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Chemical Treatment of Jordanian Zeolitic Tuff Using Dimethyl Sulfoxide and Thiourea

ABDULAZIZ N. AMRO†, RUSHDI I. YOUSEF‡ and SALEM M. MUSLEH*
Chemistry Department, Prince Abdullah Bin Ghazi Faculty for Science and Information Technology, Al- Balqa Applied University, Al-Salt, 19117,Jordan
E-mail: smusleh@lycos.com

Jordanian zeolitic tuff was chemically treated with dimethyl sulfoxide and thiourea. The treated and untreated zeolitic tuff samples were characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF) and scanning electron microscopy (SEM). The XRD and XRF results showed that the chemical treatments using dimethyl sulfoxide and thiourea do not change neither the mineral constituents nor the Al_2O_3 and SiO_2 contents of the zeolitic tuff. The SEM figures showed clearly loading amounts of both dimethyl sulfoxide and thiourea on the zeolitic tuff surface. The ability of treated and untreated zeolitic tuff samples to remove some heavy metals ions from their acidic aqueous solutions was investigated. The results revealed that treatment with thiourea enhances the tuff ability for Pb(II), Cd(II), Zn(II) and Ni(II) cations uptake. In general, the metals uptake by zeolitic samples was found to decreased in the order Pb(II) > Cd(II) > Zn(II) > Ni(II).

Key Words: Jordanian zeolitic tuff, Chemical treatment, Dimethyl sulfoxide, Thiourea, Heavy metal cations uptake.

INTRODUCTION

Natural zeolites are low cost aluminosilicates, with a cage-like structure suitable for ion exchange due to isomorphous replacement of Al^{3+} with Si^{4+} in the structure, giving rise to a deficiency of positive charge in the framework. This is balanced by mono and divalent exchangeable cations such as Na^+, Ca^{2+}, K^+ and Mg^{2+}. Zeolite structure contains channels and pores filled with a certain amount of water and the exchangeable cations. Some cations constituents may be exchangeable from the zeolite inner cavities and pores without any major changes of zeolite structure[1].

Zeolitic tuff deposits were discovered in Jordan in 1987 in the eastern part of the country at Jabal Aritayn, 30 km NE of Azraq[2]. 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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†Environmental Research Center, Royal Scientific Society, Al-Jubaiha 11941, Jordan.
‡Department of Chemistry, Faculty of Arts and Sciences, Petra University, Amman 11196, Jordan.

Chemical treatments of Jordanian zeolitic tuff using urea[3], oxalic and salicylic acids[4], acetamide and N,N-dimethylformamide[5] and cationic surfactants[6] have been studied by our group. In this work we extend the investigation on the chemical treatments of the local zeolitic tuff by treating it with dimethyl sulfoxide and thiourea. Such treatments were studied by the technique of scanning electron microscopy, powder X-ray diffraction and X-ray fluorescence techniques.

Heavy metals such as lead, cadmium, zinc and nickel are prior toxic pollutants in industrial wastewater and they also become common groundwater contaminants. These metals are not biodegradable and tend to accumulate in organisms causing numerous diseases and disorders[7,8]. They occur naturally in very limited amounts of the earth's crust, as sulfides, sulfates, carbonates or silicates with average concentrations of 15, 0.2, 70 and 75 mg/kg for lead, cadmium, zinc and nickel, respectively[9]. Among the methods such as precipitation, oxidation, ultrafiltration, reverse osmosis and electrodialysis, ion exchange on natural zeolite seems to be more effective method[10].

Natural zeolites provide an economic and effective mechanism to remove heavy metals dissolved in waste stream[8,11-14]. Consequently, several studies of using Jordanian zeolitic tuff as scavengers of inorganic as well as organic pollutants from water have been reported[3,4,15-23]. In this work, the ability of untreated as well as treated Jordanian zeolitic tuff with dimethyl sulfoxide and thiourea for the removal of Pb^{2+}, Cd^{2+}, Zn^{2+} and Ni^{2+} from their acidic aqueous solutions was investigated.

EXPERIMENTAL

Tuff preparation: Zeolitic tuff (from Jabal Aritayn in Jordan) was crushed using Jaw Crusher (Sepronic), homogenized and sieved at different meshes. The portion with the particle size of 500-1000 micron was selected[3] and labeled ZR. The ZR sample was washed several times with distilled water until clear solution and dried overnight in an oven (Memert 500) at 105 °C. A 200 g of the dried sample was washed 3 times (3 × 500 mL) with 2 M NaCl solution, 1 h each, using a magnetic stirrer (Cimraris Thermolyne, 100 rpm). The tuff was then allowed to settle down before decanting the supernatant. The wet tuff was washed with distilled water several times to get rid of any residual chloride ions (using 0.01 M $AgNO_3$ solution)[24], dried overnight in the oven at 105 °C and then kept in a desiccator over anhydrous $CaCl_2$ and labeled Z.

Treatment with dimethyl sulfoxide: A 10.0 g sample of Z was mixed with dimethyl sulfoxide (100 mL) in a flask. The mixture was stirred using the magnetic stirrer (100 rpm) for 2 h. After decanting the supernatant, wet zeolite was washed with distilled water 3 times, dried overnight in the oven at 70 °C and then weighed to estimate the amount of loaded dimethyl sulfoxide (0.62 g). The DMSO-treated zeolite was kept in a desiccator over anhydrous $CaCl_2$ and labeled ZD.

Treatment with thiourea: A solution of 9.0 g thiourea in 100 mL distilled water was poured on a 10.0 g sample of Z. The mixture was stirred using the magnetic stirrer (100 rpm) at 60 °C using a hotplate magnetic stirrer for 4 h. The supernatant was decanted and the wet zeolite was washed with distilled water 3 times. Both washing and decantation solutions were mixed and heated till dryness to estimate the amount of thiourea remain unloaded on zeolite (the loaded amount of thiourea = 0.28 g). The thiourea-treated zeolite was dried overnight in the oven at 105 °C, then kept in a desiccator over anhydrous $CaCl_2$ and labeled ZT.

Characterization of zeolitic tuff samples: Zeolitic samples were characterized by ascertaining their chemical composition and mineral constitution as well as their surface morphology. The chemical composition was determined by X-ray fluorescence technique. The operating conditions were followed as presented by the manufacturer. Thus, 0.8 g of the sample was thoroughly mixed with 7.2 g of lithium tetraborate ($Li_2B_4O_7$) 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. The resultant glassy disc was used for XRF analysis. The mineral constitution of the samples was determined by powder X-ray diffraction technique, using X'pert instrument fitted with a Phillips X-ray tube giving CoKα radiation at $\lambda = 1.7889$ Å at 40 Kv and 40 mA. The surface morphology of the samples was investigated using scanning electron microscope at 20 Kv, where all samples were carbon plated and adhere on stubs by liquid carbon to make sure that the sample conducting electrons.

Removal of heavy metals cations: Heavy metals stock solutions of 1000 ppm were prepared from $Ni(NO_3)_2 \cdot 6H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$ and $Pb(NO_3)_2$ (99 % from Fluka).

A 100 ppm standard solution of each heavy metal was prepared separately from the corresponding stock solution. The standard solution was divided into 4 portions, each with different pH value, *viz.*, 3, 4, 5 and 6. The pH values were adjusted using 0.1 M NaOH/0.1 M HNO_3. A 50 mL solution from each portion of selected heavy metal was added to a 1.0 g of each zeolitic sample Z, ZD and ZT, separately. A 2.0 mL of supernatant was taken from each solution every 10 min for a period of 50 min and diluted to 25 mL with distilled water. The heavy metals concentrations were measured using atomic absorption spectrometer (Shimadsu 6800). A continuous flow experiment was performed using two 5.0 g samples of Z and ZT, which were placed independently in 2 columns each of 0.4 cm diameter prepared for this purpose. To each packed column, a 100 mL volume of 1000 ppm of Zn^{2+} solution was poured, which passed within about 10 min. A 2 mL portion of the eluted solution was diluted to 25 mL with distilled water and then measured by the atomic absorption spectrometer.

RESULTS AND DISCUSSION

Mineral constitution: The mineral constitution of the zeolitic tuff samples ZR, Z, ZD and ZT are shown in Table-1. The XRD results for the samples indicated

TABLE-1
MINERAL CONTENTS OF TREATED AND UNTREATED
ZEOLITIC SAMPLES ZR, Z, ZD AND ZT

Sample	Anorthite	Phillipsite	Hematite	Augite	Montmorillonite-15a
ZR	Major	Minor	Minor	Minor	Trace
Z	Major	Minor	Minor	Minor	Trace
ZD	Major	Minor	Minor	Trace	Trace
ZT	Major	Minor	Minor	Trace	Trace

that anorthite (feldspar) was the major mineral constituent. Phillipsite (zeolite) and hematite (oxides) were found as minor constituents and montmorillonite (clay) as a trace constituent. The augite (pyroxene) was found as a minor constituent in samples ZR and Z and as a trace in samples ZD and ZT. Such results indicate unambiguously that the mineral constitution of the zeolitic tuff was not affected by the chemical treatment using dimethyl sulfoxide and thiourea.

Surface morphology: The surface morphology of the zeolitic tuff samples Z, ZD and ZT was investigated by the scanning electron microscopy (SEM). Figs. 1 and 2 show the presence of anorthite and phillipsite in the zeolitic tuff sample Z. The chabazite mineral (zeolite) was also detected in sample Z as shown in Fig. 3, which is often accompanied with phillipsite in Jordanian zeolitic tuff[25].

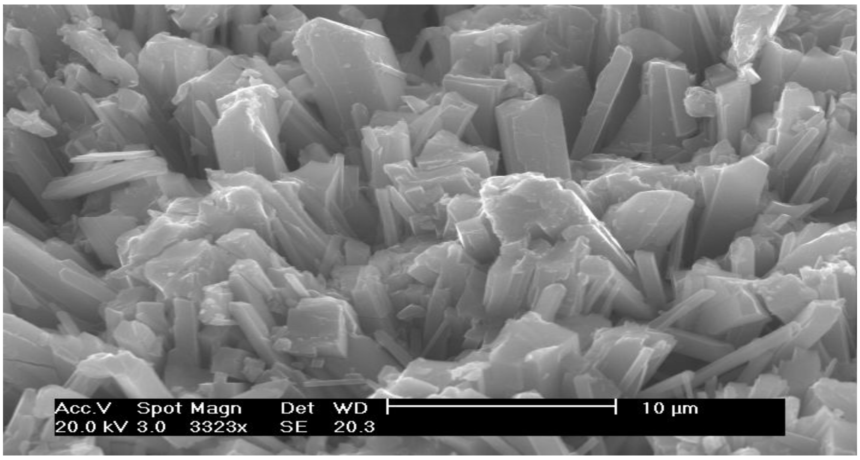
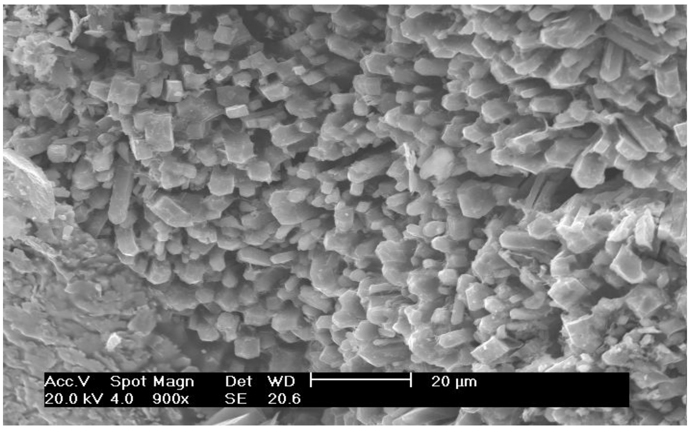


Fig. 1. SEM Graph of anorthite in sample Z

The SEM graph, Fig. 4, for the dimethyl sulfoxide-treated zeolitic tuff sample ZD shows clearly the coating of phillipsite by DMSO molecules. In a similar manner, the phillipsite surface in ZT sample shows nearly a complete surface coverage by thiourea, with an evidence of weathering represented by cracks formed as shown in Fig. 5.



Fi. 2. SEM Graph of phillipsite in sample Z

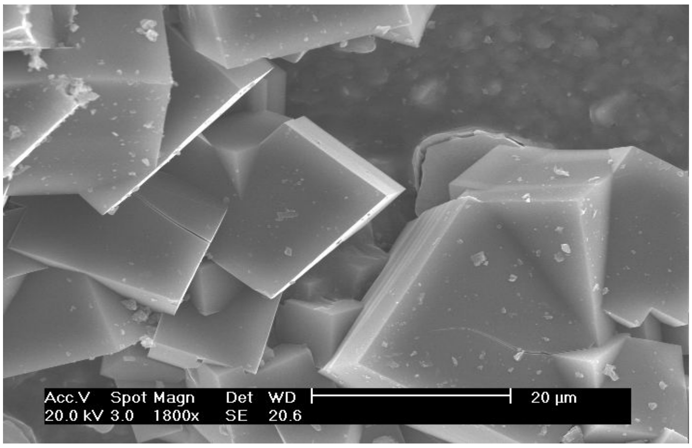


Fig. 3. SEM Graph of chabazite in sample Z

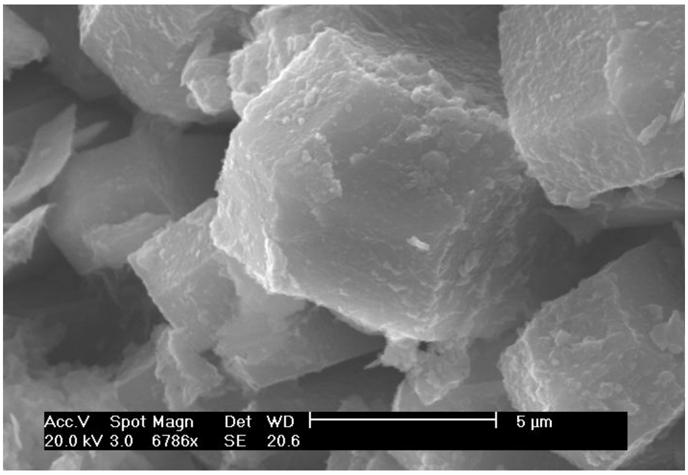


Fig. 4. SEM Graph of phillipsite coated with DMSO in sample ZD

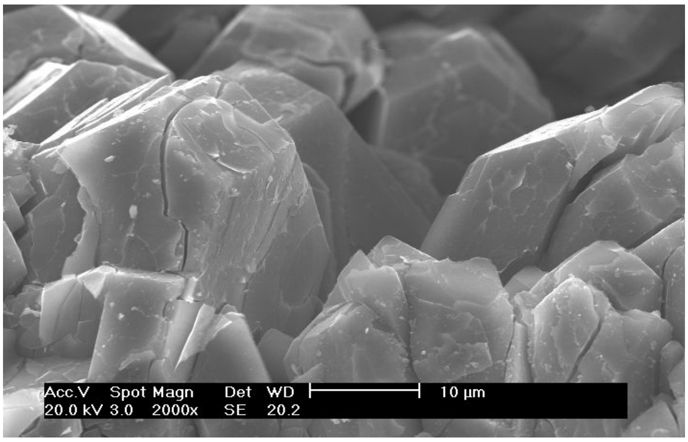


Fig. 5. SEM Graph of phillipsite coated with thiourea in sample ZT

Chemical composition: The zeolitic tuff samples ZR, Z, ZD and ZT were characterized by X-ray fluorescence technique. The percentages of metal oxides in the zeolitic tuff samples are shown in Table-2. These percentages did not add up to 100 % since the remainder (loss on ignition, L.O.I.) is lost upon the sample preparation for XRF measurements as combined water, carbonate, sulfate or volatile chlorides[3].

TABLE-2
CHEMICAL COMPOSITION (%) OF TREATED AND UNTREATED ZEOLITIC SAMPLES ZR, Z, ZD AND ZT

Sample	ZR	Z	ZD	ZD_{corr}[a]	ZT	ZT_{corr}[a]
Fe_2O_3	17.8	11.3	10.2	10.8	11.4	11.7
MnO	5.14	0.33	0.31	0.33	0.62	0.64
TiO_2	2.15	2.15	1.98	2.09	2.16	2.22
CaO	8.48	8.42	7.43	7.85	8.05	8.26
K_2O	1.17	0.93	0.86	0.91	0.91	0.93
P_2O_5	0.14	0.43	0.42	0.44	0.43	0.44
SiO_2	39.7	42.0	40.6	42.8	41.0	42.1
Al_2O_3	12.3	14.1	13.8	14.6	13.7	14.0
MgO	9.82	10.3	8.96	9.46	9.69	9.94
Na_2O	1.18	1.92	1.76	1.86	1.65	1.69
L.O.I.	1.45	8.04	13.4	8.90	10.6	8.27

[a]Corrected for deposited amount of DMSO (5.36 %) and thiourea (2.56 %) calculated on the assumption of constant water content of 8.04 % as in Z.

Washing the raw zeolitic tuff (ZR) with distilled water and with brine has nearly affected the amounts of all metal oxides except TiO_2 and CaO. Such pretreatments decreased the amount of Fe_2O_3 (40 %), MnO (90 %) and K_2O (20 %), which may be attributed to the loss of clay during washing processes. Percentages of other metals oxides were relatively increased reflecting the stability of these metals in the zeolitic tuff structure. The Na_2O content showed an increase of 60 % due to the pretreatment with NaCl solution.

The amounts of ligands loaded on zeolitic tuff could be estimated from the differences in L.O.I. values between treated and untreated samples. Thus, the amounts of DMSO and thiourea loaded on zeolitic tuff were found to be 5.4 and 2.6 %, respectively, which are in agreement with the values obtained from the gravimetric results (6.2 % for DMSO and 2.8 % for thiourea).

Concerning the effect of chemical treatment on the chemical composition, the treatment with DMSO affected the percentages of the metal oxides to a < 10 %. On the other hand, treatment with thiourea affected the percentages of most metal oxides to a < 5 %. However, the amount of MnO in ZT sample was increased to a 90 % and that of Na_2O decreased to about 10 %.

Although the natural zeolitic tuff sample Z contains non-zeolitic minerals, *i.e.* anorthite, augite and montmorillonite, the over all characteristic behaviour seems to be that of zeolites as indicated by the atom composition calculations[26] given in Table-3 and the indicator ratios[27] shown in Table-4.

TABLE-3
NUMBER OF ATOMS OF ELEMENTS IN THE ZEOLITIC SAMPLES Z, ZD AND ZT[a]

Element	Z	ZD	ZT
Si	7.476	6.855	7.134
Al	2.955	2.749	2.780
Fe	1.581	1.297	1.486
Mn	0.150	0.045	0.091
Mg	2.740	2.258	2.513
Ca	1.604	1.346	1.500
K	0.212	0.184	0.203
P	0.064	0.061	0.063
Na	0.675	0.577	0.556
Ti	0.288	0.252	0.281
H	9.543	15.07	12.26
O	32.00	32.00	32.00

[a] Calculated from data given in Table-2 on the basis of 32 oxygen atoms [Ref. 26].

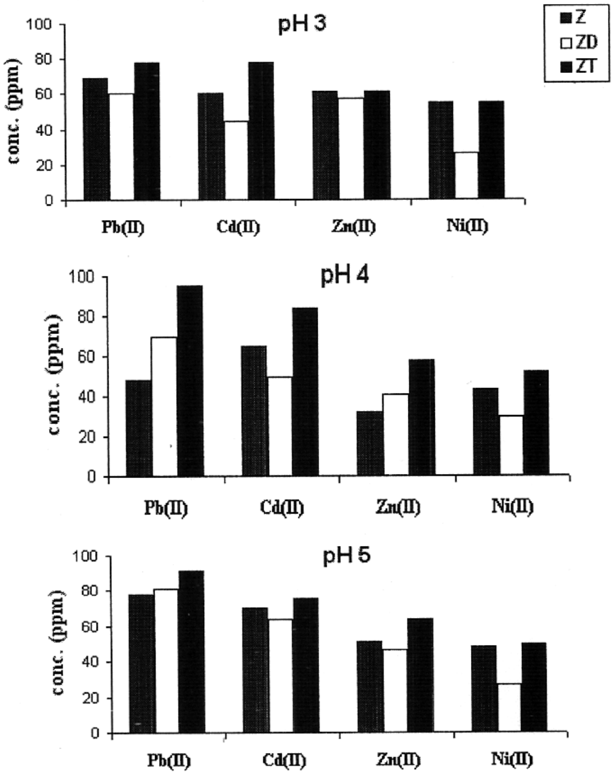
TABLE-4
INDICATOR RATIOS FOR ZEOLITIC SAMPLES Z, ZD AND ZT [Ref. 27]

Indicator ratio (R)	Z	ZD	ZT
(Si)/(Si + Al)	0.699	0.714	0.720
Si/Al	2.530	2.494	2.566
(Si + Al)/O	3.575	3.048	3.238
$(SiO_2)/(Al_2O_3)$	2.980	2.938	3.024
(Mg + Ca + Na + K) Oxides/(Al_2O_3)	1.530	1.378	1.497

The indicator ratio Si/(Si+Al) was found to be within the range of intermediate ordered zeolites, *i.e.*, 0.625 < R < 0.75, due to the scale reported by Gottardi[27], who divided zeolites to basic, acidic and intermediate according to Si/(Si+Al) ratio. The Si/Al ratio, which can vary considerably within the limits of one structural type, depending upon the compositions of original solutions and conditions of crystallization[28] was found to be nearly the same for treated and untreated samples. Other interesting atom ratio is (Si + Al)/O, which shows a small deviation from the values for zeolites[25], this is to be expected, as this ratio is quit sensitive to the mixture composition of the samples.

The ratios of the oxides, *i.e.*, SiO_2/Al_2O_3 and (Mg + Ca + K + Na) oxides/Al_2O_3, for typical zeolites are ~ 2 for the former and ≈1 for the latter. These indicator ratios, which are given in Table-4, show that treatments with thiourea and DMSO have no significant effect on Al_2O_3 and SiO_2 contents.

Removal of heavy metals: The uptake of heavy metals cations, *viz.*, Pb^{2+}, Cd^{2+}, Zn^{2+} and Ni^{2+} by zeolitic samples Z, ZD and ZT was investigated at different pH values, *viz.*, 3, 4, 5 and 6 as shown in Fig. 6. The uptake experiments were performed in acidic media because heavy metals precipitate as hydroxides, $M(OH)_2$, in basic media. As shown in Fig. 6, the metals uptake was slightly influenced by the change of the pH value in the acidic range 3-6, such slight effect was reported elsewhere[8]. However, the sequence of metal cations uptake was found to follow the order $Pb^{2+} > Cd^{2+} > Zn^{2+} > Ni^{2+}$. Similar uptake behaviour of heavy metal cations on zeolites has been presented in literature[7,29,30].



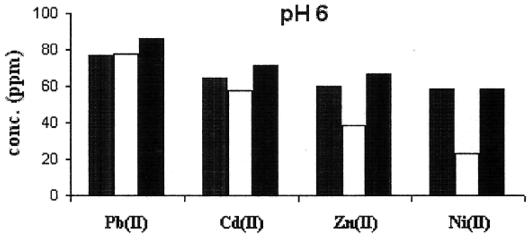


Fig. 6. Uptake (in ppm) of lead, cadmium, zinc and nickel cations for zeolitic samples Z, ZD and ZT at pH 3, 4, 5 and 6 after 50 min contact time

The zeolite pores may be closed by thiourea and DMSO molecules. Thus, retarding the possibility of ion exchange among heavy metals cations in the aqueous solution and the exchangeable cations of the zeolite framework. Therefore, the mechanism of adsorption of heavy metals on treated zeolitic tuff can be proposed to be through bonding of metal cations with the non-bonding electrons of ligands loaded on zeolitic tuff. Batch experiments results revealed, in general, that the heavy metals cations uptake decreases in the order ZT > Z > ZD. Thus, treating zeolitic tuff with thiourea enhances the ability of the tuff for removal heavy metals cations due to the presence of nonbonding electrons (lone pairs) on nitrogen and sulfur atoms of thiourea. Whereas, the lone pairs electrons of oxygen atom of DMSO molecule are no longer available for complexing heavy metals cations because these electrons are often bound to the silanol (Si-OH) and aluminol (Al-OH) moieties of zeolite surface.

In the light of batch experiments results, a continuous flow experiment was conducted to investigate the uptake of Zn^{2+} from its aqueous solution using samples Z and ZT as shown in Fig. 7. The figure shows clearly the increase of Zn^{2+}-uptake capacity by thiourea-treated zeolite sample (ZT), from 8.5 mg/g Z to 10.8 mg/g ZT.

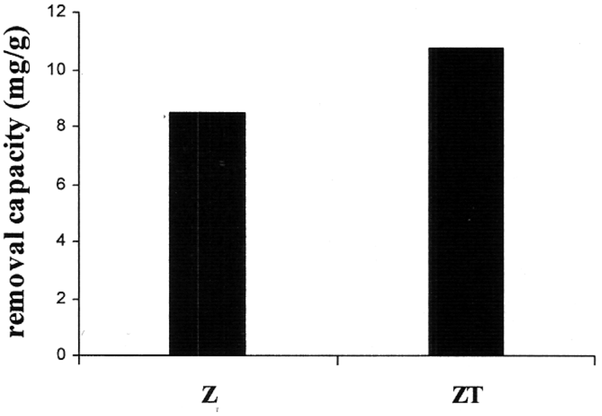


Fig. 7. Uptake capacity (in mg Zn^{2+} / g zeolite) of zeolitic samples Z and ZT

Conclusion

The chemical treatment of Jordanian zeolitic tuff with dimethyl sulfoxide and thiourea under the experimental conditions employed in the present work did not affect the tuff mineral constitution. The SEM graphs showed clearly the deposition of dimethyl sulfoxide and thiourea on phillipsite surface after these treatments. Thiourea and dimethyl sulfoxide showed no significant influence on Al_2O_3 and SiO_2 content of the zeolitic tuff.

In contrast to the DMSO-treatment, the chemical treatment of zeolitic tuff with thiourea increases the ability of the tuff for removal of heavy metals from water. However, different pH values in the acidic range 3-6 do not play a remarkable role in metals uptake.

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