

# pH influence on heavy metals absorption on natural volcanic tuffs

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**Abstract:** The adsorption behavior of natural Jordanian volcanic tuff with regard to  $\text{Cr}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Zn}^{2+}$  was studied in dependence of solution pH in order to assess its practical and economic application for wastewater treatment. A series of batch-wise experiments were conducted using fixed-bed columns under multi changing conditions, as different pH-values (2, 4, 6 and 7), varying initial solute concentrations (1, 5, 10, 20) mg/L, different temperatures (10 C°, 20 C°, 30 C°), and varying tuff particle sizes (0.35 -3.5) mm. The filtrate was analyzed using A.A.S. The breakthrough curves in regard to absorption of  $\text{Fe}^{2+}$  and  $\text{Cu}^{2+}$  were obtained under different conditions through plotting the normalized effluent metal concentrations (C/C0) versus adsorbent volume. Uptake capacity factor for Fe ions found to equal 0.417 mg/g. While that of Cu ions found to be as much as 0.151 mg/g. Obtained results showed that volcanic tuff is an efficient and low cost ion exchanger and adsorbent for removing heavy metals. Results indicate that an initial solution pH of 2·0 is favorable for obtaining high chromium ions removal. Lead favour the pH=4 to be absorbed and removed from aqueous solution. Equilibrium modeling of the removal showed that the adsorption of the metal ions follows the linear adsorption isotherm.

**Keywords:** Natural volcanic tuff, heavy metals, absorption, pH, wastewater.

## 1.0 Introduction

Several toxic heavy metals have been discharged into the environment as industrial wastes, causing serious soil and water pollution problems.  $\text{Pb}^{+2}$ ,  $\text{Cu}^{+2}$ ,  $\text{Fe}^{+2}$ ,  $\text{Zn}^{+2}$  and  $\text{Cr}^{+3}$  are especially common metals that tend to accumulate in organisms, causing numerous diseases and disorders [1]. Toxic heavy metals 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. Heavy metal ions can be removed from wastewaters using a wide range of methods such as precipitation, solvent extraction, vacuum evaporation, membrane technologies, adsorption and ionic exchange. 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 [2]. The main advantages of ion exchange over chemical precipitation are: the removal of metal ions, selectivity and the less produced sludge. The region of middle east are well known by the limited water resources and this necessitates that much effort is put into water conservation, health protection and environmental protection. The expansion of industrial activities, including metal-based industries, and the excessive use of chemicals increase the pollution of waters with heavy metals. All these require the availability of low-cost technology and materials for wastewater treatment. Volcanic and zeolite tuff is widely distributed in Jordan. The North Arabian basalt plateau covers an area of about 11,000 km<sup>2</sup> (called Harrat Alsham) in the northeast of Jordan and extends northwest into Syria and southeast into Saudi Arabia [3]. 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). The huge reserves and the availability of the volcanic tuff as low cost material encouraged the authors to carry out this research. In addition The development of new and cost effective methods to remove heavy metals from ground water, drinking water and wastewater also becomes one of the research priorities.

**Table 1: Natural Resources Authority (NRA) estimation of volcanic tuff reserves in various areas in Jordan.**

Area	Geological Reserves (million ton)
Tal Rimah	46.0
Al-Aritayn	170.0
Tlul Al-Shahba	9.2
Northeast Areas	472.0
Other areas	1340.0



Figure 1: The natural Jordanian volcanic tuff used in experiments

One of the most promising approaches to improve the efficiency and increase the capacity of wastewater treatment plants in removing heavy metal cations without increasing size is based upon application of natural volcanic tuff rich in zeolites in the aeration basin. Zeolite particles are good carriers of bacteria, which adsorb on the zeolite surface resulting in increased sludge activity. They are considered to be, next to clay iron-oxide-coated sands and activated carbons, low-cost sorbents and offer a potential for a variety of industrial uses.

In literature there are many studies dealing with removing heavy metal by using natural zeolite in batch experiments [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11], but not enough data about using the column experiment are available.

This research study aims to assess the adsorption behavior of different heavy metal ions  $\text{Cr}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$  on natural untreated volcanic tuff material under changing the solution pH and to find the optimum pH for fixation of particular heavy metals.

## 2. Materials and Methods

### 2.1 Materials used in the study

Glass columns with different heights (40 -70 cm) were used in batch-wise experiments. The columns are filled with natural tuff aggregates having different sizes ranging from 0.5 – 0.3 mm. The conventional mineral processing techniques of volcanic tuff used are starting with crushing the materials followed by autogenously tumbling milling and then low intensity magnetic and gravity separation. Volcanic tuff was ground and then sieved to different fractions of which the fraction of 0.5 -3.0 mm were selected and used.

Table 2: grain size distribution of the used volcanic tuff material

Grain size (mm)	Weight (g)	Percentage (%)	Class
< 3	1000	100	coarse
<2	954.3	95.43	moderate
<1	439.15	43.92	fine
<0.5	46.68	4.67	fine

The tuff was not exposed to any pre - treatment or modification. Samples were just washed and dried at 103.5 °C and kept in desiccators for 24 h to ensure complete drying out. The initial aqueous solution concentrations of metals (1, 5, 10, 20) mg/L were prepared using standard solution for each metal.

### 2.2. Setup of Experiments

A batch-scale column system using coarse and fine volcanic tuff was developed to investigate the continuous removal of heavy metals under the influence of changing the pH. In these experiments, the effects of flow rate, hydraulic detention time, particle size of tuffs, column height, initial solution concentration and the pH on removal efficiency were investigated. In one-dimensional experiments with volcanic tuff aggregates filled columns of different sizes (fine, middle and coarse aggregates), were fed with synthetic wastewater containing metal solutions from top. The fixed bed columns, which will allow the most experimental variations, are filled with a layer of fine aggregates < 1mm at the bottom, over which a layer of tuff (different grain sizes) is placed. The hydraulic conductivity can be controlled by recording the time required to collect the injected sample outflow (hydraulic detention time). Samples from the wastewater inflow and outflows are taken for chemical analyses, where as volcanic tuff samples are analyzed for chemical parameters.

The dry mass of volcanic tuff used in one column weighs 79.52 g which forms a height of 10 cm. The volume of wastewater sample added each batch over the columns is 40 ml.

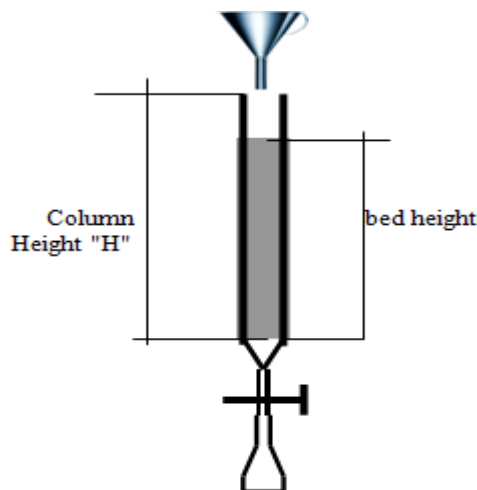


Figure 2: Column Experiment

### 2.3 Methodology

Jordanian volcanic tuff was studied for its absorbing potential for different metal ions ( $\text{Cu}^{+2}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cr}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Zn}^{2+}$ ) The batch technique of metal ions from solution was carried out at specific conditions, defined as:

- at pH of 1.0, 3.0, 4.0, 6.0 and 7,
- at temperatures 10, 20.0°C, 30.0°C and 45.0°C,
- at different contact time and with the same ionic strength (0.1M  $\text{NaClO}_4$ ).

Analysis of data will be based on adsorption models such as Langmuir, or Freundlich isotherms. Adsorption kinetics were applied in order to determine adsorption mechanism and adsorption characteristic constants. Representative samples of Jordanian volcanic tuff were investigated by using optical microscopy, scanning electron microscopy (SEM), X-Rays diffraction (XRD).

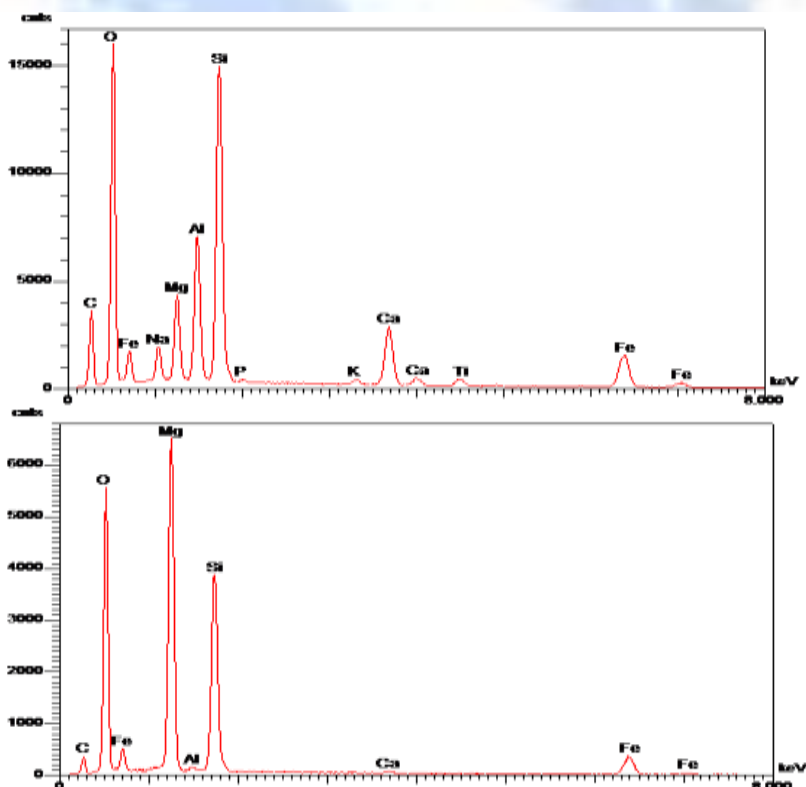
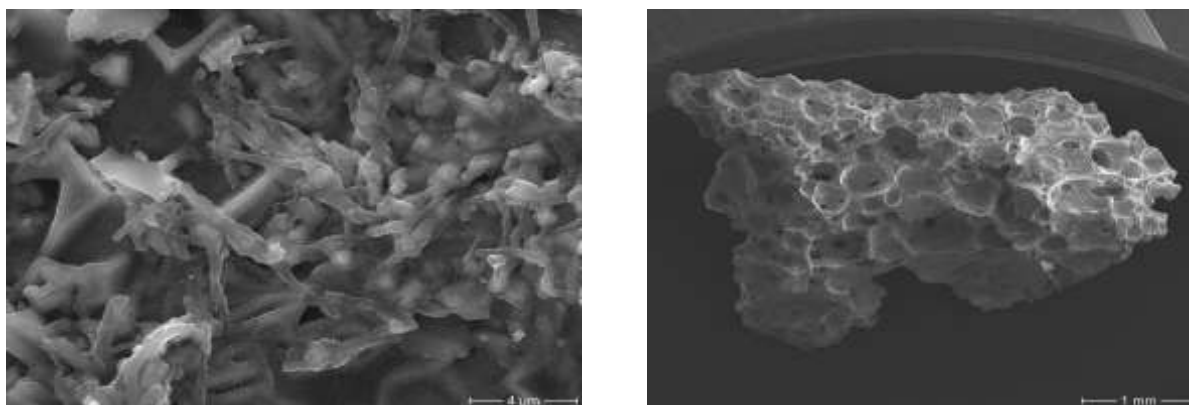


Figure 3: X-Rays diffraction spectrum of Jordanian volcanic tuff



**Figure 4: SEM images of Jordanian volcanic tuff shows tabular crystals associated with small fibrous crystals**

For a better understanding the removal efficiency of tuff, a chemical analysis of the mineral is performed. The chemical composition in (%) of the tuff material is presented in table 3.

**Table 3: Chemical analysis of Jordanian volcanic tuff used in experiments**

SiO <sub>2</sub>	70.08
MnO	0.04
Al <sub>2</sub> O <sub>3</sub>	11.72
Na <sub>2</sub> O	1.55
CaO	3.18
K <sub>2</sub> O	3.78
MgO	0.96
TiO <sub>2</sub>	0.16
Fe <sub>2</sub> O <sub>3</sub>	1.20

Water content ~ 4 %

### Sampling procedure

The effect of solution pH on uptake of the metal ions by tuff material was studied at room temperature to assess and understand the maximum removal efficiency. For these investigations, a series of 50 mL glass test tubes were employed. Each test tube received 40 mL of a metal ion solution (each batch has different initial concentration) and adjusted to the desired pH from 2.0 to 7.0 by employing a pH meter. The pH of the solution was adjusted using dilute solution of hydrochloric acid HCl or sodium hydroxide NaOH. A known amount of volcanic tuff (10 mg) was added into each test tube. A continuous shake of tubes were performed to maintain an equilibrium and complete mixing. The effluent suspension was diluted (if necessary) to an appropriate concentration range for the elemental analysis by atomic absorption spectroscopy (A.A.S). The detention time denoted as DT in minutes which reflects the real detention time of the aqueous solution within the fixed bed. Each batch consists of 4 effluent samples with detention times varying from zero to 10 minutes. The first sample (sample # 1) is poured over the fixed bed and collected immediately at the bottom, practically with a detention time zero (denoted by CF0). The second sample (sample # 2) is collected after lasting in the bed for 1 minute (denoted as CF2), the third sample (sample # 3) lasts 5 minutes (denoted CF5), where the fourth sample (sample# 4) is allowed to last 10 minutes within the bed before discharge (denoted CF10).

## 3. Results and Discussions

### 3.1 The sorption capacity of volcanic tuff material

In experimental performance by the batch method, due to the small ratio of volumes of zeolite/solution, the kinetics of the removal is determined by diffusion through the natural volcanic tuff particles. The experiments are carried out at different pH values (2, 4, 6 and 7) and with different initial concentrations (1, 5 and 10 mg/L). The results show that the ionic exchange reactions took place for all samples considered in the experiments. The most obvious result obtained for all metals considered and at different initial concentrations, is the decrease in the initial concentration. Therefore it is to conclude that volcanic tuffs are an active material in the absorption/ ionic exchange process and can be strongly recommended for removal of heavy metals from aquatic solutions.



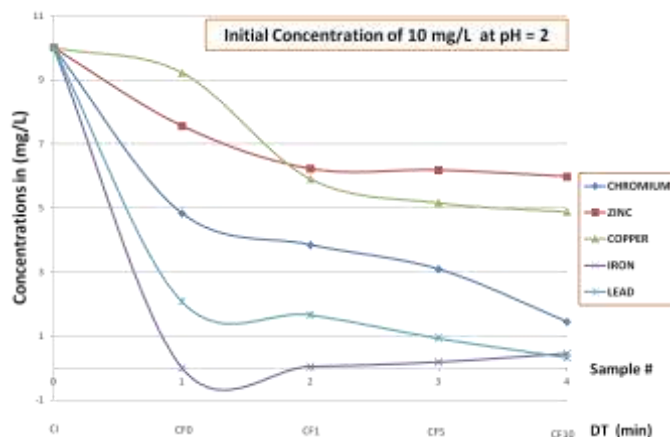


Figure 1. Absorption behavior of metal ions at pH =2

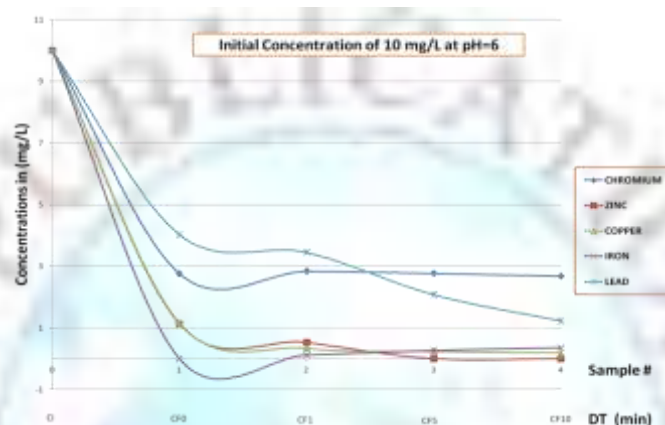


Figure 2: Absorption behavior of metal ions at pH = 6

Figures (1 and 2) show the varying behavior of heavy metal ions applied to the fixed volcanic tuff bed in relation to pH. As per figure (1), at pH =2, the highest removal efficiency can be obtained for lead and for iron ions, while the lowest removal efficiency is for zinc and copper. The removal sequence in dependence to pH =2 can be written as  $Fe^{+2} \gg Pb^{+2} \gg Cr^{+2} \gg Cu^{+2} \gg Zn^{+2}$ . By pH = 6, a sequence for the ability for removal in the form of  $Fe^{+2} \gg Cu^{+2} \gg Zn^{+2} \gg Cr^{+2} \gg Pb^{+2}$  can be written. It is to pinpoint that all experiments are repeated for every aqueous solutions to a new volcanic bed each time with the aim to avoid the interference of heavy metals among each other.

### 3.2 Metal uptake as a function of pH

The solutions containing heavy metals ions have been adjusted to different pH values (2, 4, 6 and 7), this is performed in order to examine the elimination of these ions at different acidic conditions. The experiments and obtained results indicate clearly the decrease in initial concentrations of metal ions as a direct function of pH.

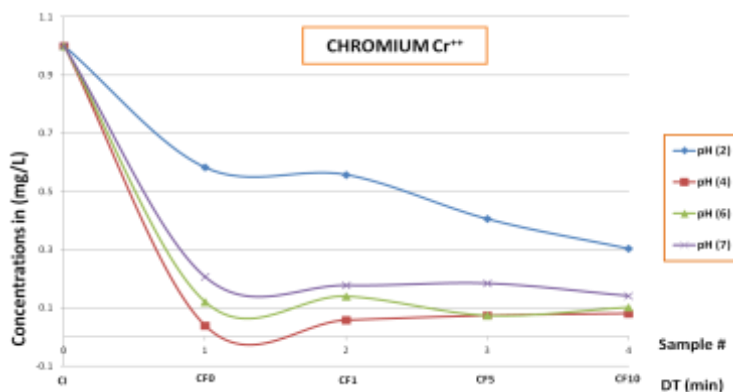


Figure 6: Chromium uptake behavior by different pH

In figure (6), chromium ions show little ability to be absorbed by bed material by applying an aqueous solution with pH = 2 when compared to the ability to be absorbed at pH = 4 or pH = 6. Similarly, lead ions show a higher ability to be absorbed by fixed bed material at pH = 4 than at pH = 6 as shown in figure (7).



Figure 7: Lead ions uptake behavior by different pH

### 3.3 The uptake capacity of volcanic tuff on metal ions .

The experimental results of the fixation of heavy metals ions on natural volcanic tuff indicate a varying behavior of tuff material in absorbing metal ions in regard to initial concentration and fixed pH vale. The plots in figure 8 , 9 and figure 10, show the uptake degree of each heavy metal ion as a function of the initial concentration. The uptake degree is defined as:  $\alpha = (C_i - C_e/g \text{ tuff})$  measured in mg/L/g.

$C_i$  being the initial concentration, and  $C_e$  final concentration of the particular ion. It is to emphasis that the volume of all solutions considered was 40 ml for each application. The experiments show that applying solutions containing heavy metal ions is an efficient method of removal of heavy metal ions from wastewater containing lower metal concentrations. On the other hand, the metal uptake is shown to be selective. The quantity of particular ionic species ( $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cr}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Zn}^{2+}$ ) bound in dependence on the initial concentrations, indicates that the removal efficiency from the liquid phase follows the sequence  $\text{Fe}^{2+} > \text{Cu}^{2+} > \text{Pb}^{2+} > \text{Cr}^{2+} > \text{Zn}^{2+}$  when keeping the pH at 4 and follows the sequence  $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Fe}^{2+} > \text{Cr}^{2+} > \text{Pb}^{2+}$  when keeping the pH at 6.

At pH= 7 the removal efficiency sequence can be written as  $\text{Cu}^{2+} > \text{Fe}^{2+} > \text{Pb}^{2+} > \text{Cr}^{2+} > \text{Zn}^{2+}$ . For instance, when flowing through a fixed bed with solutions of different metals, the material prefers copper and iron ions to zinc or chromium at pH =4 . At pH = 6 the material prefers zinc, copper and iron ions to lead or chromium.

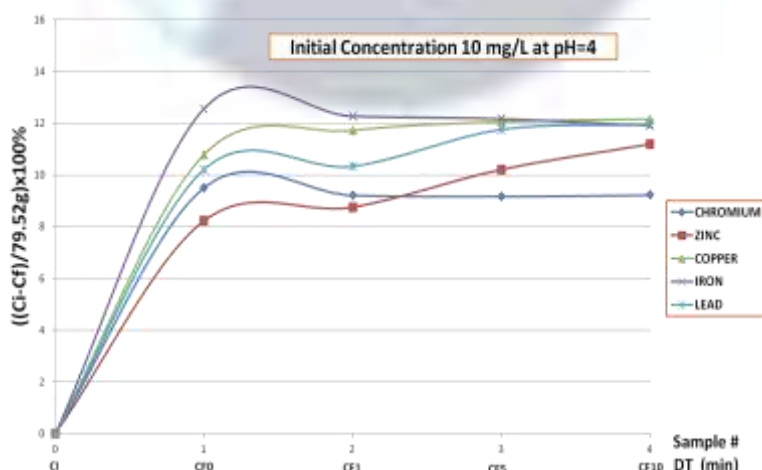


Figure 8.1

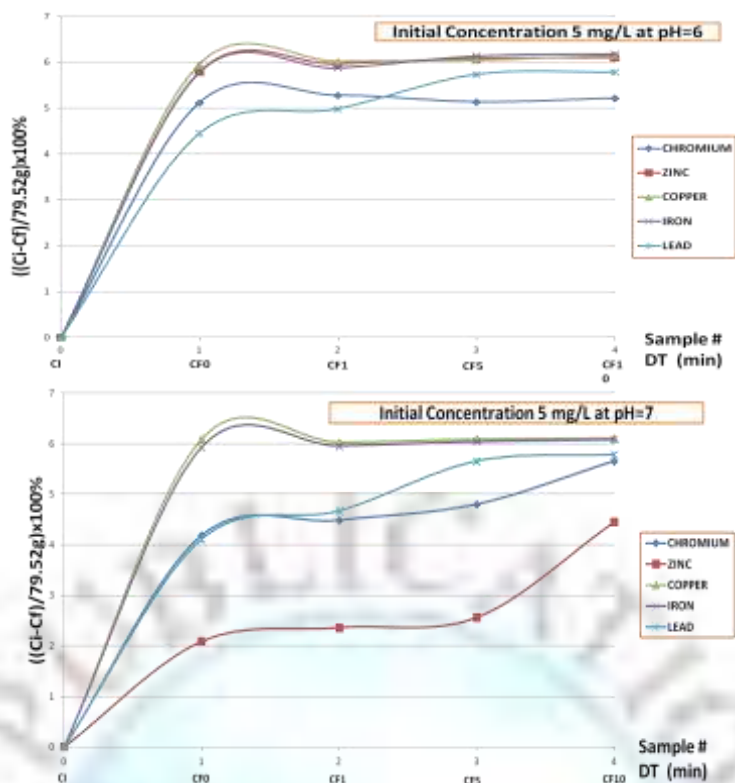
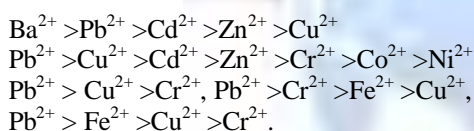


Figure 8.1, 8.2 and 8.3: Binding of metals on fixed bed material at different pH values as a function of initial concentration applied.

Several selectivity sequences have been reported in the literature (mainly conducted in a single solution) for natural zeolites [12, 13, 14]:



The observed differences in selectivity sequences were considered to be due to the specifics of the adsorbents and to the differences in the experimental techniques used.

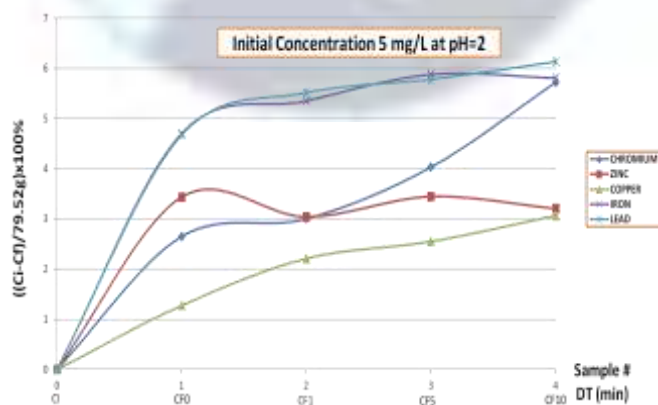


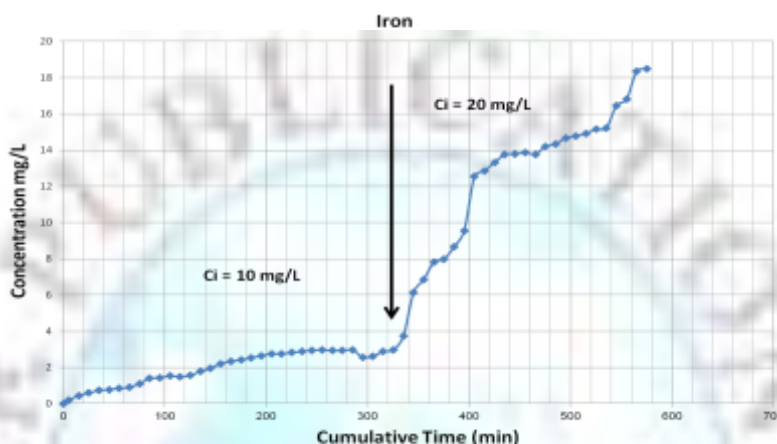
Figure 9: metal uptake at pH = 2 and initial concentration of 5 mg/L

### 3.4 Breakthrough curves

The breakthrough curve experiment of heavy metals on natural zeolite was carried out using the batch method. Batch experiments were conducted using 10 g of adsorbent with 40 ml of solutions containing heavy metal ions of desired concentrations at constant temperatures (25° C).

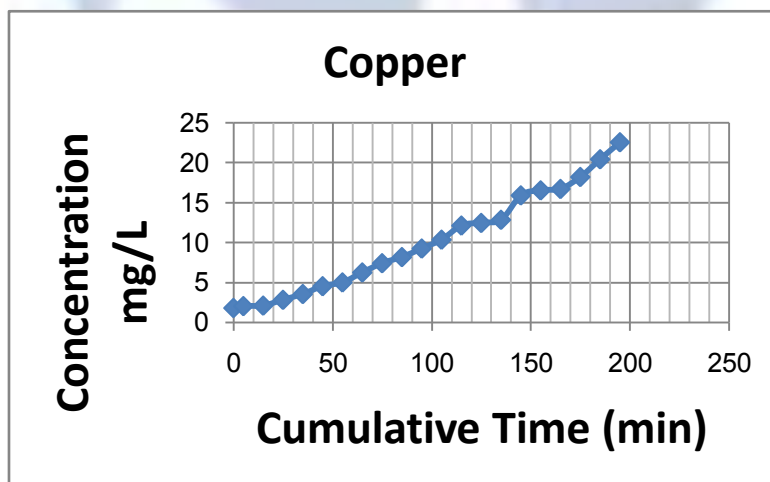
Two metals iron and copper are applied to a fixed bed column filled with 10 g of volcanic tuff in order to examine the time of saturation of material with these two metal ions. The batch adsorption experiment were conducted (started first with iron solution) with an initial concentration of 10 mg/l. 40 ml of this solution is applied to the column containing 10 g of bed material every 10 minutes. The discharge is taken and analyzed. After exactly 335 minutes the analysis of the sample taken shows that the final concentration of iron in samples is still low, which means that the adsorption capacity of material is high. In order to fasten the saturation of the bed material, the experiment is then continued with an initial concentration of iron = 20 mg/l also here with 10 minutes tact. After exactly 580 minutes the final concentration stabilizes and starts to increase, this gives a belief that the material is saturated with iron and reaches its ultimate absorbing capacity.

It is to emphasize that iron is selected with the belief that because iron is a major component of the natural material and the absorbing capacity of the material for iron can be limited when compared to the absorbing capacity of tuff on other metal ions that are less present. It is conclude that the material possesses a high absorbing capacity on heavy metals ions similar or even higher that its capacity to absorb iron ions. This gives the evidence that the material is very suitable to remove heavy metal ions from aqueous solutions when coming to contact with the material.



**Figure 10.1: Iron breakthrough curve**

Figure 10: shows the breakthrough curve for copper. The experiment is repeated for copper solution with an initial concentration of 10 mg/l using the same bed that is previously brought to saturation with iron ions. It is to observe that after exactly 192 minutes the material is completely saturated with copper ions.



**Figure 10.2: Copper breakthrough curve**

### 3.5 Uptake capacity factor for Iron and copper

The quantity of adsorbed heavy metal on the tuff; i.e. uptake capacity, was calculated by the difference of the initial and final equilibrium concentrations using following mass balance equation:

$$UP = (V/m) \times (Ci - Cf)$$



where UP is the quantity of heavy metal adsorbed on the tuff (mg metal/gm tuff), that is the metal loading at a given time period until saturation point, Ci is the initial metal concentration in the solution and Cf (mg/L) is the equilibrium or final metal concentration in the solution, m is the amount of tuff in grams and v is the volume of solution.

The iron breakthrough curve experiment involves the adding of: 35 applications (batches) each 40 mL of liquid with an initial concentration of  $Fe^{+2} = 10$  mg/L followed by 24 applications with an initial concentration of 20 mg/L. The added iron loading is completely absorbed by the 79.52 g bed material before reaching the saturation point. An uptake capacity factor can be calculated using these data as follows:

$$\text{Total added } Fe^{+2} \text{ loading : } 35 \times 0.040 \text{ L} \times 10 \text{ mg/L} + 24 \times 0.040 \text{ L} \times 20 \text{ mg/L} = 33.2 \text{ mg}$$

So, The uptake capacity factor:

$$UC_{Fe} = 33.2/79.52 \text{ g} = 0.417 \text{ mg/g.}$$

In regard to  $Cu^{+2}$  absorption and in order to reach the saturation point, 30 applications were needed with initial concentration = 10 mg/L. An uptake capacity factor can be calculated using these data as follows:

$$Cu^{+2} \text{ loading: } 30 \times 0.04 \text{ L} \times 10 \text{ mg/L} = 12 \text{ mg.}$$

So, an uptake capacity factor,  $UC_{Cu} = 12.0 \text{ mg}/79.52 \text{ g} = 0.151 \text{ mg/g.}$  was obtained . An  $UP_{Fe}/UP_{Cu}$  ratio is found as much as 2.76

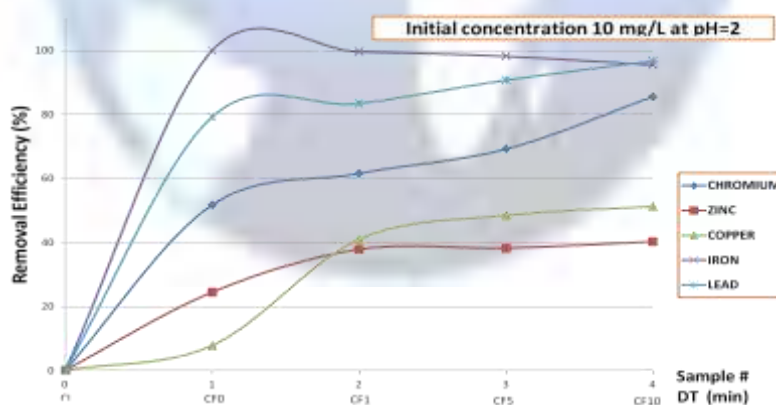
### 3.6 Adsorption Efficiency of volcanic tuff:

The efficiency (%) of volcanic tuff on absorbing heavy metal ions can be determined using following equation:  $\eta = (Ci - Cf / Ci) \times 100\%$ .

The percent adsorption (%) and distribution ratio (Kd) were calculated using the equations:

$$\% \text{ adsorption} = (Ci - Cf / Cf) \times 100,$$

where Ci and Cf are the concentrations of the metal ion in initial and final solutions, respectively, and Kd = amount of metal in adsorbent amount of metal in solution  $\times V / m$  ml/g, V = volume of the solution (ml) and m is the weight of the adsorbent (g) [15].



**Figure 11: removal efficienc (%) of tuff in absorbing heavy metal ions.**

As figure 11 shows, that the tuff possess different potentials in regard of absorbtion of metal ions. The acidic condition (pH =2) plays a detrimental role in obtained results. A removal efficiency sequence for the given conditions (Ci = 10 mg/L and pH=2), can be given in the form of  $Fe^{+2} \gg Pb^{+2} \gg Cr^{+2} \gg Cu^{+2} \gg Zn^{+2}$ .

The amount of contaminant fixed on the volcanic tuff is a function of the initial concentration of contaminant in solution  $p = f(Ci)$ . This relationship can be easily seen by examining the breakthrough curves for  $Fe^{+2}$  and  $Cu^{+2}$ . Because all experiments are conducted using the same procedure, the same weight and volume of tuff material and the same volume of aqueous solution added each batch, the results of concentration decrease within the fixed bed can be taken to represent uptake capacity of the fixed bed material. The concentration decrease in dependence of the intial concentration of the aqueous solution is presented in following figures.

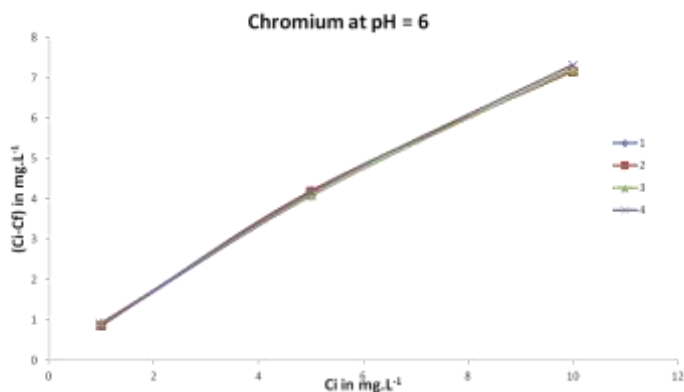


Fig. 12: Uptake of Zinc ions in relation to initial concentration at pH = 6.

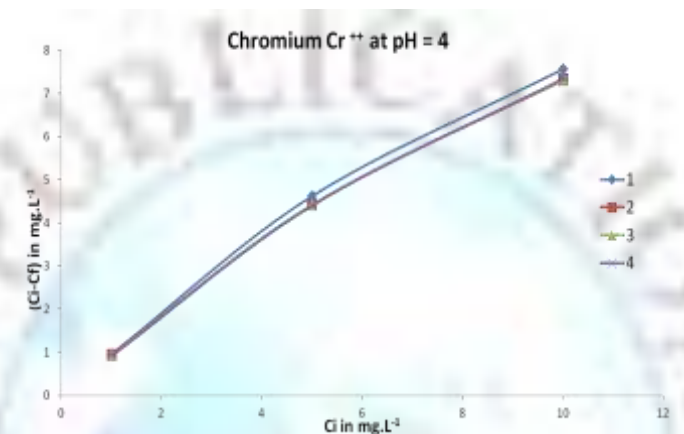


Fig. 13: Uptake of Chromium ions in relation to initial concentration at pH = 4.

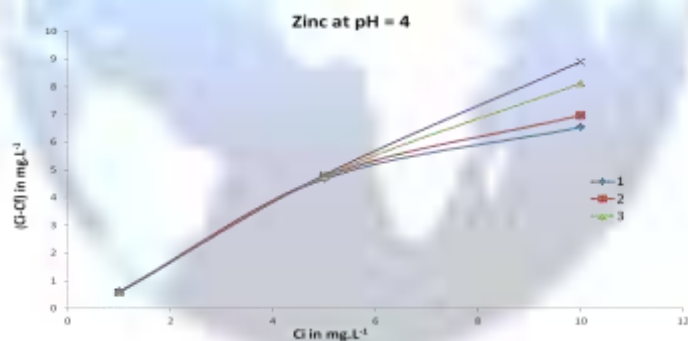


Fig. 14: Uptake of Zinc ions in relation to initial concentration

Figures 12, 13 and 14 represent the uptake of metal ions by the fixed bed material in relationship to their initial concentration increase. In fitting these obtained data to one of the adsorption isotherm models it is to conclude that the results clearly indicate that the uptake capacity of the material is behaving following the linear adsorption model.

### Conclusions

The present study indicated the efficient ability of the natural volcanic tuff as a low-cost material in removing mixed heavy metal ions, in particular copper [Cu<sup>+2</sup>], zinc [Zn<sup>+2</sup>], chromium [Cr<sup>+3</sup>], lead [Pb<sup>+2</sup>] and iron [Fe<sup>+2</sup>], from aqueous solutions. One of the most relevant parameters for effective removal are the acid condition of the aqueous solution (pH value). The natural volcanic tuff possess, on the one hand good retention capacity for cationic metals. On the other hand, the metal uptake is selective and depends strongly on prevailing pH condition. For instance, when flowing a solution with two metals through the fixed bed, the material prefers some ions to others. It showed that the selectivity sequence of metal ions by the adsorbents was dependent on the system employed, and was mainly dependent on the initial concentrations of the metal ions and the initial pH of the solution.

Acidic metal solutions reduce the performance of natural volcanic tuff in retarding the movement of heavy metals and affect the mineralogical composition of the materials. Results obtained were modeled using one of the adsorption isotherm models. The results clearly show that the uptake capacity of the used tuff is behaving following the linear adsorption model.

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