

## Chemical Modification of Natural Jordanian Zeolitic Tuff using Acetamide and N,N-Dimethylformamide

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A low priced locally natural occurring zeolitic tuff was chemically treated with acetamide and N,N'-dimethyl formamide (DMF) compounds. The chemical and structural properties of the treated and untreated tuff were studied using scanning electron microscopy (SEM), powder X-ray diffraction (XRD), X-ray fluorescence (XRF) and infrared spectroscopy (FTIR) techniques. The XRD data revealed that chemical treatments do not affect the mineral content of the zeolitic tuff. The results of SEM, XRF and FTIR techniques indicated some changes in the zeolite surface. The results of the uptake of Pb(II), Cd(II), Ni(II) and Cu(II) from their aqueous solutions for the zeolitic tuff samples revealed that treatment with acetamide increases slightly the removal ability of zeolitic tuff, while treatment with DMF decreases the tuff removal ability.

**Key Words:** Zeolitic tuff, Chemical treatment, Acetamide, N,N-Dimethyl formamide, Heavy metals uptake.

### INTRODUCTION

Natural zeolite minerals can be defined as crystalline hydrated alumino-silicates of alkali and alkaline earth cations that consist of infinite or finite three dimensional crystal structure of (Si,Al)O<sub>4</sub> tetrahedra. These tetrahedra linked together by the sharing of oxygen atoms<sup>1-3</sup>. Zeolite structure contains channels and pores filled with a certain amount of water and exchangeable cations. Some cations constituents may be exchangeable from the zeolite inner cavities and pores without any major changes of zeolite structure<sup>3</sup>. Zeolites are considered as rigid crystalline sponges capable for imbibing large amounts of molecules small enough or of the right shapes to pass through their surfaces and enter the intracrystalline pores, while they are unable to sorb molecules having the wrong sizes or shapes<sup>4</sup>.

Zeolitic tuff deposits were discovered in Jordan in 1987 in the eastern part of the country at Japal Aritayn, 30 km NE of Azraq<sup>5</sup>. The dominant zeolite mineral in these deposits is phillipsite, which is thought to be the product of alteration of alkaline basaltic tuff deposits.

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Chemical treatments of Jordanian zeolitic tuff using urea and thiourea<sup>6</sup>, oxalic acid and salicylic acid<sup>7</sup> and cationic surfactants<sup>8</sup> have been studied by our group. In this work, the investigations on the chemical treatments of the local zeolitic tuff by treating it with acetamide and N,N-dimethylformamide (DMF) are extended. Such treatments were studied by the several techniques such as scanning electron microscopy (SEM), powder X-ray diffraction (XRD), X-ray fluorescence (XRF) and infrared spectroscopy (FTIR) techniques.

Heavy metals occur naturally in very limited amounts of the earth's crust, as sulfides, sulfates, carbonates or silicates with average concentrations of 15, 0.2, 75 and 50 mg/kg for lead, cadmium, nickel and copper, respectively<sup>9</sup>.

The contamination by heavy metals occurs in aqueous waste streams in many industrial activities, such as metal finishing, mining and mineral processing, coal mining, oil refining, tanneries and metal plating facilities, among others. It is noteworthy that the heavy metals are not biodegradable and tend to accumulate in organisms, causing numerous diseases and disorders<sup>10,11</sup>. The removal of heavy metal cations from solutions can be achieved by several processes such as chemical precipitation, adsorption on activated carbon, solvent extraction, ultrafiltration, or ion exchange<sup>12-15</sup>. Natural zeolites provide an economic and effective mechanism to remove heavy metals dissolved in waste stream<sup>11,16-19</sup>. Consequently, several studies of using Jordanian zeolitic tuff as scavengers of inorganic as well as organic pollutants from water have been reported<sup>6,7,20-25</sup>. In this work, the ability of untreated as well as treated Jordanian zeolitic tuff with acetamide and N,N-dimethylformamide for the removal of Pb<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup> and Cu<sup>2+</sup> from their acidic aqueous solutions was investigated.

## EXPERIMENTAL

**Tuff preparation:** Zeolitic tuff rocks were obtained from Jabal Aritayn in Jordan. This raw material was crushed using jaw crusher (Sepornic), homogenized and sieved at different meshes according to the particle size. A 500.0 g sample of the particle size of 500-1000 micron was selected<sup>6</sup> and washed with distilled water three times until clear solution. Then the sample was dried at 105 °C in an oven (Memert 500) for 12 h and kept in a desiccator over anhydrous CaCl<sub>2</sub> and labeled ZW. Subsequently, a 200.0 g sample of ZW was stirred with 500 mL of 2 M NaCl solution for 1 h using magnetic stirrer (Cimraris Thermolyne, 200 rpm). Then the mixture was allowed to settle and the supernatant was decanted. After repeating the treating with NaCl solution three times, the sample was washed with distilled water several times until no chloride ions were detected in the eluted water (Mohr's method). The wet sample was dried in an oven overnight at 105 °C and kept in a desiccator over anhydrous CaCl<sub>2</sub> and labeled Z.

**Chemical treatments with amides:** To a 5.00 g sample of acetamide (99 % from Riedel-deHaen) in 100 mL ethanol 10.00 g of Z was added. The mixture was stirred using the magnetic stirrer (200 rpm) for 2 h. The supernatant was decanted

whereas the zeolitic tuff was washed with ethanol (50 mL) three times and decanted each time. Then the four decanted supernatants were collected and heated over water bath (Memert) for 4 h at 70 °C to remove ethanol. The wet zeolitic tuff was dried in an oven overnight at 70 °C and kept in a desiccator over anhydrous CaCl<sub>2</sub> and labeled ZA. The loaded amount of acetamide was estimated by comparing masses of dried ZA and acetamide (from supernatants).

A 100 mL of N,N-dimethyl formamide (98 % from GCE) was stirred with 10.00 g of Z for 2 h using the magnetic stirrer (200 rpm). After decanting the supernatant, the wet zeolitic tuff was washed with distilled water (50 mL) three times, dried in an oven overnight at 105 °C and then weighed in order to estimate the amount of loaded N,N-dimethyl formamide. The dry loaded zeolitic tuff was kept in a desiccator over anhydrous CaCl<sub>2</sub> and labeled ZF.

**Characterization of zeolitic tuff samples:** Samples Z, ZA and ZF were characterized by ascertaining their mineral constitution, chemical composition and chemical characterization, as well as their surface morphology. The mineral constitution of the samples was determined by powder XRD technique, using X'pert instrument fitted with a Philips X-ray tube giving CuK<sub>α</sub> radiation at  $\lambda = 1.7889 \text{ \AA}$  at 40 kV and 40 mA. The chemical composition was determined by XRF technique using Diano-2023 instrument according to the following operating conditions. A 0.8 g of zeolitic sample was mixed with 7.2 g of lithium tetraborate (Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>) in a platinum crucible, which was introduced into an automatic fluxer (Leco Corp., model FX-200) where a temperature program was affected starting from room temperature to 1200 °C. The melt was then poured into a casting dish and allowed to cool to form a glassy disc. The chemical characterization of the samples was investigated by FTIR spectroscopy using Jascow FTIR-410 spectrophotometer. Samples were ground with dried KBr using an agate mortar and pestle and the transparent disks were obtained using a hydraulic press at 5 ton/m<sup>2</sup>. The surface morphology of the samples was studied using scanning electron microscope (SEM) type XL-30 W/TMP/2000 at 20 kV.

**Removal of heavy metals:** Stock heavy metals solutions (1000 ppm each) were prepared independently from their nitrates, *i.e.* Pb(NO<sub>3</sub>)<sub>2</sub>, Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (99 % from Fluka).

**Batch system:** From the corresponding stock solutions, a 100 ppm solution of each heavy metal was prepared separately and then divided into four portions of pH values 3, 4, 5 and 6, respectively (using 0.1 M NaOH/0.1 M HNO<sub>3</sub>). A 50 mL of each portion (100 ppm of heavy metal solution at certain pH value) was stirred with 1.00 g of one of zeolitic tuff samples (Z, ZA, or ZF) at 21 °C. While stirring, a 2 mL of supernatant was withdrawn every 10 min for a period of 50 min. Then diluted with distilled water to 25 mL in a volumetric flask to determine the concentration of metal remained in liquid using atomic absorption spectrometer (Shimadzu 6800).

**Continuous flow system:** A 5.00 g of zeolitic tuff (Z or ZA) was packed in a glass column (0.4 cm diameter) prepared for this purpose. A 100 mL of stock solution of heavy metal (Cd<sup>2+</sup> or Ni<sup>2+</sup>) of pH 4 (using 0.1 M NaOH/0.1 M HNO<sub>3</sub>) were

poured into the packed column which were passed (downstream, without pumping) within 10 min. A 2.0 mL of the eluted solution was diluted to 100 mL with distilled water before determining the concentration of metal using the atomic absorption spectrometer.

## RESULTS AND DISCUSSION

**Mineral constitution and surface morphology:** The XRD results revealed that the mineral contents of the water washed-(ZW) and the brine washed-zeolitic tuff (Z) are identical. As shown in Table-1, the anorthite (feldspars) was the major constituent, while phillipsite (zeolites), augite (pyroxenes) and hematite (oxides) were minors. Montmorillonite-15A clay was found in a trace amount. Such mineral constitution was clearly observed in the scanning electron micrographs of sample Z (Figs. 1 and 2), which show the presence of the characteristic crystals of phillipsite beside anorthite, augite and montmorillonite-15A.

TABLE-1  
MINERAL CONSTITUTION OF ZEOLITIC TUFF SAMPLES ZW, Z, ZA AND ZF

Sample	Anorthite	Phillipsite	Augite	Hematite	Montmorillonite-15a
ZW	Major	Minor	Minor	Minor	Trace
Z	Major	Minor	Minor	Minor	Trace
ZA	Major	Minor	Minor	Trace	Trace
ZF	Major	Minor	Trace	Minor	Trace

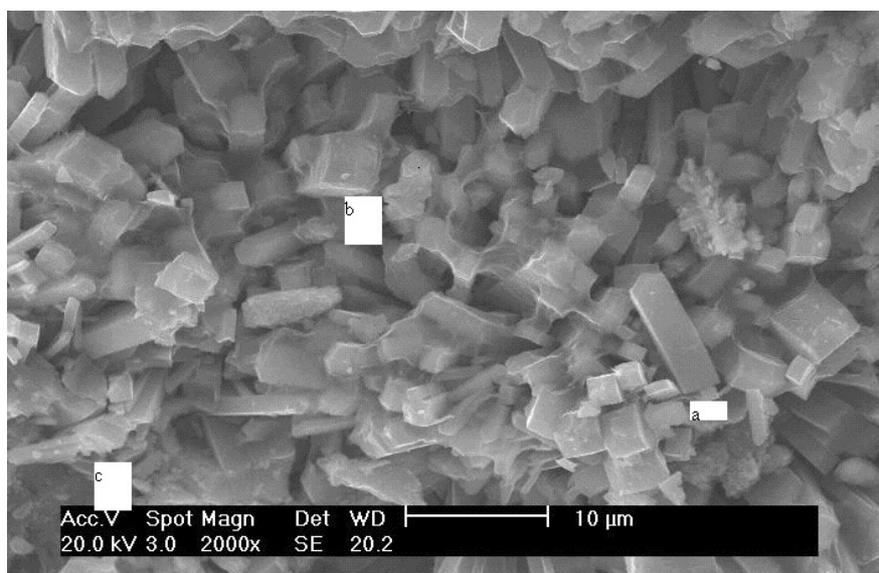


Fig. 1. SEM image of (a) phillipsite, (b) augite and (c) anorthite in sample Z

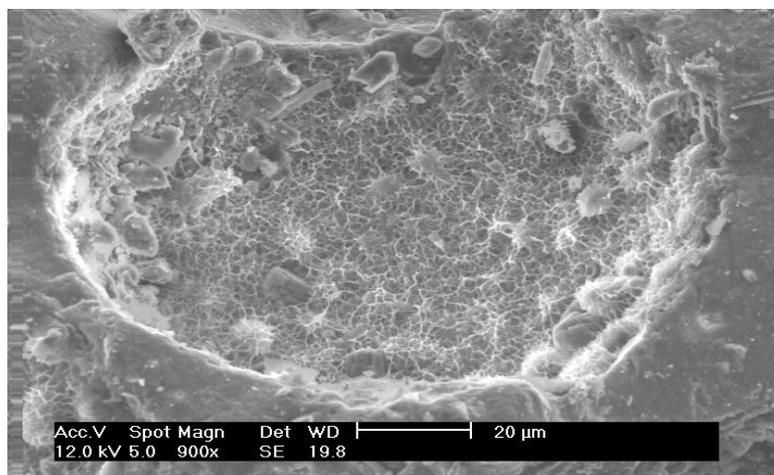


Fig. 2. SEM image of montmorillonite in sample Z

The chemical treatments of sample Z by acetamide and by N,N-dimethyl formamide (DMF) were nearly kept the same mineral content. The only changes in ZA (zeolite-acetamide) and in ZF (zeolite-DMF) samples were the trace amounts of hematite and augite (Table-1). Keeping identical mineral content through chemical treatment of Jordanian zeolitic tuff has been reported in literature<sup>6,7</sup>. The scanning electron micrographs of ZA and ZF samples show that phillipsite (Fig. 3) and montmorillonite (Fig. 4) were coated with acetamide, whereas the coating of phillipsite, anorthite and augite with N,N-dimethylformamide were observed in Fig. 5. Such coating, in other words, unambiguously show the deposition of acetamide and N,N-dimethyl formamide on the surface of the zeolitic tuff.

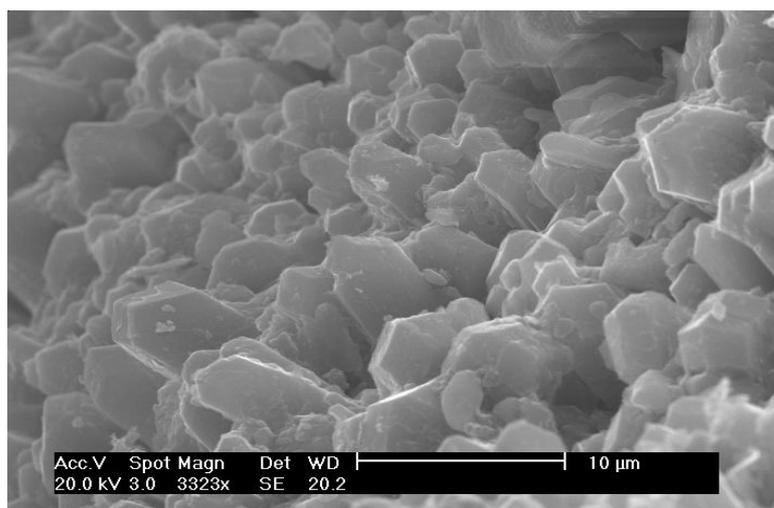


Fig. 3. SEM image of phillipsite coated with acetamide in sample ZA

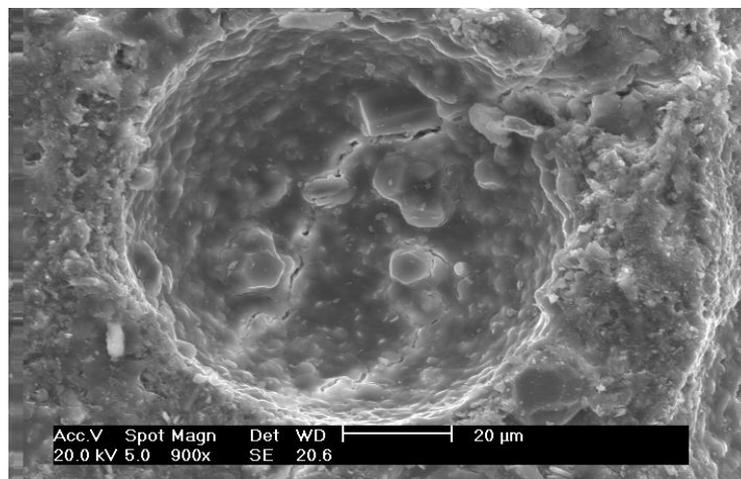


Fig. 4. SEM image of montmorillonite coated with acetamide in sample ZA

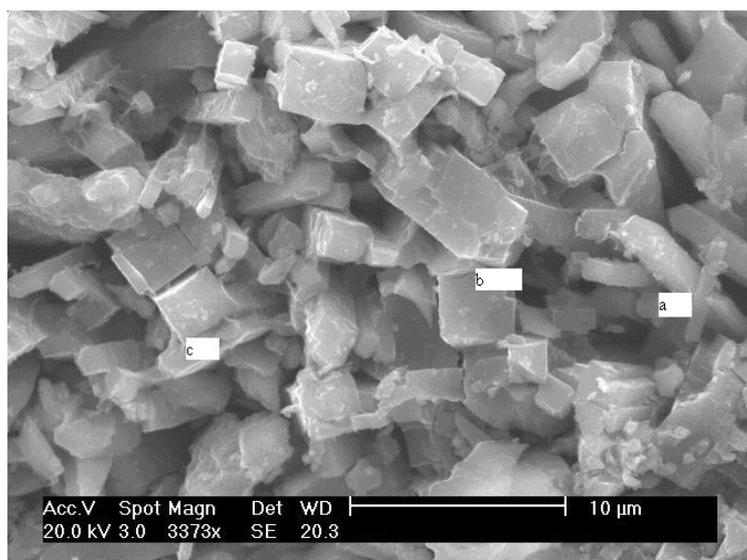


Fig. 5. SEM image of (a) phillipsite, (b) anorthite and (c) augite coated with N,N-dimethyl formamide in sample ZF

**Chemical composition:** The XRF results for ZW (water washed zeolite), Z (brine washed zeolite), ZA (zeolite-acetamide) and ZF (zeolite-DMF) samples are tabulated in Table-2. Washing samples with brine affected the amounts of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  which were nearly doubled; the amount of  $\text{MnO}$  was decreased to about one fifth of its origin value. The  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio was slightly changed from 3.17 in ZW to 2.98 in Z revealing that aluminosilicate structure of the sample was not greatly affected. Other metals oxides were nearly unaffected.

TABLE-2  
CHEMICAL COMPOSITION (%) OF ZEOLITIC TUFF SAMPLES ZW, Z, ZA AND ZF

Sample	Fe <sub>2</sub> O <sub>3</sub>	MnO	TiO <sub>2</sub>	CaO	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	Na <sub>2</sub> O	L.O.I
ZW	12.57	1.55	2.13	8.45	0.55	0.37	42.11	13.29	10.11	0.88	7.99
Z	11.34	0.33	2.15	8.42	0.93	0.43	42.01	14.10	10.33	1.92	8.04
ZA	10.94	0.36	2.10	7.94	0.99	0.40	41.95	13.51	9.57	1.80	10.44
ZF	10.84	0.27	2.06	7.87	0.89	0.42	41.09	13.88	9.52	1.81	11.35

L.O.I. = Loss of ignition.

The percentages of the metals oxides in ZA and ZF samples were not significantly affected by the amides loading whereas the summation of changes in ratios describes the increase in L.O.I. (loss on ignition) for these samples. The amount of ligand adsorbed on zeolitic tuff may be roughly estimated from the difference in L.O.I. values between loaded and unloaded samples. As shown in Table-2, the amounts of acetamide and N,N-dimethyl formamide loaded on the zeolitic tuff in samples ZA and ZF, are 2.40 and 3.31 %, respectively. These values, however, are almost in agreement with the values of 2.5 % for acetamide and 3.5 % for N,N-dimethyl formamide, which were estimated gravimetrically as the difference in mass of zeolitic tuff before and after treating with amides.

Although the zeolitic tuff samples contain some important non-zeolitic minerals, as revealed by XRD results, the overall characteristic behaviour seems to be that of zeolites as indicated by the atom composition calculation<sup>1</sup> given in Table-3 and by the indicator ratios<sup>2</sup> shown in Table-4. Thus the indicator ratios Si/(Si+Al) of Z, ZA and ZF samples, which range between 0.715 and 0.725 fall within the range of 'intermediate ordered zeolites', *i.e.*  $0.625 < R < 0.75$ , according to the scale reported by Gottardi<sup>2</sup>. The Si/Al ratio which can vary considerably within the limits of one structural type depending upon the compositions of the original solutions and conditions of crystallization<sup>26</sup> was found to be nearly the same, 2.53, 2.64 and 2.51 in Z, ZA and ZF samples, respectively.

TABLE-3  
NUMBER OF ATOMS OF ELEMENTS IN THE ZEOLITIC  
TUFF SAMPLES Z, ZA AND ZF\*

Element	Z	ZA	ZF
Si	7.476	7.280	7.070
Al	2.955	2.763	2.815
Fe	1.581	1.431	1.404
Mn	0.150	0.053	0.039
Mg	2.740	2.478	2.442
Ca	1.604	1.479	1.451
K	0.212	0.218	0.196
P	0.064	0.058	0.061
Na	0.675	0.606	0.604
Ti	0.288	0.275	0.266
H	9.543	12.085	13.027
O	32.000	32.000	32.000

\*Calculated from data given in Table-2 on the basis of 32 oxygen atoms [Ref. 1].

TABLE-4  
INDICATOR RATIOS FOR SAMPLES Z, ZA AND ZF [Ref. 2]

Indicator ratio	Z	ZA	ZF
(Si)/(Si + Al)	0.717	0.725	0.715
Si/Al	2.530	2.635	2.512
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	2.979	3.105	2.960
(Mg + Ca + Na + K) oxides/Al <sub>2</sub> O <sub>3</sub>	1.532	1.503	1.447

The ratios of the oxides, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and (Mg + Ca + Na + K) oxides/Al<sub>2</sub>O<sub>3</sub>, for typical zeolites are  $\geq 2$  for the former and  $\approx 1$  for the latter, were found to be almost the same in Z, ZA and ZF samples. As shown in Table-4, the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios were found to be 2.98, 3.10 and 2.96, whereas the (Mg + Ca + Na + K) oxides/Al<sub>2</sub>O<sub>3</sub> ratios were found to be 1.53, 1.50 and 1.45 for Z, ZA and ZF samples, respectively.

**Chemical constitution:** The wave numbers of some of characteristic bands of Z, ZA and ZF samples with their assignments are given in Table-5. The band at 450 cm<sup>-1</sup> in zeolite sample (Z), which assigned to bending vibration,  $\beta$ [Si-O-Si(Al)], has shifted to 463 and 453 cm<sup>-1</sup> in zeolite-acetamide sample (ZA) and zeolite-DMF (ZF) samples, respectively. The main characteristic band of asymmetric stretching vibration,  $\nu_{asy}$ [Si-O-Si(Al)], which appears at 1025 cm<sup>-1</sup> in Z has not strongly shifted due to acetamide and DMF treatments; thus appears at 1024 and 1016 cm<sup>-1</sup> in ZA and ZF, respectively. Moreover, the band of symmetric stretching vibration,  $\nu_{sym}$ [Si-O-Si(Al)], at 1440 cm<sup>-1</sup> in the untreated zeolite sample (Z) has shifted to 1429 and 1439 cm<sup>-1</sup> in ZA and ZF samples, respectively.

TABLE-5  
SOME INFRARED ABSORPTION BANDS (cm<sup>-1</sup>) OF SAMPLES Z, ZA AND ZF

Z	ZA	ZF	Assignment
1633	1661	1658	$\beta$ (H <sub>2</sub> O) of anorthite (1635), augite (1630) <sup>1</sup> and phillipsite (1648) <sup>27</sup>
1440	1429	1439	$\nu_{sym}$ [Si-O-Si(Al)] of anorthite <sup>28</sup>
1025	1024	1016	$\nu_{asy}$ [Si-O-Si(Al)] of anorthite (1028), phillipsite (1018) and augite (1023) <sup>29</sup>
450	463	453	$\beta$ [Si-O-Si(Al)] of phillipsite (445) <sup>27</sup>

The band at 1633 cm<sup>-1</sup>, which is assigned to bending vibration of water molecules in sample Z,  $\beta$ (H<sub>2</sub>O), has shifted to higher frequencies appearing at 1661 and 1658 cm<sup>-1</sup> in ZA and ZF, respectively as illustrated in Fig. 6. Such shifts in the wave numbers can be understood as another indication of zeolite surface modification.

**Removal of heavy metal cations:** It was reported in literature that the pretreatment of zeolite with NaCl increases the zeolite ability to remove heavy metals from their solutions<sup>17,18,30-32</sup>. It may be due to the increased rate of metal ions immobilization by zeolite transformed in Na form. In other words, heavy metal ions are more strongly bound to zeolite pretreated with NaCl compared to natural zeolite. Therefore, in this work the zeolitic tuff was treated with NaCl solution before modification with acetamide and N,N-dimethyl formamide.

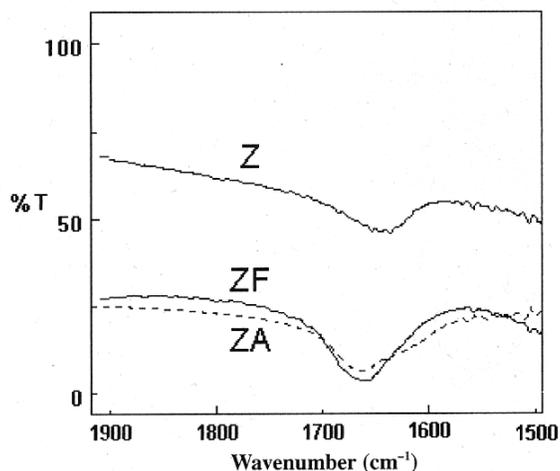


Fig. 6. Infrared spectra of samples Z, ZA and ZF in the region 1900 to 1500  $\text{cm}^{-1}$

The batch experiments were conducted at pH's 3, 4, 5 and 6. The pH values were selected to be in the acidic region since in the basic region metals hydroxides will precipitate. The metal cations [Pb(II), Cd(II), Ni(II) and Cu(II)] uptake for untreated zeolite (Z), zeolite-acetamide (ZA) and zeolite-DMF (ZF) samples are shown in Fig. 7. The heavy metals uptake was found to follow the order Pb(II) > Cd(II) > Ni(II) ~ Cu(II). Such order of heavy metal cations uptake on zeolites was also reported<sup>10,12,24</sup>.

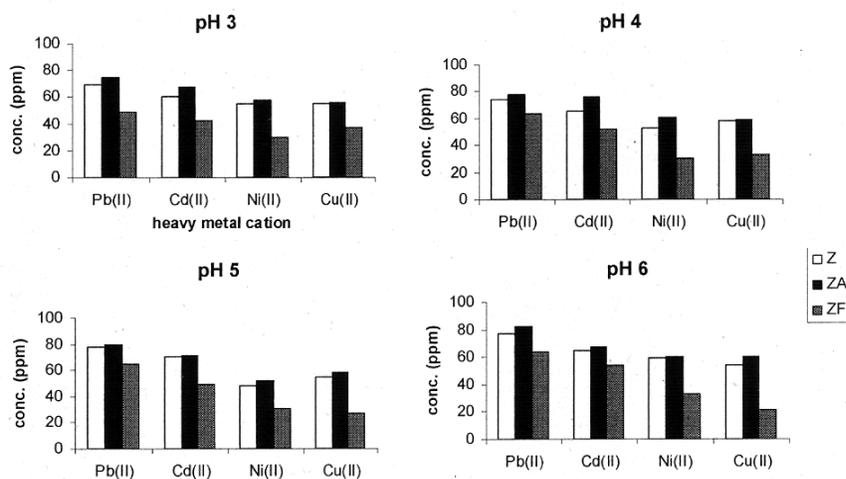


Fig. 7. Uptake (in ppm) of lead(II), cadmium(II), nickel(II) and copper(II) for zeolite samples Z, ZA and ZF at pH 3, 4, 5 and 6 after 50 min contact time according to batch experiments

Although amides blocked some of the holes and channels in the tuff, thus preventing the ions from being attracted to the negatively charged groups in the tuff, the uptake data, shown in Fig. 7, revealed that the removal ability of treated and untreated zeolitic tuff samples follows the sequence  $ZA > Z > ZF$ . The mechanism of heavy metals uptake on treated zeolitic tuff can be proposed to be through bonding of metal cations with the nonbonding electrons of nitrogen and/or oxygen atoms of amide. The zeolitic tuff treated with acetamide (ZA) could compensate this blockage effect and improve to some extent the uptake due to the presence of the lone pairs on the nitrogen/oxygen atom(s) of acetamide. On the other hand, the lower removal ability of ZF sample relative to ZA can be attributed to the steric effect on the availability of electron pair on the nitrogen atom. The two methyl groups on the nitrogen of DMF reduce the ability of electron pair to interact with metal cation. Furthermore, the enolic form of acetamide molecule,  $H_3C-C(O)-NH_2 \rightleftharpoons H_2C=C(OH)-NH_2$ , facilitates the interaction ability of acetamide with metal cation.

The uptake of cadmium and nickel cations by Z and ZA samples using continuous flow experiments are shown in Fig. 8. The uptake results revealed that the adsorption capacities of Cd(II) and Ni(II) were increased from 12 mg Cd(II)/g Z to 14 mg Cd(II)/g ZA and from 9 mg Ni(II)/g Z to 10.9 mg Ni(II)/g ZA, respectively. Such increase in the uptake ability supports the batch experiments' results that treatment of zeolitic tuff with acetamide enhances to some extent the tuff ability for removal of heavy metal cations.

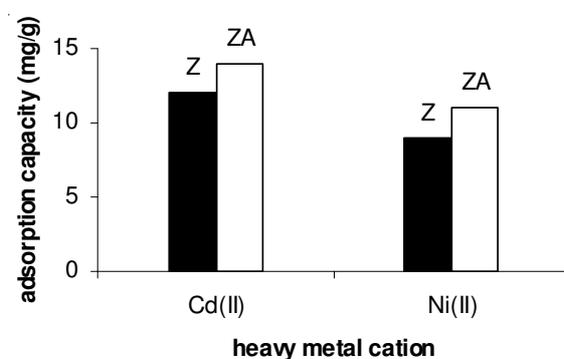


Fig. 8. Adsorption capacity (in mg metal/g zeolite) of zeolite samples Z and ZA toward cadmium(II) and nickel(II) at pH 4; according to continuous flow experiments

## Conclusion

The XRD results revealed that the chemical treatment of Jordanian zeolitic tuff using acetamide and N,N'-dimethyl formamide doesn't change the mineral content of the local tuff. The scanning electron microscopy, the XRF and the FTIR results gave a clear picture of the deposition of both acetamide and N,N'-dimethyl formamide on the zeolitic tuff surface.

The zeolitic tuff pretreated with NaCl can be used as a scavenger for Pb(II), Cd(II), Ni(II) and Cu(II) cations from their acidic aqueous solutions. Treating this tuff with acetamide improves slightly the removal ability of the tuff, whereas treating with N,N'-dimethyl formamide decreases the tuff ability for heavy metal cations uptake.

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