

## **Mn<sup>+2</sup> and Cd<sup>+2</sup> Removal from Industrial Wastewater Using Phillipsitic Tuff from Jabal Uniza, Southern Jordan**

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### **ABSTRACT**

Southern Jordanian natural zeolitic tuffs outcropped in Uniza volcano have been investigated and tested for their heavy metals' removal capacity. The main species identified in Uniza natural zeolitic tuffs are: phillipsite and, subordinately, chabazite. The effects of particle size and stirring time were examined in the removal experiments. Two types of Uniza phillipsitic tuff were used in the removal of Mn<sup>+2</sup> and Cd<sup>+2</sup> from treated industrial wastewater. The first type is the reddish bulk sample (UZ1), while the second type is the separated size (UZ2) fraction between 1 and 0.3 mm. Batch and column tests were performed to determine the removal capacity of Mn<sup>+2</sup> and Cd<sup>+2</sup> from treated industrial wastewater. In batch experiments (static regime), the use of UZ2 type shows a higher removal percentage of Mn<sup>+2</sup> and Cd<sup>+2</sup> compared to UZ1 type for the same time. The results of column experiments indicate that toxic metal ions such as Mn<sup>+2</sup> and Cd<sup>+2</sup> can be removed with approximately 100% efficiency from industrial wastewater containing similar ions using Jordanian zeolitic tuff. In dynamic regime, by using UZ1 the manganese ions (Mn<sup>+2</sup>) were completely removed up to 57 BV (1.71 L) and the zeolite exhaustion took place after more than 112 BV (3.36 L), while by using UZ2 the manganese ions were completely removed up to 67 BV (2.01 L) and the zeolite exhaustion took place just around 114 BV (3.42 L). For an efficient cadmium ions removal, the use of UZ1 sample showed a complete removal up to 85 BV (2.55 L) and the zeolite exhaustion took place after more than 129 BV (3.87 L), while the use of UZ2 showed that the Cd<sup>+2</sup> ions were completely removed after 151 BV (4.53 L) and the zeolite exhaustion took place after more than 205 BV (6.15 L).

**KEYWORDS:** Natural zeolite, Uniza, Phillipsitic tuff, Wastewater, Phillipsite, Heavy metals.

### **INTRODUCTION**

Zeolites are a group of hydrated aluminum-silicates of the alkali or alkaline earth metals (sodium, potassium, magnesium, calcium) characterized by low mining cost, availability, bulk density and high resistance to alteration (Mercer and Ames, 1978). Zeolites have a three-dimensional crystalline framework of tetrahedral silica or alumina anions strongly bonded at all corners, and they contain channels filled with water and exchangeable cations.

The structure is suitable for ion exchange due to

isomorphism: the replacement of Al<sup>3+</sup> with Si<sup>4+</sup> 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<sup>+</sup>, Ca<sup>2+</sup>, K<sup>+</sup> and Mg<sup>2+</sup>. The main consequence of this structure type is represented by the reversibility of the hydration and cation exchange processes that preserve the original network. Thus, they present specific properties (e.g., adsorption-desorption capacity, ion exchange capacity, catalytic properties), which confer to this group of minerals important and diverse possibilities of usage.

Ion exchange capacity and cation selectivity are the most important properties for zeolite as a natural molecular sieve material for wastewater treatment. Ion

exchange is defined as a process in which an insoluble substance removes ions of positive or negative charge from an electrolytic solution and releases other ions of like charge into the solution in chemically equivalent amounts (Benfield, 1982). Cation selectivity refers to the preference order of zeolite for cations based on the various factors which determine the selectivity; ion size, valence and hydration energies are important factors in determining the selectivity of a given ion in a specific system. The zeolite prefers or is highly selective for certain cations and does not prefer or is less selective for others (Colella, 1996). Ames (1960) has demonstrated that zeolites can be used in radioactive wastewater treatment due to their high ion exchange selectivity and resistance to degradation from radiation. Pansini *et al.* (1996) found that zeolite removes heavy metals from natural and industrial wastewaters. Mercer *et al.* (1970) have used natural zeolite to remove ammonium ions from wastewater. Simes and Hindin (1978) have demonstrated that the preferred method for removing traces of  $\text{NH}_4^+$  from fresh hatchery water is a possible method to satisfy the standard for water reuse. The proposed design has used an ion exchange using natural clinoptilolite. Blanchard *et al.* (1984) have indicated that clinoptilolite has a good selectivity for the ammonium ion. The efficiency order is as follows:



The above heavy metals as well as ammonium in wastewater can be treated by passing it through clinoptilolite columns. Semmens (1978) has suggested that clinoptilolite is highly selective for barium and lead, but is less selective for copper, cadmium and zinc.

Zeolites in Jordan were first discovered by Dwairi (Dwairi, 1987). The Jordanian phillipsitic tuff has a good efficiency in ammonium removal from wastewater, as well as Hungarian clinoptilolite, but, phillipsite is more selective for ammonium ions (Dwairi, 1991). In addition, Dwairi (1992) has found that the Jordanian phillipsite is of good efficiency for cesium fixation and immobilization from nuclear waste in comparison with phillipsitic rich tuff from California and moderately rich tuffs from Arizona and Nevada. Atilli (1992) has evaluated the Jordanian phillipsitic tuff for applications in water softening, removal of ammonium and toxic heavy metal ions in laboratory and

pilot plant scale. Al-Rashdan (1994) has evaluated the effect of Jordanian phillipsitic zeolitic tuff from Jabal Aritayn on the removal of ammonium and phosphate from domestic wastewater. It was concluded that phillipsitic zeolitic tuffs have shown acceptable efficiency in the removal of pollutants from the effluent. Ibrahim *et al.* (2002) and Ed-Deen (1998) have evaluated zeolites from Tell Rimah for industrial wastewater treatment. The results have indicated that Tell Rimah zeolitic tuff showed high selectivity for the removal of Cu, Cr, Ni and Zn from electroplating factory effluents and could be used for removing Pb and Fe from the wastewater of the battery factory. Ibrahim and Akashah (2004) found that faujasite tuff from Jordan has a good selectivity for lead from wastewater.

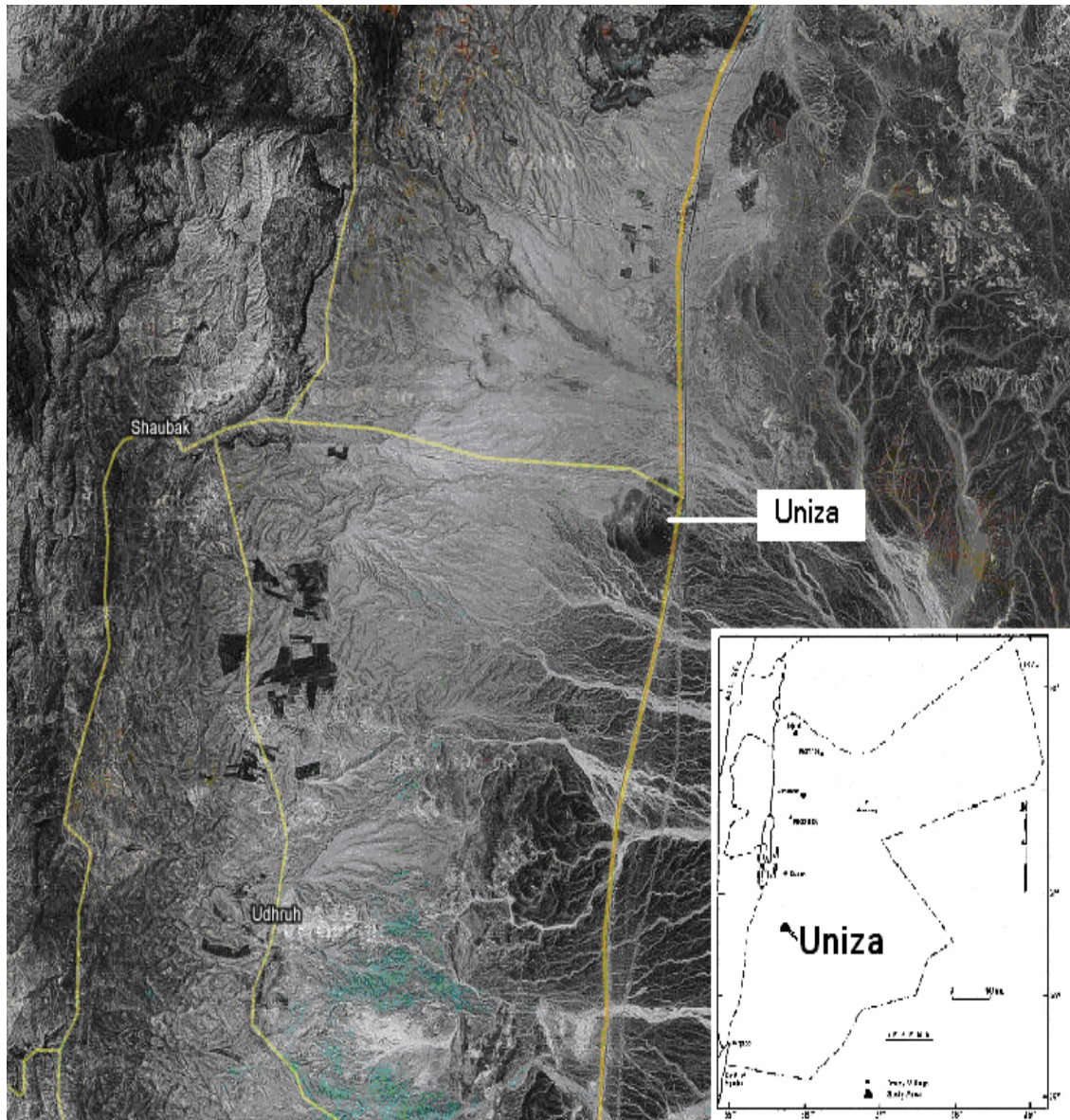
Al Dwairi (2007) studied the characterization of Jordanian zeolitic tuff and its potential use in wastewater treatment. He studied the mineralogy and geochemistry of all zeolitic tuff localities in Jordan and evaluated Jordanian natural zeolitic tuffs obtained from Hannoun (HNZ) and Mukawir (MNZ) volcanoes for removing selected heavy metals (Zn and Pb) and total organic carbon from domestic wastewater. The results show that HNZ and MNZ are suitable for domestic wastewater treatment. Ibrahim and Jbara (2009) have used natural phillipsite-faujasite tuff from Jordan to remove paraquat from synthetic wastewater. They found that natural zeolites are suitable to remove paraquat.

Al Dwairi (2009) evaluated the Jordanian phillipsitic tuff from Al-Ataita volcano for applications in wastewater treatment. He concluded that Al-Ataita phillipsitic tuff shows good removal percentages of ammonium from municipal wastewater.

Southern Jordan volcanic eruptions consist of many volcanic cones. Uniza volcano is one of these cones (Figure 1). It lies about 175 km south of Amman with a height of 1144 m above the sea level (Ibrahim, 1987). Lithologically, Uniza volcanic rocks are 110 meters thick and comprise well bedded lapili and ash (Aritayn type), welded tuff, poorly bedded (Hassan type) and basaltic flows. Figure 2 shows a columnar section in the northeast part of the volcano (Ghrir, 1998). The dominating zeolites in Uniza zeolitic tuff are phillipsite as major (phillipsitic zeolitic tuff) and chabazite as minor minerals as shown in the X-ray pattern for zeolites from Jabal Uniza (Al Dwairi, 2007). Because of its huge amounts of zeolitic tuff and easiness to reach

via the highway leading to Aqaba, this location has been chosen from the southern Jordanian zeolitic tuffs to be used as pollutant control in removing heavy metals from industrial wastewater plants. This location has not been

studied before for its industrial ore environmental application. In addition, the information available on using phillipsite in wastewater treatment is very low in comparison with other natural zeolites.



**Figure 1: A location map showing Uniza volcano in south Jordan**

## MATERIALS AND METHODS

Two types of phillipsitic tuff were used in the experiments. These are Uniza bulk sample (UZ1) and Uniza processed sample (UZ2). Two systems of experiments were carried out: batch and bench scale (column) experiments.

## Sample Preparation

Phillipsitic tuff samples were prepared as follows:

- 1- Uniza bulk sample (UZ1) was collected as channel sample, crushed using a crusher with an aperture of 5 cm and then sieved into the size (2-1mm).
- 2- Uniza processed sample (UZ2) was crushed using a jaw crusher with an aperture of 5 cm and sieved

into the size (1-0.3 mm), which is characterized by a high content of zeolitic minerals reaching about 85% (Al Dwairi, 2007).

3- Powdered samples from (UZ1 And UZ2) were prepared for batch experiments.

| Location       | Thickness | Horizon                      | Lithology   | Description  |
|----------------|-----------|------------------------------|---|--|
| Uneiza Volcano | 20        | Upper Zone Sideromelane Zone |   | Agglomerated, bad sorted bed cemented, dominated by basaltic to scoriaeous bombs and show variation in color form violet to black, with carbonate. |
|                |           | Middle zone Palagonite       |   | Normal grading ashes, well sorted, well cemented, laminated  |
|                |           |                              | Normal grading lapilli, well sorted, well cemented with carbonate and silicious lithic, dominated by small rounded bombs at the lower part. |  |
|                |           |                              | Ashes, well sorted well cemented with carbonate   |  |
|                |           |                              | Normal grading lapilli, well sorted, well cemented, brownish color, carbonate and shale lithic.   |  |
|                |           |                              | Ashes, well sorted, well cemented, laminated, brownish color.   |  |
|                | 10        | Lower Zone Zeolite Zone      |   | Normal grading lapilli, well sorted, well cemented, with few small bombs.  |
|                |           |                              |   | Medium to coarse lapilli, bad sorted, well cemented, brownish red color, dominated by bombs.   |
|                |           |                              |   | Fine to coarse lapilli, bad sorted, well cemented with carbonate lithic, dominated by small bombs, reddish brown color highly zeolite content.     |
|                | 0         |                              |   |  |

Figure 2: A columnar lithological section and authigenic zonation in Uniza volcano after (Ghrir, 1998)

Natural zeolitic tuff samples were used in the removal experiment without any modification or chemical treatment.

Wastewater used in all experiments was obtained from the effluent of Al Tafila wastewater treatment plant in south Jordan. The samples were first filtered using filter paper to get rid of suspended solids, then spiked by 20 ppm concentration for each individual heavy metal at pH of 7.7 for all removal experiments.

**Experimental Methods**

In the batch method, the two types of phillipsitic zeolitic tuff were ground to powder, and the removal experiments were carried out by using polyethylene bottles containing a specific volume (50 ml) of effluent

wastewater and a fixed mass (1 gram) of powdered phillipsitic zeolitic tuff (UZ1 and UZ2) at a temperature of 25°C The containers were shaken for different periods of times (1, 2, 4, 8,12 and 24 hours) as shown in Table 1. The treated wastewater was filtered and analyzed for Mn<sup>+2</sup> and Cd<sup>+2</sup> concentrations. Column method was carried out using a bench scale plant consisting of a glass column with a length of 50 cm and a base area of 1 cm<sup>2</sup>. This column has been filled with 30 cm of two types of phillipsitic zeolitic tuff for each column as shown in Figure 4.

The column experiment was carried out using the following test conditions: a flow rate of 5 ml/min (10BV/h) for UZ2 and 10ml/min (20BV/h) for UZ1, original concentration for C<sub>0</sub> of 20 mg/L, and pH of 7.7.

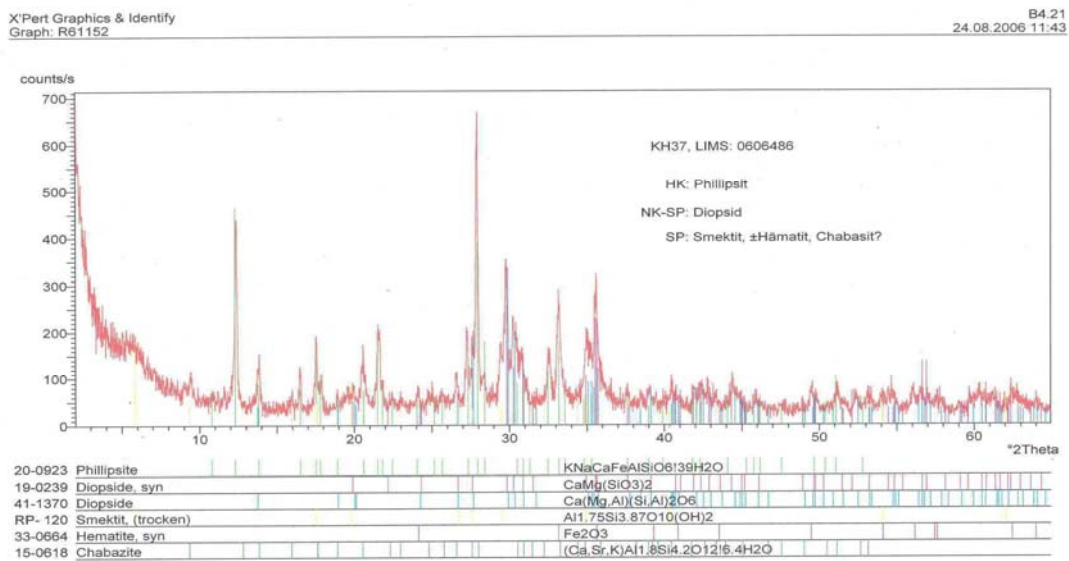


Figure 3: XRD pattern of phillipsite zeolitic tuff from the study area

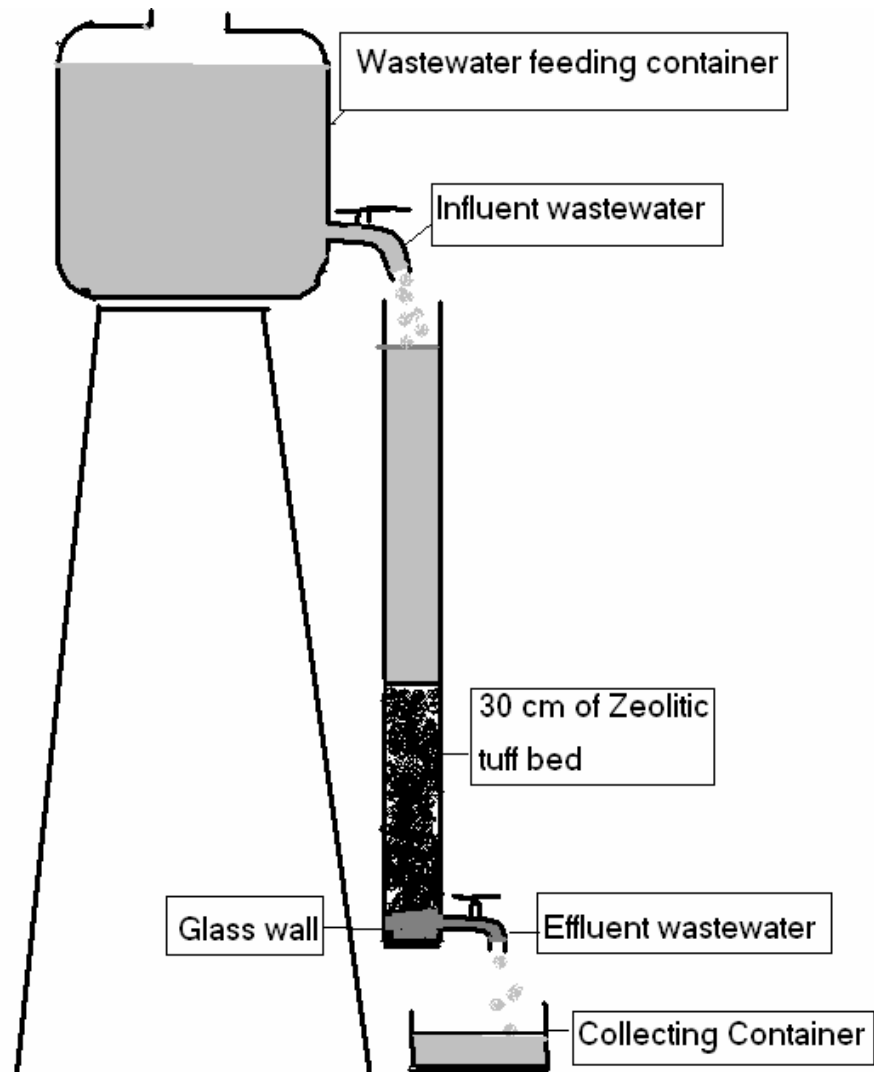


Figure 4: Bench scale plant method using 30 cm of Jordanian phillipsitic zeolitic tuff

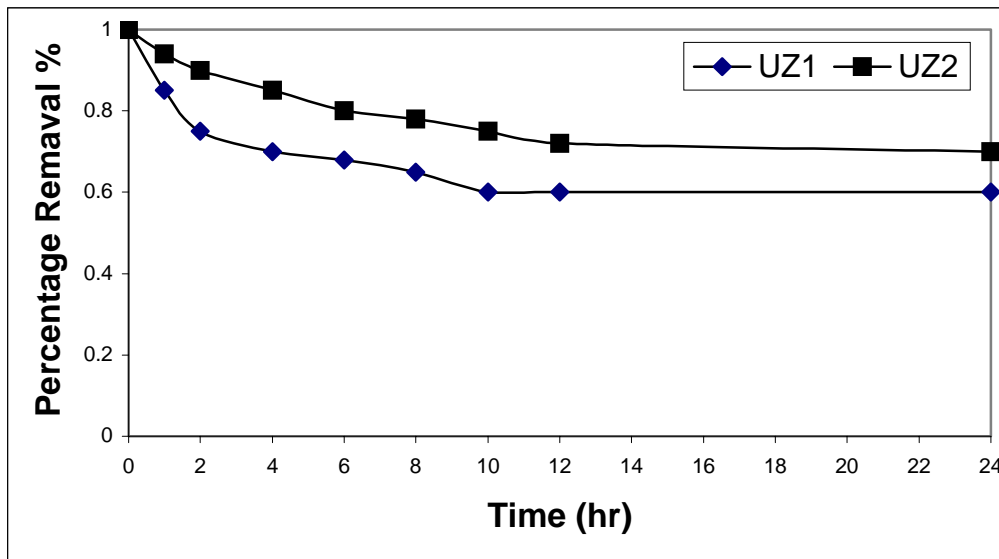


Figure 5: Decay curve of Mn<sup>2+</sup> from industrial wastewater using UZ1 and UZ2 phillipsitic zeolitic tuff

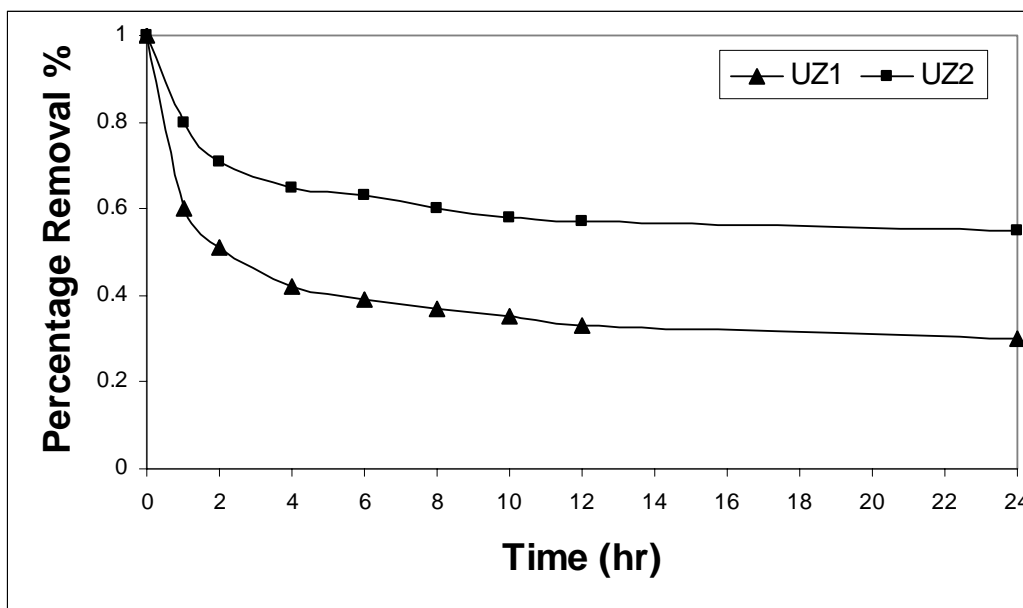


Figure 6: Decay curve of Cd<sup>2+</sup> from industrial wastewater using UZ1 and UZ2 phillipsitic zeolitic tuff

### Methods of Chemical Analysis

Chemical analysis of original and treated wastewater samples was conducted according to the standard methods of the examination of water and wastewater. The determination of heavy metal concentration was carried out using an Atomic Absorption Spectrophotometer (PYE Unica Spg).

### RESULTS AND DISCUSSION

#### Results of the Batch Experiments

Bach experiments were carried out for the two types of phillipsitic zeolitic tuff. The results obtained from these experiments were as follows :

The percentage removal [%] of Mn<sup>2+</sup> and Cd<sup>2+</sup> ions from industrial wastewater using powdered phillipsitic

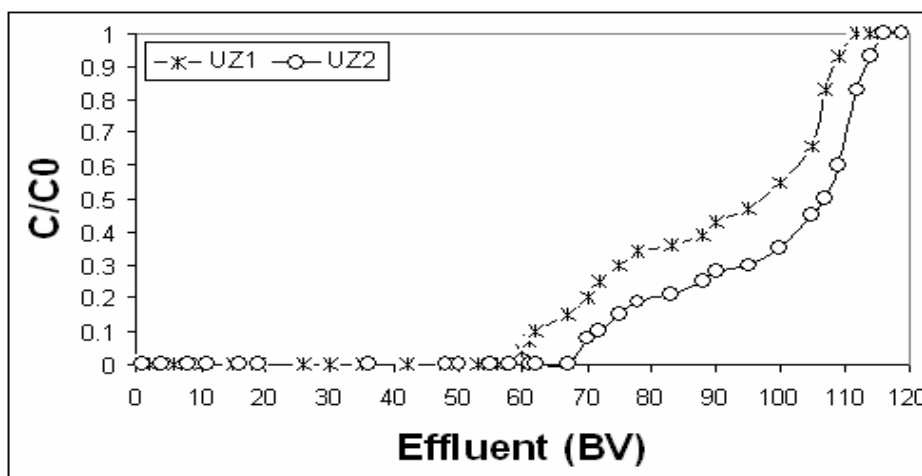
zeolitic tuff size of UZ1 and UZ2 for the different shaking times is listed in Table 1 and illustrated in Figures 5 and 6.

The batch method results show that the percentage removal for Mn<sup>+2</sup> ranges between (92.7%) and (96.6%)

and ranges between (93.3%) and (97.7%) by using UZ1 and UZ2, respectively. The percentage removal of Cd<sup>+2</sup> ranges between (93.1%) and (97.1%) and between (93.9%) and (97.9%) by using UZ1 and UZ2, respectively.

**Table 1: Percentage removal obtained from batch experiments for Mn<sup>+2</sup> and Cd<sup>+2</sup>**

| Phillipsitic zeolitic tuff | Shaking time (hours) | Percentage removal % Mn <sup>+2</sup> | Percentage removal % Cd <sup>+2</sup> |
|----------------------------|----------------------|---------------------------------------|---------------------------------------|
| UZ1                        | 1                    | 92.7                                  | 93.1                                  |
|                            | 2                    | 93.2                                  | 94.2                                  |
|                            | 4                    | 94.1                                  | 94.9                                  |
|                            | 8                    | 96.0                                  | 95.8                                  |
|                            | 12                   | 96.7                                  | 96.3                                  |
|                            | 24                   | 96.9                                  | 97.1                                  |
| UZ2                        | 1                    | 93.3                                  | 93.9                                  |
|                            | 2                    | 94.1                                  | 95.1                                  |
|                            | 4                    | 95.4                                  | 96.1                                  |
|                            | 8                    | 96.5                                  | 96.6                                  |
|                            | 12                   | 97.0                                  | 97.2                                  |
|                            | 24                   | 97.7                                  | 97.9                                  |



**Figure 7: Breakthrough curve for Mn<sup>+2</sup> sorption using UZ1 and UZ2 phillipsitic zeolitic tuff**

### Results of Column Experiments

The results of column experiments of Mn<sup>+2</sup> and Cd<sup>+2</sup> adsorption are represented by breakthrough (S) curves as shown in Figures 7 and 8 by using UZ1 and UZ2 natural Jordanian phillipsitic zeolitic tuff.

The adsorption of Mn<sup>+2</sup> and Cd<sup>+2</sup> using UZ2 samples in the column system shows breakthrough and exhaustion points higher than those observed in UZ1 samples in the same experiments by using a 30 cm thick fixed bed of Jordanian phillipsitic zeolitic tuff. In column fixed bed UZ1 and UZ2 show a good selectivity

for Mn<sup>+2</sup> and Cd<sup>+2</sup>. The selectivity for Cd<sup>+2</sup> ions is higher than that for Mn<sup>+2</sup> ions by using the two types of phillipsitic tuff (Cd<sup>+2</sup> > Mn<sup>+2</sup>), but the use of UZ2 shows the highest selectivity for Cd<sup>+2</sup> ions. The higher adsorption capacity for UZ2 can be explained by the accumulation of phillipsite in finer fractions due to the difference between the hardness of minerals and related to the fact that UZ2 sort is characterized by a low average diameter. In case of Cd<sup>+2</sup>, the ionic exchange capacities are higher due to the selectivity of phillipsite.

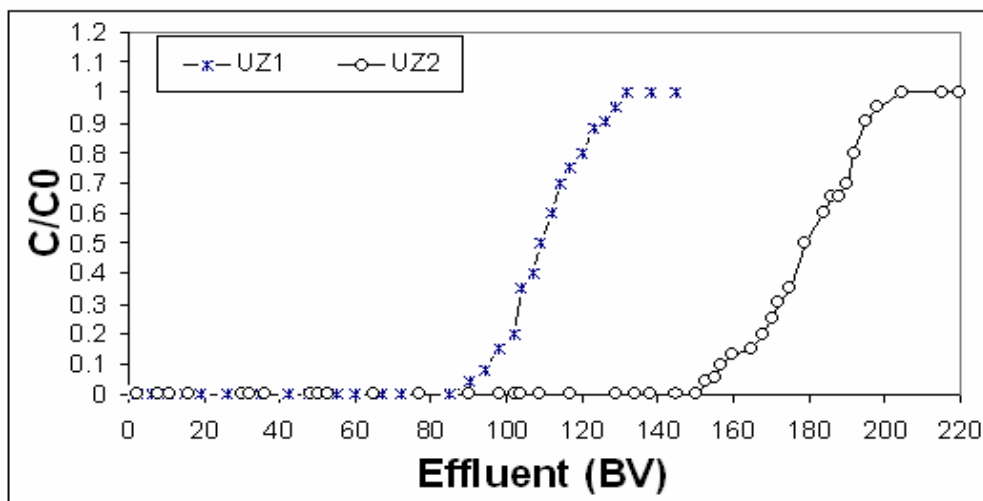


Figure 8: Breakthrough curve for Cd<sup>2+</sup> sorption using UZ1 and UZ2 phillipsitic zeolitic tuff

### CONCLUSIONS

The use of Jordanian natural phillipsitic zeolitic tuffs from Uniza area, southern Jordan (UZ1 and UZ2) as adsorbents is effective and suitable for the removal of heavy metals from industrial wastewater, either as a fixed bed of zeolite ion exchangeable material or by mixing the phillipsitic zeolitic tuff with the industrial wastewater.

The utilization of zeolite can be an alternative for removing of Mn<sup>2+</sup> and Cd<sup>2+</sup> ions, and the efficiency of the process is influenced by the different diameters of particles. UZ2 sample with size fractions (0.3-1mm) is

suitable for the removal of Mn<sup>2+</sup> and Cd<sup>2+</sup> ions from industrial wastewater. In the batch experiment, the increase of shaking time has increased the removal of heavy metals.

The zeolites have slightly higher preferences for Cd<sup>2+</sup> comparable with Mn<sup>2+</sup>. The utilization of the sort with a low average diameter of particles Mn<sup>2+</sup>, in static regime, to equilibrium adsorption capacity (for 24 h contact range) is higher for UZ2. In case of dynamic regime, a low average diameter of particles leads to a delay in reaching the penetration moment of the ionic column, obtaining a higher ionic exchange total capacity corresponding to the exhaustion of the column.

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