolite was performed by heating the natural zeolite sample in a furnace for 30 minutes at 100, 200 and 300°C. Although the thermal treatment process can affect the adsorption capacity, mostly up to $200C^0$, as the temperature rate increases more, there is a decrease in the level of the effect of the thermal treatment process on adsorption and the adsorption process gets slower.

It was observed that the thermal treatment samples at 200°C adsorbed more metal ions of $Cd^{2+,}$ Pb^{2+} ions from solution, around %50 better than the thermal treatment samples at 300°C adsorbed less metal ions as shown in Figure(3.13), but the efficiency decreased when zeolite was treated at very high temperatures.

The increase in the efficiency of heavy metal removal from solution as a result of thermal treatment may be due to the removal of water and hydroxyl groups from the natural zeolite structure. This removal of water and hydroxyl group results in a change in the surface area of the samples and also leaves the channels more vacant and available. Hence the adsorption capacity is improved since the heavy metal ions had better access to exchangeable sites within the natural zeolite (Turner *et al.,* 2000; Tatsuo and Nagae, 2003). However, the decline in the efficiency for zeolite treated at very high temperatures was related to the possible collapse of the zeolite structure and the loss of porosity, which reduced the activated surface area (Tatsuo and Nagae, 2005,Akdeniz *et al.,* 2007).



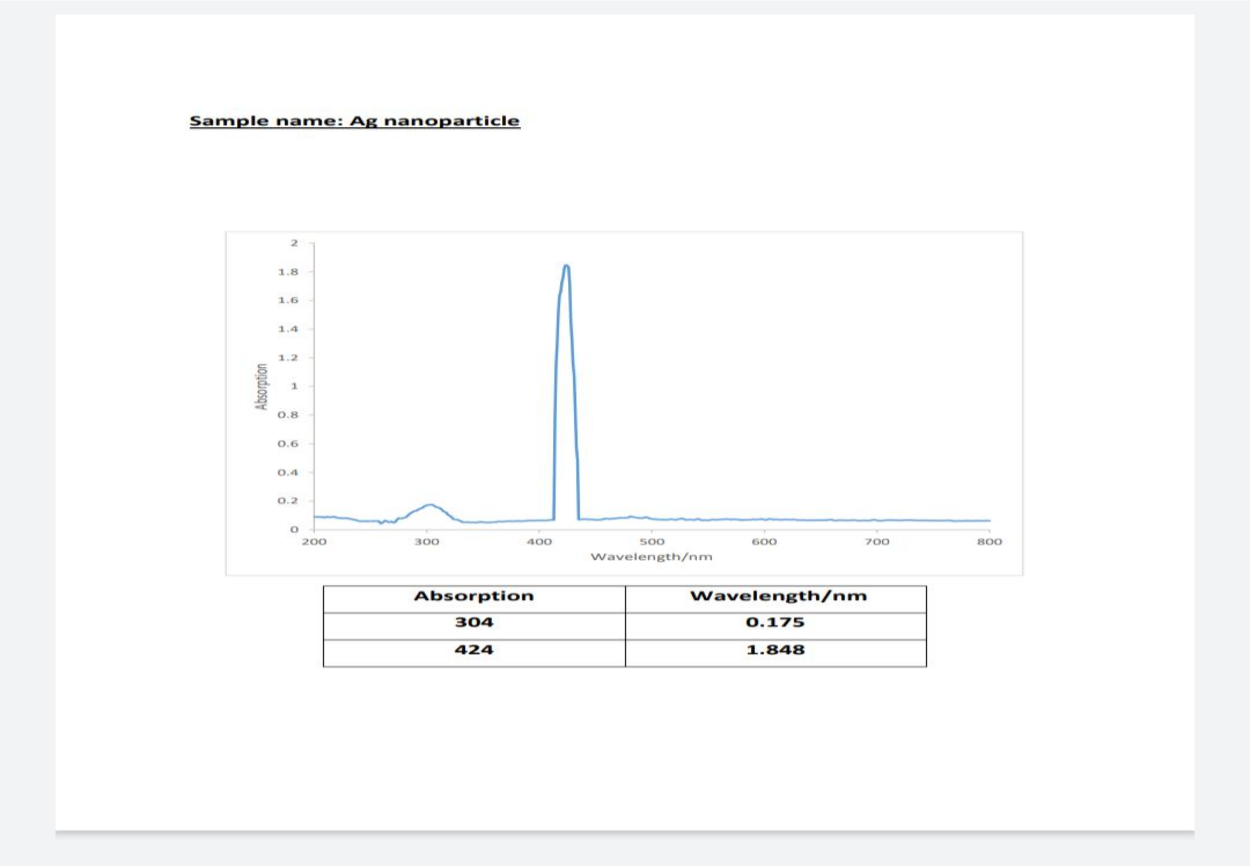
Fig(3.13) Removal of Cd^{+2} and pb^{+2} in different values of temperature

3.4Results of silver nanoparticle characterization

3.4.1The UV\visible

Figure (3.14) shows the uv-vis spectra of the silver nanoparticle in the range 300

600nm.The absorption band invisible light region (350-500)nm ,plasmon peak at 430nm is typical for silver nanoparticle. The plasmon peak and the full-width of half- maximum depends on the extent of nanoparticle aggregation (yamomto,s.etc2004)



Sample name: Ag nanoparticle

Absorption	Wavelength/nm
304	0.175
424	1.848

Fig(3.14) The UV- spectrum of nano Ag

3.4.2 Silver nanoparticle morphology

The SEM images, elemental analysis measurements confirmed the presence of silver nanoparticles in solution (figs 3.15) therefore, they exhibit distribution and capacity for aggregation depending on the sample

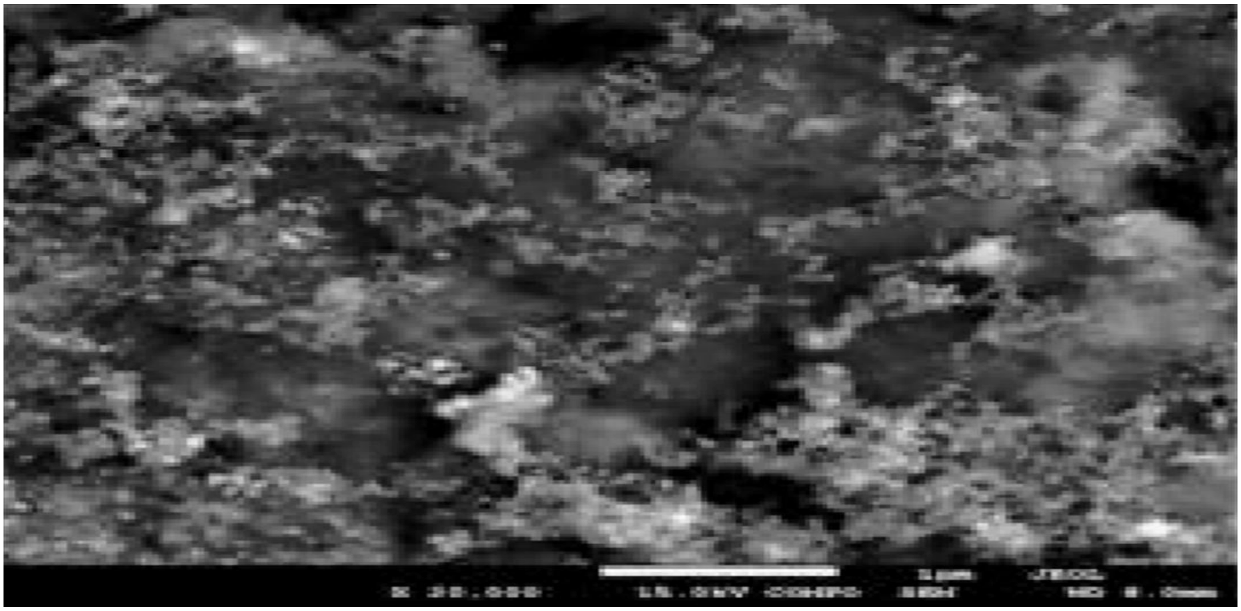
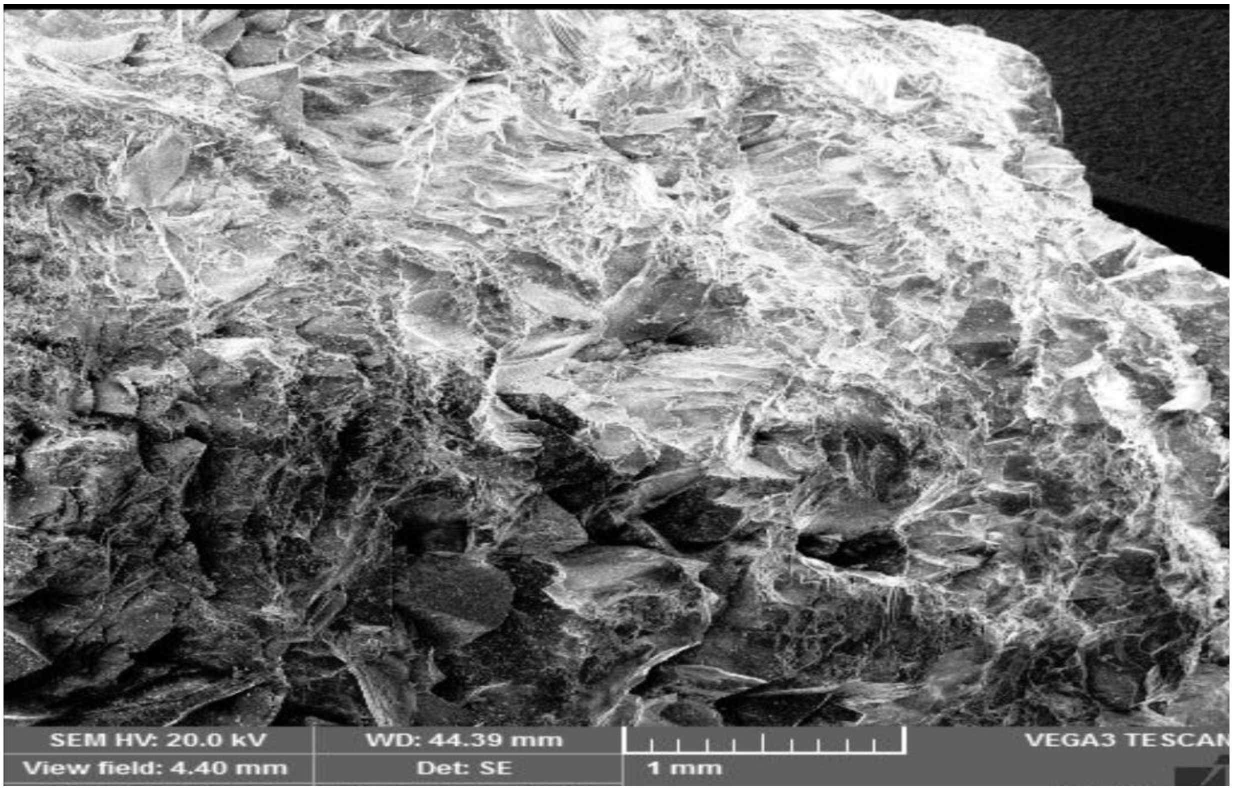


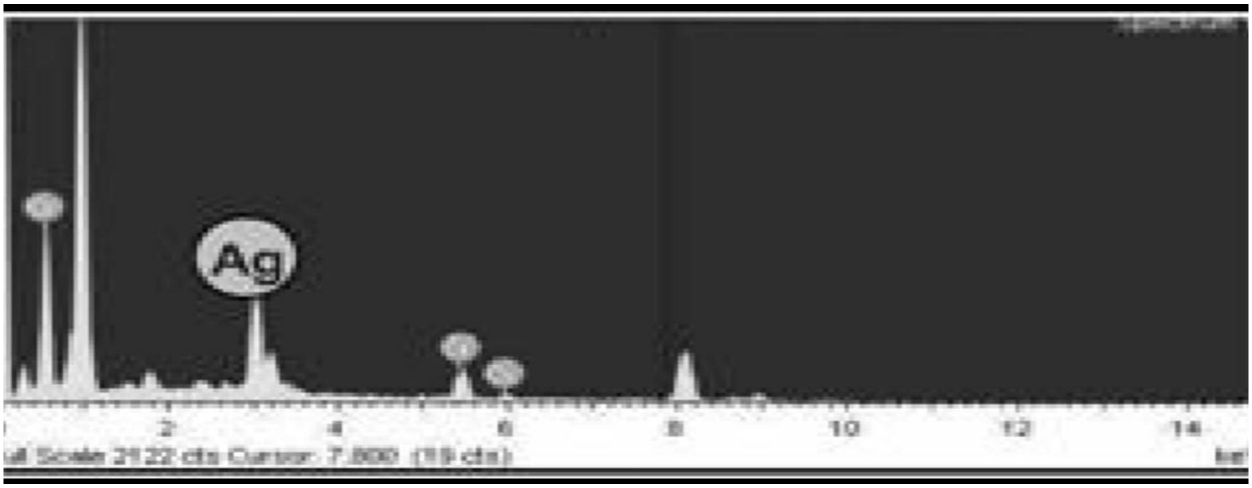
fig (3.15) SEM image of Ag nano

3.4.3 Morphology

The morphology characterization of the zeolite, before and after Ag deposition, was investigated by scanning electron microscopies (SEM) ,fig(3.16) show the SEM images of pure zeolite and Ag-zeolite , it was observed that the morphology of zeolite did not have noticeable changes after doped Ag nano of a low amount of Ag.



Fig(3.16) SEM image of nano-silver doped zeolite



Fig(3.17) EDS image of nano-silver zeolite

3.5 Removed of Cd, Pb ions using silver nano-zeolite

The heavy metal ion concentrations in the waste water solution were determined using AAS . The standard solutions for metal analysis using the AAS were prepared from standard metal solutions to determine the amount of Cd^{2+}, Pb^{2+} present in the solutions before and after the ion exchange shows the behaviour of adsorbents, factors that affect the rate of adsorption and maximum effective capacity of natural zeolite towards $Cd^{2+,}$ Pb^{2+} ions removal.ion concentration analysis using the AAS. After a mathematic calculation the results were presented either by plotting a presenting data in a table

Table (3.5) removal of Cd and Pb by nano silver zeolite

pH	Initial conc. Ci (mg\L)	Final conc. Ce(mg\L)	Removal%	Cd
4	200	0.5	98.50	
	300	2.0	97.43	
	400	11.0	95.90	
				Pb
4	200	0.3	98.73	
	300	3.8	98.00	
	400	16.5	95.88	

Batch studies were used in order to investigate the behaviour of both natural zeolite and silver nano zeolite and to understand the metal removal efficiency from solution. The results show that the uptake of heavy metal cations from solution using nana zeolite mostly occurs and the highest removal ratio of Cd^{2+}, Pb^{2+} ions was achieved > 98 % . The percentage adsorbed value of heavy metal cations from solution using natural zeolite passed 95% . Hence, the metal removal efficiency from solution of nano zeolite is higher than that of natural zeolite.

GENERAL CONCLUSIONS

In this work the specific aims of this study are reviewed to present an overview of the conclusions of the study and to make a critical evaluation. In this study, the potential of natural zeolite as a low cost adsorbent material was assessed for the removal of cadmium, and lead from synthetic industrial waste metal solutions. In order to determine this potential a number of experiments were carried out such as the characterisation of zeolites, as well as equilibrium.

This study also involved the development of nano silver zeolite from Al-Gadarff state as a source of production for these important industrial materials. The application of zeolites and nano zeolite, especially in the areas of ion exchange, is well known; hence the use of local raw materials such as AL- Gadarff is meant to offer an alternative and cheaper means of producing this unique and functional material. Finally, the experiments show that both natural and nano silver zeolites can be available in commercial quantities. However, nano silver zeolites are more attractive for some specific applications, while the cheapness of a natural zeolite may favour its use. This is why this research concentrated on using cheap and available materials, which can promote green technologies and reduce the operating costs and energy requirements and reduce the amount of the waste material. That makes the processes more economical and decreases the environmental impacts.

recommendations

The experiments presented in this thesis have shown that both natural zeolite and nano silver zeolite have the potential for use in treating wastewater. Although, the initial objectives were achieved in this study, there are some other aspects that were not within the scope of this study due to the limitations of time and availability of equipment. Therefore, further research and studies are needed, taking into account that modern industrial technologies require the use of zeolitic materials and sorbents with very precisely specified parameters. There are several areas of research that could give better perspectives in terms of possible applications. Some recommendations for further studies are presented below:

1- The initial solution pH, initial solution concentration as well as pre-treatment or modification of the adsorbent in the case of batch experiments was studied while The adsorbent mass, adsorbent particle size the effect of temperature on heavy metal removal capacity was not included. However, for applied purposes on a large scale, the actual impact of all of these factors needs to be covered since they act simultaneously in solution and obviously have an effect on each other.

2- Natural zeolite was chemically (using NaCl) and thermally treated in this study. However other modifications of zeolite with solutions of H_2SO_4, HCl,

$NaNO_3$, NH_4Cl, HNO_3, $CaCl_2$, and NaOH can be used to increase the capacity and efficiency of natural zeolite in treating industrial wastewaters. This could be a potential area of further study.

3- This study has only focused on the removal of cations and did not investigate the effect of anions on the capacity and effectiveness of natural zeolite. Industrial wastewaters contain both metal cations and anions such as sulfate ($SO_4^{2-),}$ phosphoric acid ($H_2PO_4^-$), chloride (Cl^-) and nitrate (NO_3^-). To remove anions from the water Zeolite surface has to be modified with a solution of inorganic salts (for example $FeCl_3$). Further studies could be carried out to determine whether zeolite can remove anions from solution and how the anions affect the heavy metal uptake capacity and efficiency of natural zeolite in treating industrial wastewaters.

5-In this study the equilibrium studies focused on the Langmuir and Freundlich isotherms models only, while other isotherms models were not investigated. There are other isotherm models available that could be used to describe the equilibrium sorption such as: the Sips, Temkin, Toth, Redlich-Peterson and Dubinine Kaganere Radushkevich (DKR) isotherms. These isotherms models are more general and do not presume a homogeneous surface or stable sorption potential.

6-Finally, a wide range of successful environmental applications of zeolite materials are available. On this basis a variety of contaminated soil, polluted air and wastewater treatment technologies could be developed. The improvement of the long-term chemical and physical stability of modified zeolitic materials and the combination of their sorption properties with contaminant destruction could also be the subject of further academic and industrial research.

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