

Use of Natural and Modified Jordanian Zeolitic Tuff for Removal of Cadmium(II) from Aqueous Solutions

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ABSTRACT

The possibility of using natural and modified Jordanian zeolite for removal of cadmium as a model component of heavy metals has been considered. Bench-scale tests using both aqueous solutions and real water under different experimental conditions have been employed. Different parameters, including metal ion concentration, modifier type, water quality and pH, have been studied. Synthetic Zeolite Molecular Sieve (4A) as control material has been also considered for the purpose of comparison. Zeolite characterization has been investigated via XRD, XRF, BET Surface Area/pore size, TGA, FTIR analyses for the samples under consideration. The metal concentration and modification salts were found to have significant effect on sorption of cadmium by zeolite and thus on zeolite efficiency. Hardness in water was found to highly impede adsorption. Sorption equilibrium was achieved within 250 min. The equilibrium isotherm data of cadmium-zeolitic tuff were represented by Langmuir and Freundlich isotherm models, but they were well represented by Langmuir model.

KEYWORDS: Jordan natural zeolite (Phillipsite), Heavy metals, Ion exchange, Langmuir isotherm, Characterization.

INTRODUCTION

Zeolites are a group of hydrated aluminum-silicates of the alkali or alkaline earth metals (sodium, potassium, magnesium, calcium). Zeolite has a three-dimensional crystalline framework of tetrahedral silica or alumina anions strongly bonded at all corners and contains 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 (Phillipsite) was discovered in 1987 (Dwiri, 1987). Zeolitic tuff is widely distributed in Jordan. The North Arabian basalt plateau covers an area of about 11,000 km² (called Harrat Alsham) 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 extent in ground water. Therefore, their removal from water is required prior to intended use. Many

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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 the solid. The ion exchange properties of clays and zeolites have been recognized and studied for more than a century (Skoog et al., 1994; Harvey, 2000). The main advantages of ion exchange over chemical precipitation are: the removal of metal ions, selectivity and less produced sludge.

The first attempt for purifying water using naturally purifying materials containing zeolite was 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 provides low cost treatment by ion exchange process (Elbishtawi et al., 1997). It has also been found that NaCl pretreated zeolite material improves 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 the effect of different parameters on the removal efficiency of certain selected heavy metals by natural volcanic tuff obtained from Northeastern Jordan.

MATERIALS AND METHODS

Materials

Philipsite rich natural zeolite mineral used in this study was obtained in the form of volcanic tuff from Artain area, located in the east west part of Jordan. Represented zeolitic tuff samples with grain size of 0.595-1.410 mm (Sieve No. 30-14/28-12 mesh) were 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 24 hrs and then sieving into the required grain size.

The sample then underwent treatment with NaCl in which 1 gm of zeolitic tuff was added to 100 ml of 2N NaCl followed by shaking for 24 hrs. Eventually, the zeolitic tuff is converted to the Na-form, such that the zeolitic tuff structure is enriched with exchangeable Na ions. This would result in what can be referred to as Na-Z. After shaking, the zeolitic tuff samples were washed several times with deionized water in order to remove excess sodium chloride and calcium chloride. Modification has been also done by calcium chloride and hydrochloric acid solution of pH 5; these modifications result in what can be referred to as Ca-Z and H-Z, respectively.

Concentrated hydrochloric and sulfuric acid solutions (36% HCl and 96% H₂SO₄, Scharlau) diluted to 5% v/v were 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 or sodium 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. 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).

Instruments

Total dissolved solids and pH values were measured with a WTW (Wissenschaftlich-Technische Werkstätten, Germany) and pH 330 device, respectively. Metal concentrations 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

Diffractometer equipped with Cu K α radiation (Ultima IV, Rigaku, Japan). Thermal analyzer (TG 209 F1-, Netzsch, Germany) was used for thermal analysis of the samples. Fourier Transfer Infra Red (FTIR) was obtained by IR Affinity-1 (Shimadzu, Japan). XRF by S4 Pioneer, Bruker, Germany. True density (skeletal density) was measured by Ultrapycnometer 1000 (Quanto Chrome, USA). Surface area adsorption and desorption curves were determined by using N₂ as adsorptive by NOVA 2000 Series, Quanta Chrome, USA.

Bench-scale Adsorption Test

Sorption tests for cadmium were conducted at room temperature 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) and at room temperature (25±2°C). The initial pH of the solution was adjusted using either 0.1 M HCl or 1 N NaOH. At the end of the sorption process, the samples were filtered through 0.45 Whatman filter paper. The filtrate was analyzed using AAS against cadmium. 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 concentrations following the equation:

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

where q_e is the quantity of heavy metal adsorbed on the zeolite (mg metal/gm zeolite), C_i is the initial metal concentration in the solution and C_f (mg/L) is the equilibrium or final metal concentration in the solution, m is the amount of zeolite in grams and v is the volume of solution (l). The percent of metal adsorption is

calculated by the following equation:

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

Equilibrium Isotherm Models

Langmuir isotherm models the single coating layer on adsorption surface. This model assumes that adsorption takes place at 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 (Ünlü and Ersoz, 2006). The linear form of Langmuir isotherm can be written as:

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

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 another 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°C by varying metal concentrations; namely 200, 300, 400, 500 and 750 ppm. Each of these metal solutions was mixed with 1 g zeolite for 240 minutes to ensure equilibrium.

RESULTS AND DISCUSSION

Characterization of Raw Zeolitic Tuff Sample

The zeolite used in this work has been characterized

by BET, X-Ray Diffraction (XRD), Thermo-gravimetric analysis(TGA), Fourier Transform Infra-Red (FTIR) Techniques in addition to X-ray Fluorescence. The zeolite particle and BET surface area properties are displayed in Table (1).

Table 1. Particle size properties of zeolitic tuff

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

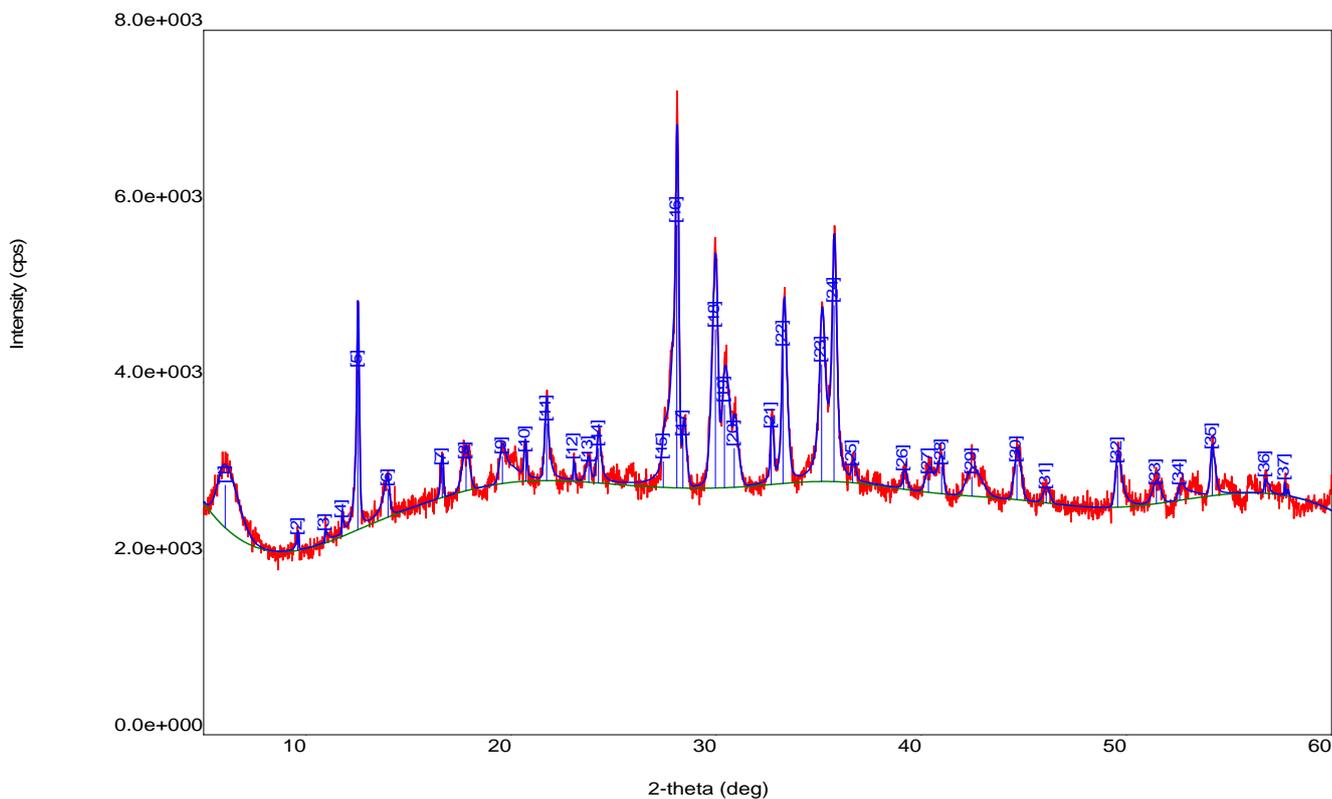


Figure (1): XRD powder diffraction chart for Jordanian zeolitic tuff

The BET of N₂ adsorption using zeolitic tuff sample seems to be of types II and IV according to Sing et al. (1984) classification. According to IUPAC classification and the BET isotherm curve, micropores and mesopores could exist in the sample in the low relative pressure and middle relative pressure, respectively.

The X-ray diffraction results (Figure 1) indicate that the examined zeolitic tuff sample is rich in Phillipsite of the formulae (Na_{0.13} (NH₄)_{1.19} (Al_{1.5} Si_{2.5} O₈) 1.92 H₂O). The other ingredients are hematite and pyroxene.

The chemical composition of the raw zeolite as determined by X-Ray Fluorescence is shown in Table 3. As presented in this table, the silica to alumina ratio

is about 3; while the Loss on Ignition (LOI) which represents water content is 7.24%. The same approximate values were found using TGA analysis. Silica to Alumina Ratio clearly indicates that this samples of Jordan zeolite is natural.

Thermal behavior of zeolitic tuff was investigated by using TGA thermogram as shown in Figure 2. The temperature ranges 50-110, 110-350 and 350-500°C correspond to loss of external water, loosely bound water and tightly bound water, respectively. The weight losses were found to be 5, 1.8 and 1.0% by weight for external, loosely and tightly bound water, respectively, for the examined zeolitic tuff. The temperature range 800-1000°C could be also related to the loss of CO₂ as a result of decarbonation of calcite.

Table 2. Phases comprising the used sample of Jordan zeolite

Phase 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 syn(0,1,2),Clinopyroxene,
15	27.41(3)	293(22)	121(80)	Clinopyroxene syn(2,2,0),Phillipsite(3,0,-1)
17	28.37(2)	564(31)	172(41)	Phillipsite(1,3,1)
22	33.252(10)	1525(50)	510(11)	Hematite syn(1,0,4),Phillipsite(1,1,2)
23	35.131(11)	1326(47)	620(21)	Clinopyroxene, syn(1,3)
24	35.737(10)	1999(58)	734(20)	Hematite, syn(1,1,0),Clinopyroxene,
34	52.60(12)	140(15)	111(18)	Clinopyroxene syn(1,5,0),Phillipsite(0,7,2)
37	57.72(5)	146(16)	13(9)	Hematite, syn(0,1,8)

Table 3. Chemical composition of Jordanian zeolitic tuff using X-Ray Fluorescence

Oxide	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	TiO ₂	CaO	K ₂ O	P ₂ O ₅	MgO	Na ₂ O	LOI	Si/Al
Wt%	41.26	12.41	15.6	0.25	2.86	7.26	1.94	0.63	7.82	2.73	7.24	2.96

The structural information of the zeolite tuff was obtained using FTIR spectroscopy. Figure 3 shows H-bonded O-H stretching at 3365-3381cm⁻¹, H₂O bending at 1645.28 cm⁻¹, a 1413.82 cm⁻¹ asymmetric stretching

vibration of the carbonate in the sample, a 1020.34cm⁻¹ strong band due to phillipsite symmetric stretching vibration of silicate group, a 750.31 cm⁻¹ symmetric stretching vibration of metal oxides (MO) and a 459.06

cm⁻¹ bending vibration for 4 single ring zeolites such as phillipsite.

Sorption Results

Equilibrium time: It can be seen that sorption takes place in two steps. The first step takes place in the first 4-5 hours (240-300 minutes). Later, in the second stage, the uptake relatively remains constant and is considered as equilibrium.

The kinetics of cadmium uptake using raw zeolitic

tuff revealed that the sorption process takes place in two steps as shown in Figure 4. The first step is relatively fast and takes place in the first hour; while the second step follows and is a slow one. This is an expected result as sorption process is normally fast. The fast step may indicate that this sorption process occurs mainly at the surface of the particles; while the slow step may indicate that intrapore diffusion occurs but is not the rate controlling one.

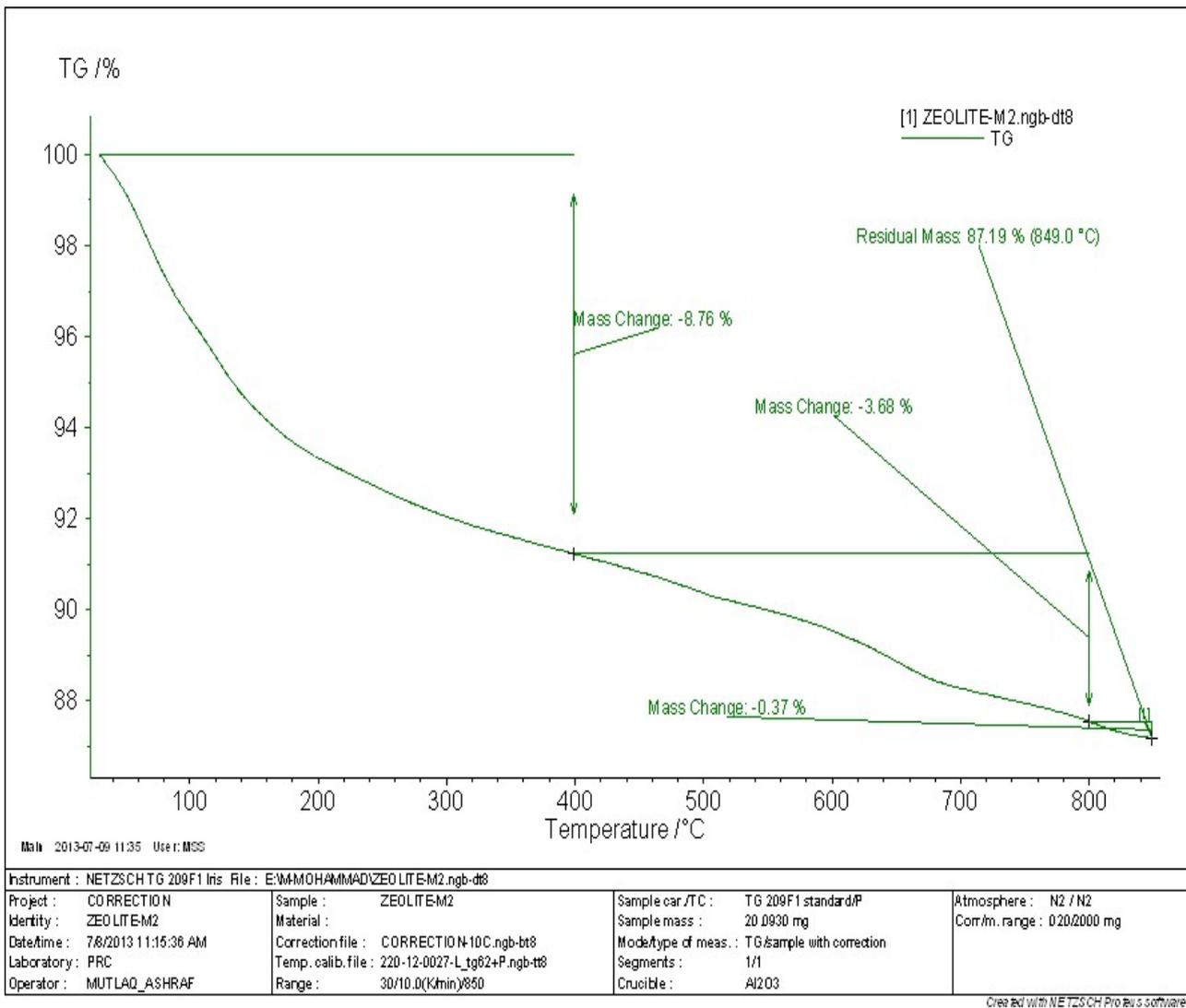
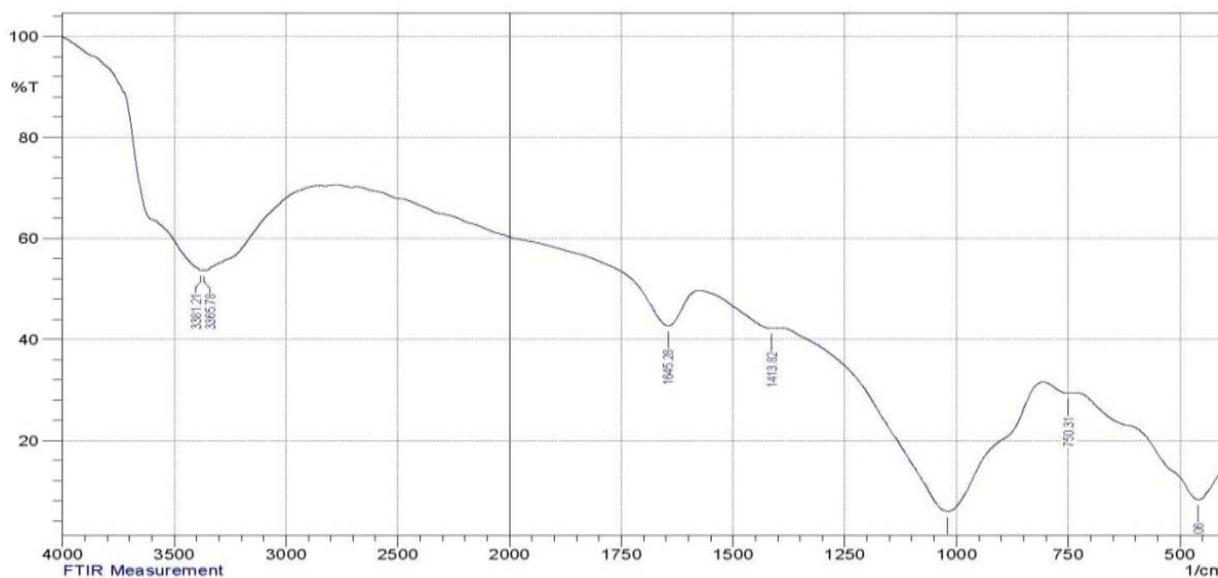


Figure (2): TGA thermogram of Jordanian zeolitic tuff

Table 4. Langmuir and Freundlich constants for different types of zeolitic tuff

Langmuir constants		Zeolite Form			
		Raw	Na-Z	Ca-Z	H-Z
Q_{max}		38.9	81	45.6	41
K_L		0.35	0.38	0.39	0.95
R^2		0.9419	0.9902	0.9374	0.9956
Freundlich constants		Raw	Na-Z	Ca-Z	H-Z
K_f		15.4	34.4	35.5	20.4
n		2.1	4.4	4.5	3.8
R^2		0.8071	0.7517	0.7438	0.3834



	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	459.06	8.2501	9.2275	729.09	399.26	251.6781	27.2447
2	750.31	29.3359	0.635	806.25	731.02	39.2595	0.4146
3	1020.34	5.9337	29.5096	1392.61	808.17	396.0468	140.2705
4	1413.82	42.152	0.9146	1575.84	1394.53	61.8882	0.6972
5	1645.28	42.6521	8.2817	2673.34	1577.77	240.5537	5.5261
6	3365.78	53.6264	0.302	3373.5	2860.43	106.0956	1.2663
7	3381.21	53.6686	0.438	4000.36	3375.43	74.4798	3.447

Figure (3): FTIR spectroscopy of zeolitic tuff

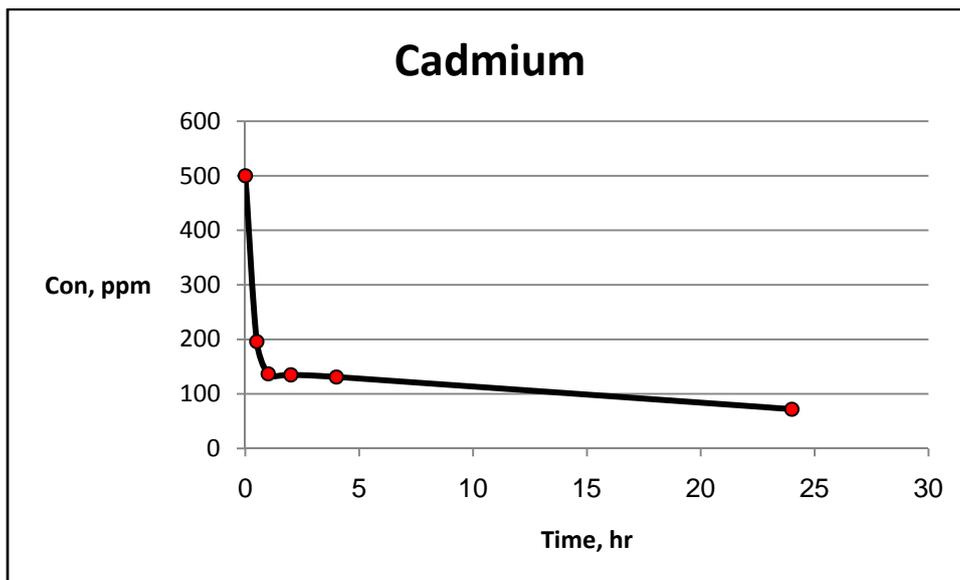


Figure (4): Residual cadmium concentration in solution versus time during sorption using zeolitic tuff (pH=4, 25°C, 1gm/100ml)

Table 5. Comparison between sorption capacity of zeolites used in this work and synthetic zeolite (1gm per 100 ml at 25°C)

Zeolite Type	Concentration(ppm)	Q_{max} (mg/gmZ)	CEC (meq/gmZ)
Raw	200-750	39	0.7
Na-Z	200-750	80.6	1.43
Synthetic 4A	300-750	77.5	1.38

Adsorption isotherm was performed by considering adsorption of cadmium by zeolitic tuff using different cadmium concentrations (in the form $Cd(NO_3)_2$) in the range 200-750 ppm. The solutions were adjusted at pH 4. One hundred ml of each of these solutions were transferred into a 250 ml flask, 1 gm of zeolite tuff was added and the systems were agitated in the shaker for 4hrs. After that, the slurry was filtered, and the supernatant was analyzed for Cd concentration using flame atomic absorption spectrometry. The Langmuir and Freundlich constants are presented in Table 4.

It can be noticed (Table 4) that the value of Q_{max} is

the highest for the case of using Na-Z (81 mg/gm). This could be attributed to the fact that complete exchange of sodium ions with those in zeolite has taken place during modification compared to that of Ca and H ions; sodium ions mobility is also higher which enables them to be replaced by Cd^{+2} ions. In case of calcium modified zeolite, the value of Q_{max} is greater than the raw zeolite but less than Na-Z zeolite. This could be also attributed to the lower mobility of calcium ions compared to that of sodium ions. The lower Q_{max} for the H-Z sample could be due to possibility of attacking aluminum atoms by acid

protons at low pH(3-4) during modification. This leads to partial or complete damage of zeolite main structure

which is called dealumination.

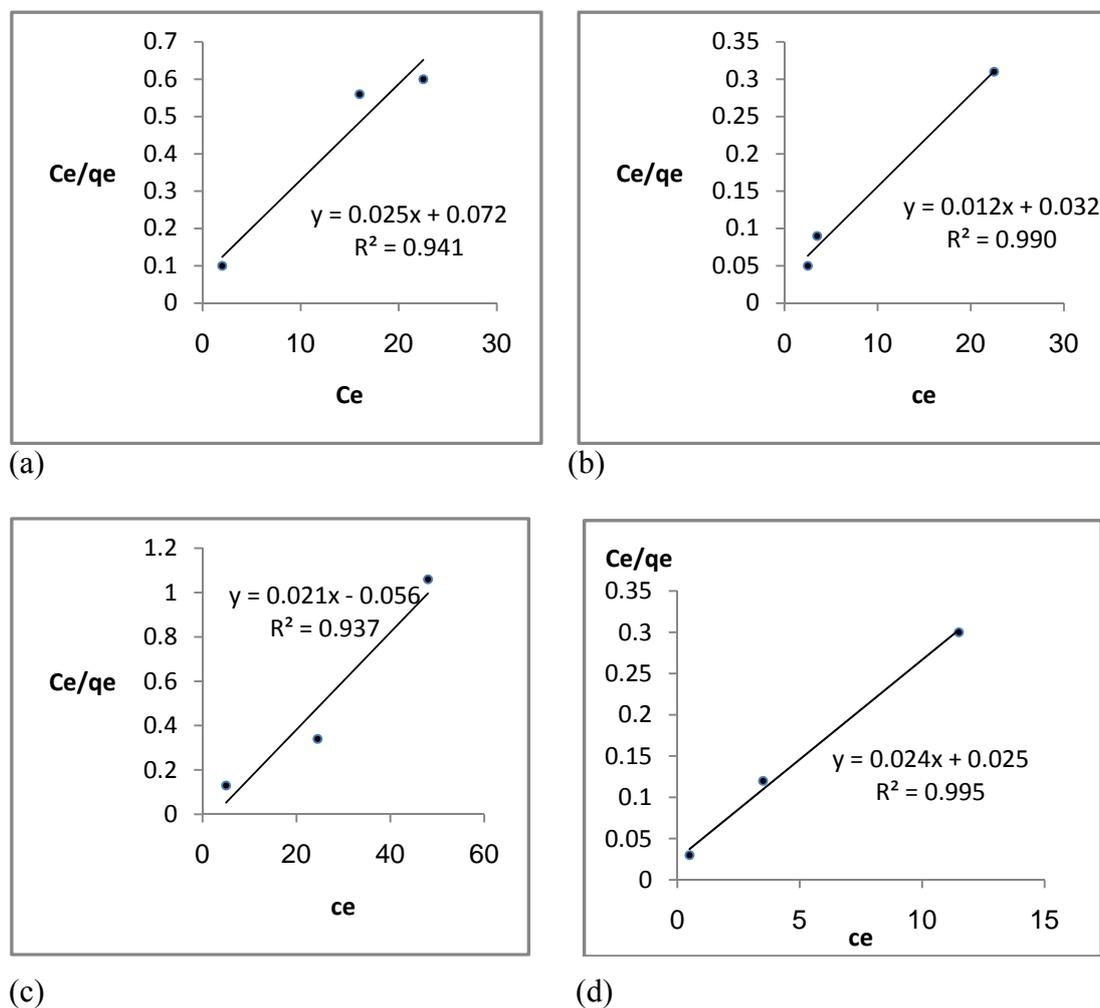


Figure (5): Langmuir isotherm plot of a- raw zeolite b- sodium modified zeolite c- calcium modified zeolite and d- acid modified zeolite

It is also noticed that the data are well represented by the Langmuir model as evidenced by R^2 values reaching acceptable values, whereas the R^2 values for the Freundlich model are very low indicating that the isotherms obtained from this work do not follow this isotherm model.

To investigate the efficiency removal of natural and modified zeolite used in this work, a control material of synthetic zeolite was tested to compare the removal

efficiency of Jordan zeolite with synthetic one. This comparison is illustrated in Table 5, where Cation Exchange Capacity (CEC) is calculated and compared between three zeolites types. It is seen that sodium modified natural zeolite has approximate efficiency to that of synthetic zeolite.

Water hardness effect on cadmium sorption by sodium zeolite was investigated. Table 6 indicates that water type and hardness have significant effects on

cadmium removal. This is attributed to the competition between hardness ions (Ca^{+2} and Mg^{+2}) and cadmium ions at the surface of zeolite, and it seems that zeolite particles have a preference to take hardness ions first. Selectivity for calcium can be attributed to its low

enthalpy of hydration as calcium will lose its coordinating water molecules fairly easily. Enthalpy of hydration values for Ca and Cd are -1593 and -1807 kJ/mol, respectively. These values and results are in agreement with those reported by Whithead (2000).

Table 6. Comparison of cadmium removal efficiency between deionized and real water

Cd Con.(ppm)	Real Water (Hardness 196ppm)		DI water (hardness 0 ppm)
	Hardness Removal	Cd Removal	Cd Removal
300	96%	55%	95%

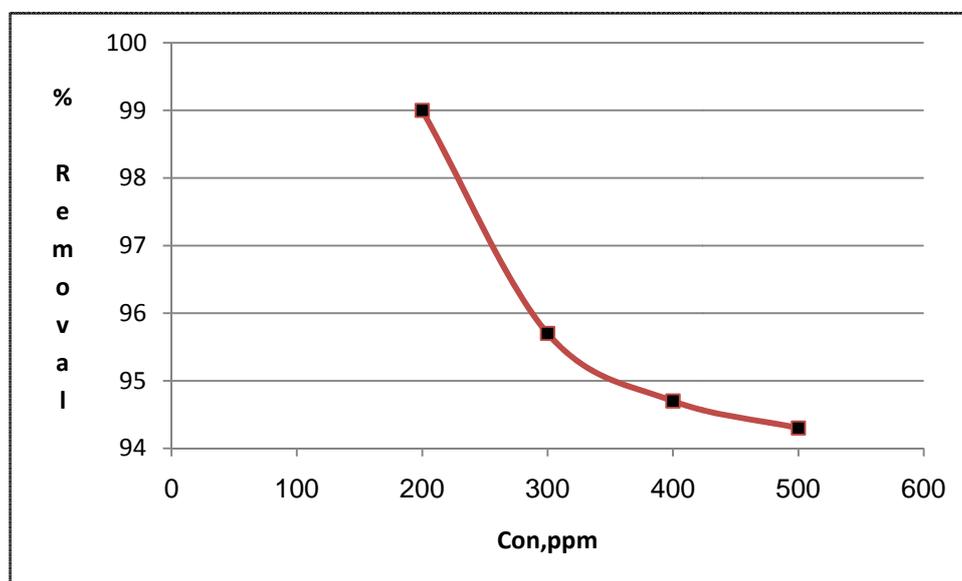


Figure 6. Cadmium removal versus its initial concentration in solution (1 g/100ml, Na- zeolite at pH4)

Sorption tests were also performed at different pH values in the range 1.5 – 4 using 1gm/100ml of Na-Z and 200-1000 ppm of cadmium in order to study the effect of pH on this sorption process. The results for pH range 1.5-2 showed undetectable cadmium uptake by zeolite, which could be 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).

The adsorption of Cd^{+2} ions onto Na-zeolite as function of cadmium concentration was studied at 25°C by varying the metal concentration from 200-750 ppm. The results are shown in Figure 6. It is noticed that the percentage removal efficiency of Cd is generally

decreased with increasing its initial concentration in the solution. These results indicate that energetically less available sites become involved as metal ion concentration increased. Similar findings are reported by Inglezakis et al. (2001).

CONCLUSIONS

The following conclusions can be drawn from the results of this work:

- Treating zeolitic tuff chemically increases its ion exchange capacity leading to an increase in its

cadmium removal efficiency.

- Sodium treated zeolitic tuff has the maximum exchange capacity among other types of calcium and acid treated zeolites tested in this work.
- Zeolite structure is damaged at pH 1-2 as removal efficiency becomes unnoticeable.
- Treated raw zeolite with 2 N NaCl has an adsorption efficiency close to that of synthetic 4A zeolite.
- Jordan zeolite can treat cadmium in aqueous solutions but pretreatment of hardness is required first.

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