Study of the Efficiency of Tuff and Modified JordanianNaturalZeolite to Remove the Iron Ions (Fe^{+2})offAqueous Solutions

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□ABSTRACT□

The possibility of using tuff and modified Jordanian naturalzeolite to remove the iron ions, a model component of heavy metals in underground water, off aqueous solution were studied. Bench-scale process was used to remove the iron ions off standard solutions and real under ground water. Different parameters affected the ion exchange have been investigated, such as concentration, modifier type and PH. Zeolite characterizations weredetermined as XRD, XRF, BET, TGA, andFTIRmethods.We found that the modified zeolite with sodium chloride had more effect than other salts and the iron ions exchange efficiency depends on concentration.Zeolite efficiency was affected by PH value. Time of sorption equilibrium achieved within 250 min. The results agree with Langmuir model.

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دراسة كفاءة الزيولايت الطبيعي الأردني الخام والمعدل في ازالة ايونات الحديد (Fe^{+2})) من المحاليل المائية

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□ملخّص□

درست امكانية استخدام الزيولايت الطبيعي الأردني الخام والمعدل لإزالة ايونات الحديد من المحاليل المائية والذي يمثل احد المعادن الثقيلةالموجودة احيانا في المياه العذبة الجوفيه. حيث تم استخدام الفلتره الثابتة لأجراء تجارب ازالة ايونات الحديد المحضر في محاليل معياريه وكذلك الموجود في مياه جوفيه حقيقتيه. درس تأثير بعض المتحولات على عملية التبادل الأيوني مثل: التركيز ، الماده المستخدمه في التعديل ودرجة حموضة المياه (PH)   وقد تم استخدام الزيولايت الصناعي (A ٖ 4)للمقارنة .

حددت مواصفات الزيولايتألمستخدمتحديد المساحه السطحيه النوعيه وفق طريقةBET، وبواسطة بعض الطرائق الأخرى مثل: XRD , XRF, TGA ,FTIR.

وجد ان الزيولايت المعدل بكلوريد الصوديوم هو الأكثر فعاليه مقارنه بالأملاح الأخرىوان كفاءة التبادل الأيوني لأيون ألحديد تعتمد على التركيز، كما وجد ان قيمة PHتؤثر بشكل واضح على فعالية الزيولايت.لقد كان زمن الاتزان الكيميائي بعد 250 دقيقه ووجد ان النتائج تتطابق مع نموذج لانغمير (Langmuir).

الكلمات المفتاحيه: التف الزيولاتي الأردني(الفلبسايت)، المعادن الثقيله، التبادل الأيوني، نموذج لانغمير، توصيف الزيولايت.

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INTRODUCTION:

Zeolites are group of hydrated aluminum-silicates of the alkali or alkaline earth metals(sodium, potassium, magnesium, calcium). Zeolites havea three–dimensional crystalline framework of tetrahedral silica or alumina anions strongly bonded at all corners and contain channels filled with water and exchangeable cations (Mumpton, 1978). These tetrahedra are the basic building blocks for various zeolite structures. Zeolites are also characterized by low mining cost, availability, bulk density and high resistance to alteration (Mercer and Ames,1987).

Jordan is rich in natural rocks and minerals..The first zeolite deposit(Philipsite) was discovered in 1987(Dwiri,1987). Zeolitic tuff is widely distributed in Jordan. The North Arabian basalt plateau covers an area of about 11,000km^2 (called Harratalsham) in the northeast of Jordan and extends northwest into Syria and southeast into Saudi Arabia(Khoury et al., 2003).Phillipsite, chabazite and faujasite are the most abundant zeolite minerals found in the Jordanian zeolitic tuff. The zeolite content in these tuffs varies from 20% to 65%. Using simple mineral processing routes, zeolite concentrates with grades up to 90% were achieved(NRA, 2013)

Heavy metals are well known toxic substances. They are found in many types of industrial water and to certain extend in ground water.Therefore, their removal from water is required prior to intended use. Many techniques exist for treating heavy metals from (waste)water; the most common ones are adsorption and ion exchange.

Ion exchange is a process by which ions held in porous, essentially insoluble solid exchange for ions in a solution that is brought in contact with solid. The ion exchange properties of clays and zeilites have been recognized and studied for more than a century (Skoog et al. 1994; Harvey, 2000). The main advantage of ion exchangeover chemical precipitation are removal of metal value, selectivity , less produced sludge

The first attempt for purifying water using naturally purifying materials containing zeolite were performed in the nineteenth century (Breck 1974). This appears to be the first practical applications of zeolite due to its cation exchangeable properties. It has been reported that the availability of natural zeolites in many countries provide low cost treatment by ion exchange process (Elbishtawi et al, 1997). It has also been found that NaCl pretreated zeolite material improve heavy metals uptake because of the improvement of the ion-exchange properties of the zeolite (Inglezakis, 2005). Zeolitic tuff can be also treated with other chemicals or heat treated in order to improve its surface functional groups.

This work aims at studying effect of different parameters on the removal efficiency of certain selected heavy metals by natural volcanic tuff from Northern east of Jordan.

MATERIALS AND METHODS:

3.1 Materials

Philipsite rich natural zeolite mineral used in this study was obtained in form of volcanic tuff from Artain area, located in the East west part of Jordan. Represented Zeolitic tuff samples with grin size of 0.595-1.410 mm(Sieve No 30-14/28-12 mesh) was used for all tests. Preparation of zeolite as sorbent material for the purpose of this study was prepared following mortar crushing, washing, drying at 105 C° for 24hrs, and then sieving into the required grain size. It, then, underwent treatment with 2N of NaCl, in which 1 g of zeolitic tuff were added to 100 ml of 2N NaCl followed by shaking for 24 hrs, eventually the zeotitic tuff is converted to the Na-form, such that the exchangeable cations

in the zeolitic tuff structure were replaced by Na^+ ions. After shaking , the zeolitic tuff samples were washed several times with deoinised water in order to remove excess sodoim chloride and calcium chloride. Modification has been also done by calcium chloride and hydrochlic acid solution of PH 5.

Nitrate salts of metals were used to prepare 1000 ppm stock solutions based on Standard Methods for the Examination of Water and Wastewater (APHA, 1995). Iron was prepared from ammonium iron(II) sulphate-6-Hydrate (Riedel-de Haen, Germany).Concentrated Hydrochloric and sulfuric acid solution(36%HCl and 96% H_2SO_4 from Scharlau) diluted to 5% v/v was used for washing glassware and polypropylene sample bottles.The pH of the samples was adjusted by using either diluted (0.1 M) solutions of hydrochloric acid orsodium hydroxide (0.1 N NaOH). All chemicals are of analytical grades and all solutions and dilutions were made using deionized water.

Synthetic zeolite of type 4A, grade S14, 8-12 mesh, beads, effective pore size 4 Angstrom (Base: Aluminium-Silicon, Cation : Sodium. Product of W.R.Grace&Co. Fisher Scientific, Davison chemical Division,USA) was used.

3.2- Instruments

Total dissolved solids and pH values were measured with a WTW(Wissenschaftlich-TechnischeWerkstatten, germany) and pH 330 device, respectively. All metal analysis were measured using Atomic Absorption Spectrometry (AAS 96,Varian). The experiments were performed using a shaker (GFL 1083). After preparation of raw and modified zeolite rich mineral samples,thermal and adsorption-related properties of the samples were determined.X-ray diffraction (XRD) by X-Ray Difractometer equipped with Cu Kα radiation (Ultima IV, Rigaku, Japan). Thermal analyser (TG 209 F1-, Netzsch,germany) was used for thermal analyses of the samples.Fourier Transfer Infra Red (FTIR) was obtained by IR Affinity-1 (Shimadzu, Japan).XRF by XER-1800, Shimadzu. True density(skeletal density) was measured by Ultrapyncometer 1000 (Quanto Chrome, USA).Surface area Adsorption and desorption curves were determined by using N2 as adsorptive by NOVA 2000 Series, Quanta Chrome, USA.

3.3- Bench-scaleion exchange test

Sorption tests for iron and other metals were conducted at roomtemperature at different metal concentrations (namely 200, 300,400,500, 750, and 1000 ppm). Solutions were prepared using nitrate salts.A 100-ml metal solution mixed with 1 g zeolite were maintained in a shaker at a preset speed (rpm), at room temperature (25 ± 2^oC). The initial pH solutions was adjusted using either 0.1 MHClor 1 N NaOH. At the end of the sorption process, the samples were filtered through 0.45 Whatman filter paper. The filtrate wasanalyzedusing AAS against iron. Blank tests were conducted without adsorbent and metal concentration was the same before and after the shaking process indicating no adsorption at the surface of the flask nor metal precipitation at all metal concentration and operating conditions.

The quantity of adsorbed heavy metal on the zeolite, i.e. uptake,was calculated by the difference of the initial and final equilibrium concentration following the equation :

$$q_e = \frac{C_i - C_f}{m} \times v$$ ……………………………………….. (1)

where $q_e$is the quantity of adsorbed heavy metal on the zeolite (mg ironmetal/gm zeolite), C_i is the initial metal concentration in the solution and C_f is the equilibrium or final metal concentration in the solution(mg/l)., m is the amount of used zeolite (g) and $v$is

the volume of used solution (l).The percent of metal adsorption is calculated by the following equation:

$$\text{Adsorption \%} = \frac{(C_i - C_f)}{C_i} 100\% \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

3.4- Equilibrium isotherm models

Langmuir isotherm models the single coating layer on adsorption surface. This model assumes that adsorption takes place at a specific adsorption sites at the surface of adsorbent. It also assumes that the attraction between molecules decreases as they are getting further from the adsorption surface (Ünlüa and Ersoz, 2006). The linear form of Langmuir isotherm can be written as:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

where q_e is the metal concentration on zeolite at equilibrium(mg of metal ion/gm of zeolite); q_{max} (mg/gm) and K_L are Langmuir constants related to the maximum adsorption capacity (corresponding to complete coverage of available adsorption sites) and adsorption energy (equilibrium adsorption constant). These constants can be obtained from the slope and intercept of the linear plot of C_e/q_e versus C_e.

Freundlich isotherm (Freundlich, 1932) is the other often used isotherm model; it considers adsorption on heterogeneous surfaces. The linear form of Freundlich model can be written as:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e$$

where K_f and n are Freundlich constants related to sorption capacity and sorption intensity, respectively. These constants can be determined from the slope and intercept of linear plot of $\log q_e$ versus $\log C_e$.

The isotherm studies were conducted at 25^oC by varying metal concentrations;namely 200,300,400,500,750, 1000 ppm.Each of these metal solution was mixed with 1 g zeolite for 240 minutes to ensure equilibrium.

Results and Discussion:

4.1- Characterization of natural raw zeolitic tuff sample:

The used zeolite has been characterized by BET, X-Ray Diffraction (XRD), Thermo gravimetric analysis(TGA), Fourier Transform Infra - Red Transform(FTIR) Techniques in addition to Xray Fluorescence

4.2- Surface area and Particle Size Distribution

The zeolite particle properties can be shown in table (1)

Table (1) Summary of particle properties						
Zeolite Type	Particle Dia (µm)	Mean Dia (µm)	BET pore volume (cc/g)	BET SA (m^2/g)	Skeletal Density (kg/m^3)	Particle Density (kg/m^3)
Raw tuff	595-1410	1004	0.07	41.2	2700	1800

Results in table 1   show that zeolite have specific surface   area 41.2 m^2/gm determined by BET method .   True and particledensity was 2700 and 1800 respectively and the sample has pore volume 0.07 cc/g.Surface area plotsof raw zeolitic tuff particles can be seen in Figure 1.
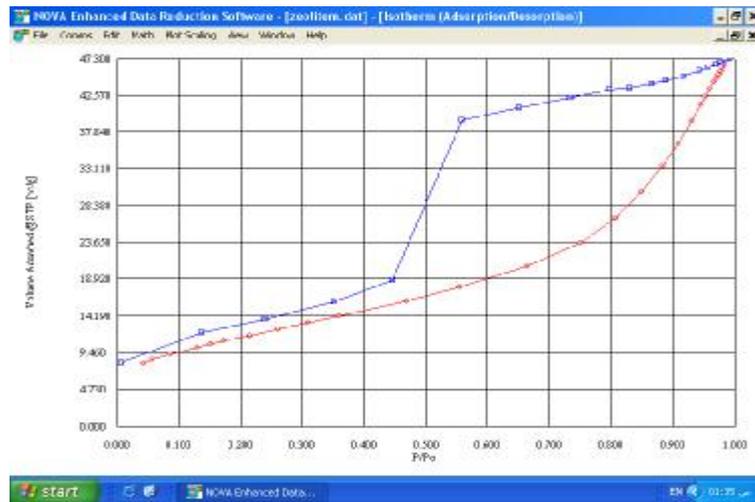
Figure(1) BET surface area of raw tuff

Fig1 shows N2 adsorption curve of zeolitic tuff sample which found of type II and IV according to Sing et al (1984). It can be seen that the sample contains pores of meso type as a result of Loop Hysteresis in the range of middle relative pressure and low percent of micro pores in the range of low relative pressure.

4.3- X-Ray Powder Diffraction Analysis

The X-ray diffraction results have indicated that the examined zeolitic tuff sample is rich in Phillipsite ($Na_{0.13}$ $(NH4)_{1.19}$ ($Al_{1.5}$ $Si_{2.5}$ O_8) 1.92 H2O along with hematite and pyroxene. Jordan natural zeolite could contain also calcite with average of 7%.(A.Abu Esnouber,1996) the XRD chart is shown in Figure (2).

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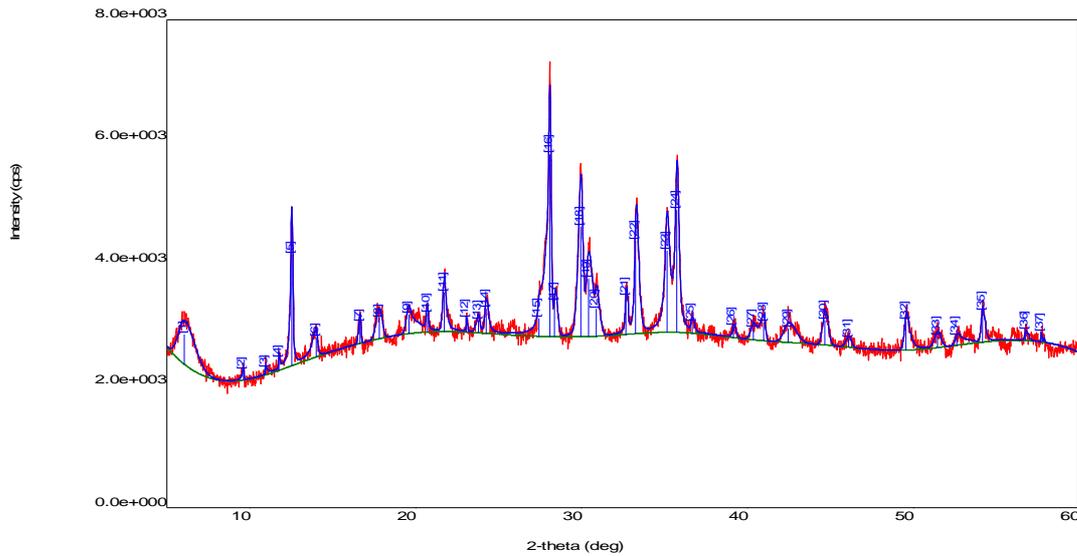
Fig(2) XRD Powder Diffraction Chart

Table(2) Phases comprising used sample of Jordan zeolite

No.	2-theta(deg)	Height(cps)	Int. I(cps deg)	Phase name
10	20.711(11)	305(23)	44(9)	Phillipsite(1,0,1)
12	23.04(5)	220(19)	17(5)	Unknown
14	24.25(3)	392(26)	117(12)	Hematite,
15	27.41(3)	293(22)	121(80)	Clinopyroxene,
17	28.37(2)	564(31)	172(41)	Phillipsite(1,3,1)
22	33.252(10)	1525(50)	510(11)	Hematite,
23	35.131(11)	1326(47)	620(21)	Clinopyroxene, syn(1,3,-
24	35.737(10)	1999(58)	734(20)	Hematite,
34	52.60(12)	140(15)	111(18)	Clinopyroxene,
37	57.72(5)	146(16)	13(9)	Hematite, syn(0,1,8)

4.4- X-Ray Fluorescence

The chemical composition of Jordan zeolite can be seen in table 3 below. Calculated Silica to Alumina ratio is 3 while Loss on Ignition(LOI) which represents water content found as 7.24. The same approximate percent found from TGA findings.

Table(3)Chemical composition

Oxide	SiO_2	Al_2O_3	Fe_2O_3	MnO	TiO_2	CaO	K_2O	P_2O_5	MgO	Na_2O	LOI	S/Al
Wt%	41.26	12.41`	15.6	0.25	2.86	7.26	1.94	0.63	7.82	2.73	7.24	3

4.5- Thermal properties

Thermal behavior of zeolitic tuff was investigated by using TGA. The TGA thermogram is given in Figure (4). The temperature ranges are 50-110, 110-350 and 350-500°C corresponding to the loss of external, loosely bound and tightly bound water, respectively. The weight losses were found as 5, 1.8 and 1.0% by weight for the external, loosely and tightly bound water for the examined zeolitic tuff. The 800-1000°C could be also related to the loss of CO_2 as a result of decarbonation of calcite.

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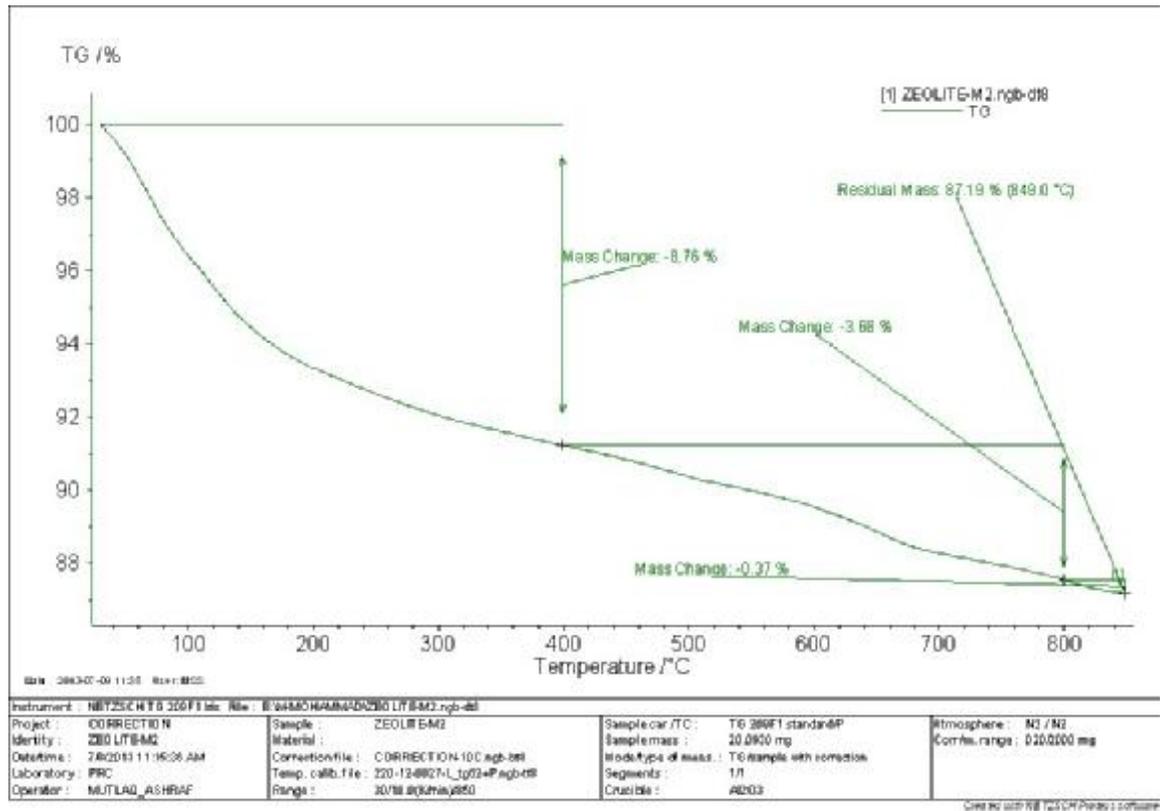
Fig (3) TGA Thermogram of zeolitic tuff

4-6- Fourier Transform Infra – Red Transform(FTIR)

The structural information of the zeolite tuff was obtained by FTIR spectroscopy Figure (5) shows H-bonded O-H stretching at 3365-3381cm^{-1}, H_2O bending at 1645.28 cm^{-1}, 1413.82 cm^{-1} asymmetric stretching vibrations of the carbonate in the sample, 1020.34 cm^{-1} strong band due to phillipsite symmetric stretching vibration of silicate group, 750.31 cm^{-1} symmetric stretching vibration of metal oxides (MO), and 459.06 cm-1 bending vibrations for single 4 rings zeolites such as phillipsite. Calcite are normally present in Jordan zeoilite.
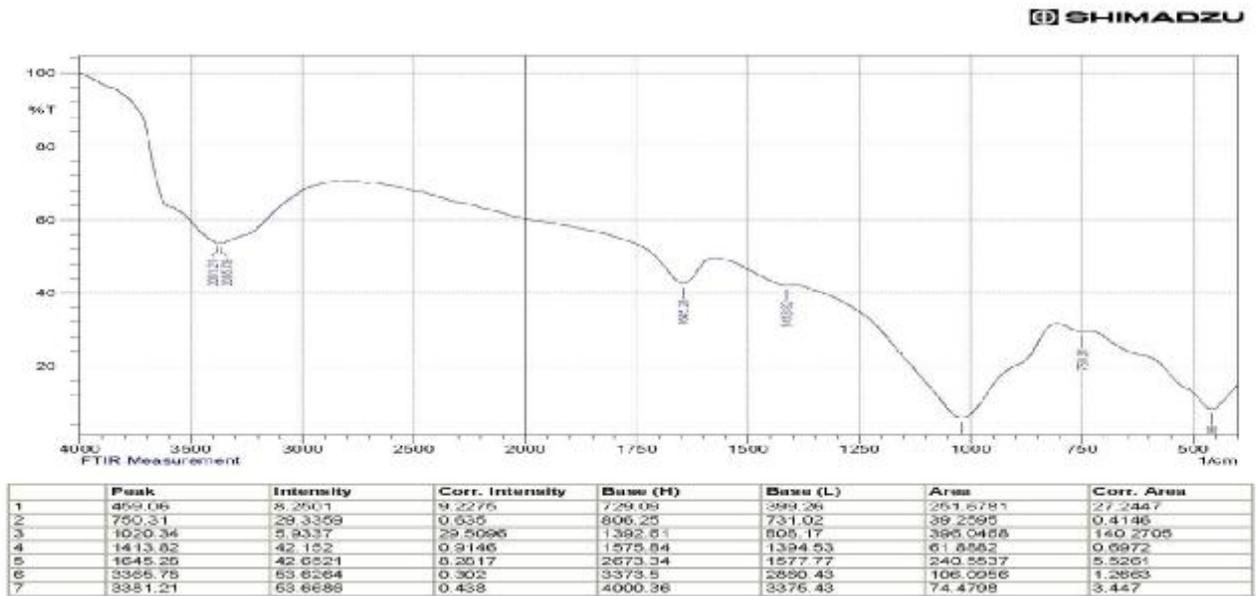
Fig (4) FTIR spectroscopy of zeolitic tuff

4-5-Ion Uptake Efficiency

4-5-1 Equilibrium time

It can be seen in Figure (5) that the sorption takes place in two steps. The first step takes place in the first 4-5 hours (240-300 minute). Later in the second stage , the concentration is relatively remains constant.
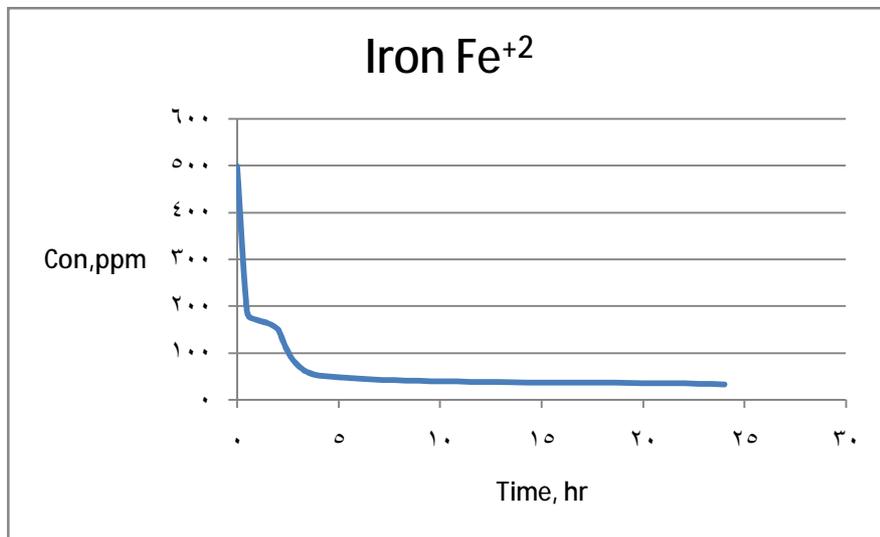
Fig(5) Equilibrium time of Iron

4-5-2- Adsorption Isotherm

1000 ppm Fe standard stock was prepared by dissolving the required amount of ferrous ammonium sulphate(Fe $(NH4)_2$ $(SO4)_2$. 6 H_2O). Concentration of 200-1000 have been also prepared by dilution from the stock. PH adjusted to 3-4 while some concentrations kept at PH1.5-2.

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100 ml of each concentration put into 100 ml flask and 1 gm of zeolite was added then mixed together in the shaker for 4 hrs. After that , the slurry is filtered and remaining ion concentration was measured by flame atomic absorption spectrometry.

Table (4): The R^2, q_m, K_L, K_F and n values obtained from Langmuir , Freundlich plots for iron.

Langmuir		Zeolite Form			
		Raw	Na-Z	Ca-Z	H-Z
Qmax		12	65	22	47
KL		0.22	0.1	0.32	0.22
R^2		0.9572	0.9814	0.9709	0.8006
Freundlich		Raw	Na-Z	Ca-Z	H-Z
Kf		33.5	2	80	0
N		7.83	1.07	3.6	0.31
R^2		0.8621	0.8169	0.4928	0.5999

(a)(b)

(c) (d)
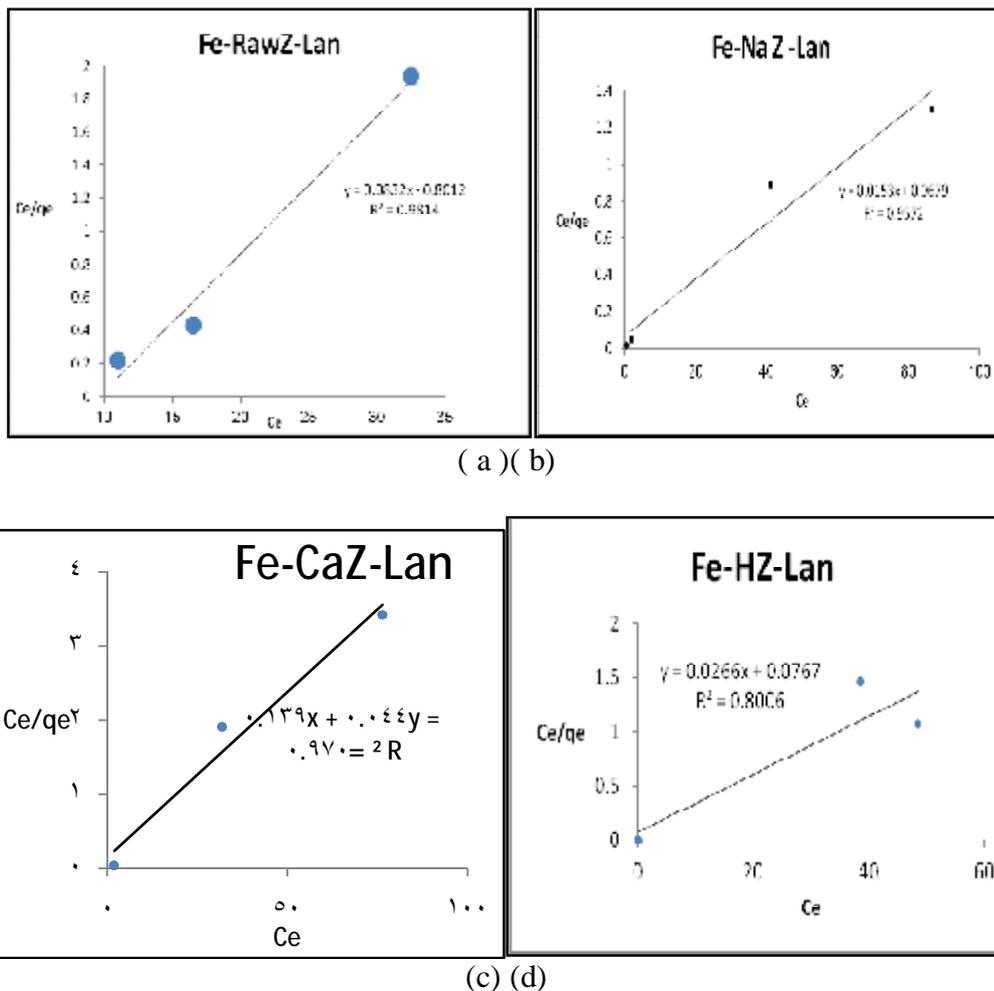
Fig(6) Langmuir isotherm plot of a- raw zeolite b- sodium modified zeolite c- calcium modified zeolite and d- acid modified zeolite.

It can be noticed from Table (4) that value of Qmax increasing in case of NaZ to 65 mg/gm. This is attributed to the fact that complete exchange of sodium ions with that in zeolite has been taken place during modification. Another reason is that sodium ions mobility is high which enable it to reach and replace high quantity of Fe^{+2}ions.

Whereas in case of calcium modified zeolite , the value of qmax is greater than the raw material but less than NaZ zeolite. This can be interpreted by the replacement of each calcium ion to two sodium ions from the zeolite structure during modification process, which is not achieved totally . From other side, mobility of calcium ions is less than that of sodium ions, consequently , exchange with iron ions is less thus Qmax decreased.

it is also noticed in all samples that correlation regression factor (R^2) is reaching acceptable values whereas this factor in acid modified sample is very low, despite the value of Qmax is greater than the raw and less than the NaZ sample. This due to possibility of attacking aluminum atoms by acid protons to aluminum at low PH during modification at low PH of 3-4. This leads to partial or complete damage of zeolite main structure which is called (dealumination).

Finally, the table shows that value of R^2 obtained by Freundlich is low which indicates that iron adsorption is not fitting with this model.

Langmuir isotherm plot of raw zeolite, sodium modiefied zeolite, calcium modified zeolite, and acid modified zeolite was determined (Figure 6).

4-5-3Comparison between materials

To investigate the efficiency removal of natural and modified used zeolite, control material of synthetic zeolite has been tested to compare removal efficiency of Jordan zeolite with synthetic zeolite, the results can be seen in Table (5) which shows that sodium modified natural zeolite has approximate efficiency of synthetic one.

Table (5) Data of Qmax and CEC of natural and synthetic zeolite

Zeolite Type	Concentration	Qe(mg Fe/g Z)	Qmax(mg/gmZ)	CEC(meq/gmZ)
Raw	300	26.75	12	0.42
	500	48.90		
	750	74.95		
Na-Z	300	29.95	65	2.32
	500	45.90		
	750	66.35		
Syn 4A	300	30.00	75	2.67
	500	47.40		
	750	74.95		

4-5-4 Effect of PH

Some experiments run at PH 3-4 whereas others run at PH (1.5-2) The results of experiments run at PH :1.5-2 showed that no any removal of heavy metals which confirm that zeolite is not working at low PH. This attributed to the damage of structure of zeolite at low PH. Acid is reported to cause leaching of Al^{3+} from zeolites, which compromises the exchange capability of the zeolite The results are complying with studies outcomes of (Bailey et al., 1999)

4-5-5Effect of concentration

The adsorption of Fe^{+2} ions onto jordan natural zeolite as function of their concentrations was studied at 25 C by varying the metal concentration from 200-750 ppm.

The results are shown in Figure(&). The percentage removal efficiency for Fe^{+2} is generally decreased with increasing of concentration. These results indicate that energetically less available sites become involved as metal iron concentration incresed Similar finding are reported by Alanbar(2007) and Karthikeyan(2005)
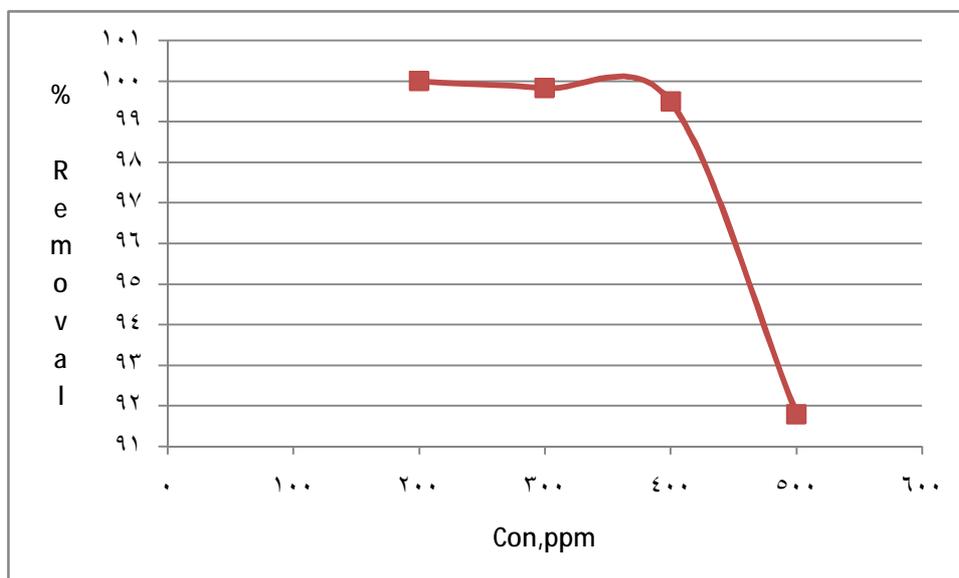
Fig(7) Con vs removal efficiency of iron by Na- zeolite

Conclusions and Recommendations

1. It has been found that modified zeolitic tuff treated with chemicals can increase iron removal efficiency as ion exchange capacity is increased.

2. Sodium treated zeolitic tuff has the maximum exchange capacity among other types of calcium and acid treated zeolites.

3. Extended exposure of philipsite samples to concentrated sodium solutions has been found to be ineffective in displacing all the cation ions from this zeolite, and the sample may require extensive conditioning over several days, with high concentration of selected cation to obtain the homoionic form.

4. Zeolite structure is damaged at PH 1-2 as removal efficiency noticed to be zero

5. Treated raw zeolite with 2 N NaCl has efficiency close to synthetic 4A zeolite

6. Jordan zeolitic tuff   containing philipsite demonstrates high treatment efficiency for removal of iron from   water at high concentration thus can remove low concentration usually present in ground water.

7. It is recommended to use sodium for treatment of raw zeolitic tuff and to avoid acid treatment.

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