

The influence of pH on heavy metals absorption on natural volcanic tuffs

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Abstract The adsorption behavior of natural Jordanian volcanic tuff with regard to Cr^{2+} , Cu^{2+} , Pb^{2+} , Fe^{2+} and 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 experiments were conducted using fixed-bed columns under multi changing conditions at 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 Atomic Absorption Spectroscopy. The breakthrough curves with regard to the absorption of Fe^{2+} and Cu^{2+} were obtained under different conditions through plotting the normalized effluent metal concentrations (C/C_0) versus absorbent volume. Uptake capacity factor for Fe ions was found to be equal to 0.417 mg/g while that of Cu ions was found to be as much as 0.151 mg/g. Results showed that volcanic tuff is an efficient and low cost ion exchanger and absorbent for removing heavy metals. Results also indicated that an initial solution pH of 2.0 was favorable for obtaining high chromium ions removal, while the pH=4 was deemed to be favorable for lead to be absorbed and removed from the aqueous solution. Equilibrium modeling of the removal showed that the adsorption of the metal ions followed the linear adsorption isotherm.

Key words: Absorption, Heavy metals, Natural volcanic tuff, pH, Wastewater

1. INTRODUCTION

Several toxic heavy metals have been discharged into the environment as industrial wastes, causing serious soil and water pollution problems. Pb^{+2} , Cu^{+2} , Fe^{+2} , Zn^{+2} and Cr^{+3} are especially common metals that tend to accumulate in organisms, causing numerous diseases and disorders (Lin and Juang, 2002). 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 methods.

Ion exchange is a process by which ions are 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 (Almjadleh et al., 2014). The main advantages of ion exchange over the chemical precipitation are the removal of metal ions, the selectivity and the less produced sludge. The region of Middle East is well known for its limited water resources and this necessitates that much effort has to be 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 km² (called the Harrat Alsham) in the Northeast of Jordan and extends northwest into Syria and southeast into Saudi Arabia (Al-Shaybe and Khalili, 2009).

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 (Table 1). 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 has also become one of the research priorities.

Table 1. The 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

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.

There are many studies dealing with removing heavy metal by using natural zeolite in batch experiments (Ali and El-Bishtawi, 1997; Dwairi, 1998; Çelik et al., 2001; Hrenovij et al., 2003; Payne et al., 2004; Bergero et al., 2008; Aydin and Saygili, 2009; Bedeleian et al., 2009), 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 including Cr^{2+} , Pb^{2+} , Zn^{2+} , Cu^{2+} and 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

Glass columns with different heights (40 -70 cm) were used in batch-wise experiments. The columns were filled with natural tuff aggregates having different sizes ranging from 0.5 – 0.3 mm. The conventional mineral processing techniques of volcanic tuff used began with crushing the materials followed by autogenously tumbling milling and then low intensity magnetic and gravity separation. Volcanic tuff was grounded and then sieved to different fractions (Table 2) 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 did not go through under any pretreatment or modification. Samples were just washed and dried at 103.5 °C and were kept in desiccators for 24 hours 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.

2.1 EXPERIMENTAL SETUP

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, were filled with a layer of fine aggregates < 1mm at the bottom, over which a layer of tuff (different grain sizes) was placed. The hydraulic conductivity was controlled by recording the time required to collect the injected sample outflow (hydraulic detention time). Samples from the wastewater inflow and outflows were taken for chemical analyses, whereas volcanic tuff samples were analyzed for chemical parameters. The dry mass of volcanic tuff used in one column weighted 79.52 g, which formed a height of 10 cm. The volume of wastewater sample added each batch over the columns was 40 ml.

2.2 METHODOLOGY

Jordanian volcanic tuff was studied for its absorbing potential for different metal ions (Cu^{+2} , Pb^{2+} , Cr^{2+} , Fe^{2+} and Zn^{2+}). The batch technique of metal ions from solution was carried out at specific conditions of pH (1.0, 3.0, 4.0, 6.0 and 7), temperatures (10, 20.0°C, 30.0°C and 45.0°C), and at different contact time and with the same ionic strength (0.1M NaClO_4).

Analysis of data was based on adsorption models such as Langmuir, or Freundlich isotherms. Adsorption kinetics were applied in order to determine the 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). For a better understanding the removal efficiency of tuff, a chemical analysis of the mineral was 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

Component	Percentage
SiO_2	70.08
MnO	0.04
Al_2O_3	11.72
Na_2O	1.55
CaO	3.18
K_2O	3.78
MgO	0.96
TiO_2	0.16
Fe_2O_3	1.20
Water content	~ 4 %

2.3 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 shaking of tubes were performed to maintain the equilibrium and complete mixing. The effluent suspension was diluted (if necessary) to an appropriate concentration range for the elemental analysis by Atomic Absorption Spectroscopy (AAS). The detention time (DT) in minutes reflected the real detention time of the aqueous solution within the fixed bed. Each batch consisted of 4 effluent samples with detention times varying from zero to 10 minutes. The first sample (sample # 1) was poured over the fixed bed and collected immediately at the bottom, practically with a detention time zero (denoted as CF0 in Figures 1-2 and Figures 4-5). The second sample (sample # 2) is collected after lasting in the bed for 1 minute (denoted as CF1), the third sample (sample # 3) lasted 5 minutes (denoted as CF5), whereas the fourth sample (sample# 4) was allowed to last 10 minutes within the bed before discharge (denoted as 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 was determined by diffusion through the natural volcanic tuff particles. The experiments were carried out at different pH values (2, 4, 6 and 7) and with different initial concentrations (1, 5 and 10 mg/L). The results showed 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, was the decrease in the initial concentration. Therefore, it is to conclude that volcanic tuffs was an active material in the absorption/ionic exchange process and can be strongly recommended for the removal of heavy metals from aquatic solutions.

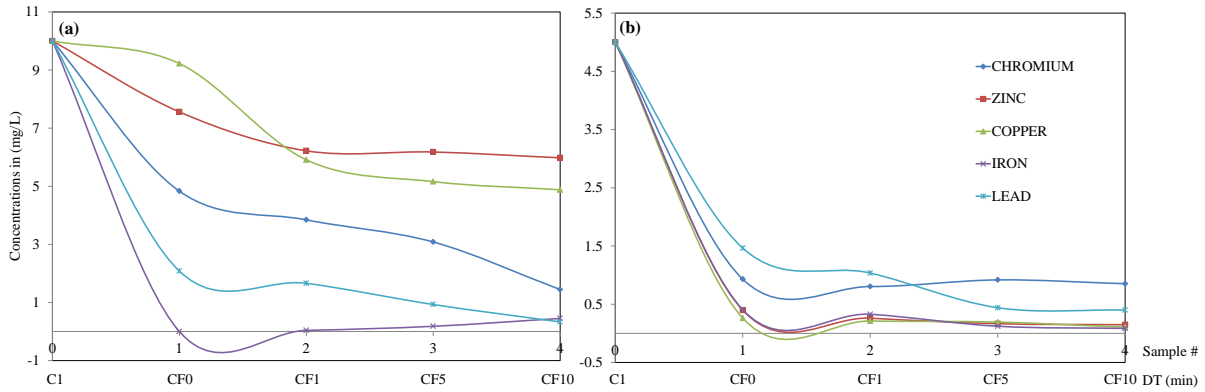


Figure 1. Absorption behavior of metal ions at; (a) pH = 2, and (b) pH=6

Figures 1(a) and 1(b) show the varying behavior of heavy metal ions applied to the fixed volcanic tuff bed in relation to pH. As shown in Figure 1(a), at pH=2, the highest removal efficiency can be obtained for lead and for iron ions, while the lowest removal efficiency was for zinc and copper. The removal sequence in dependence to pH=2 can be written as $Fe^{+2} \gg Pb^{+2} \gg Cr^{+2} \gg Cu^{+2} \gg Zn^{+2}$. At pH = 6, a sequence for the ability of removal in the form of $Fe^{+2} \gg Cu^{+2} \gg Zn^{+2} \gg Cr^{+2} \gg Pb^{+2}$ can be written (Figure 1(b)). It is to pinpoint that all experiments were 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 ADSORPTION EFFICIENCY OF THE VOLCANIC TUFF

The efficiency (%) of volcanic tuff on absorbing heavy metal ions can be determined using following equation:

$$\eta = (C_i - C_f / C_i) \times 100\% \tag{1}$$

The percent adsorption (%) can calculated using the equation (2).

$$\% \text{ adsorption} = (C_i - C_f / C_i) \times 100 \tag{2}$$

Where C_i and C_f are the concentrations of the metal ion in initial and final solutions, respectively (Erdem et al., 2004).

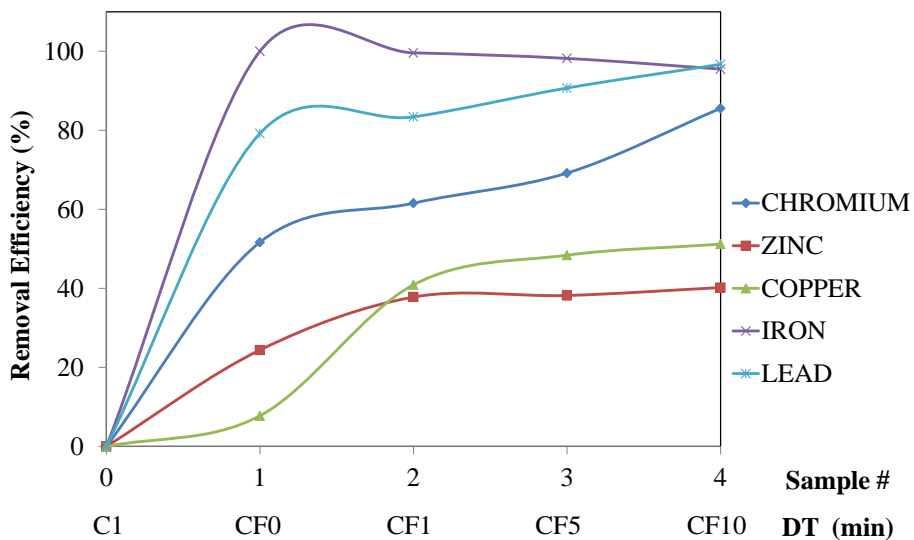


Figure 2. The removal efficiency (%) of tuff in absorbing heavy metal ions for initial concentration of 10mg/l at pH=2

As Figure 2 shows, the tuff possessed different potentials in regard of absorption of metal ions. The acidic condition (pH =2) plays a detrimental role in obtained results. A removal efficiency sequence for the given conditions ($C_i = 10 \text{ mg/L}$ 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 $p = f(C_i)$. This relationship can be easily seen by examining the breakthrough curves for Fe^{+2} and Cu^{+2} .

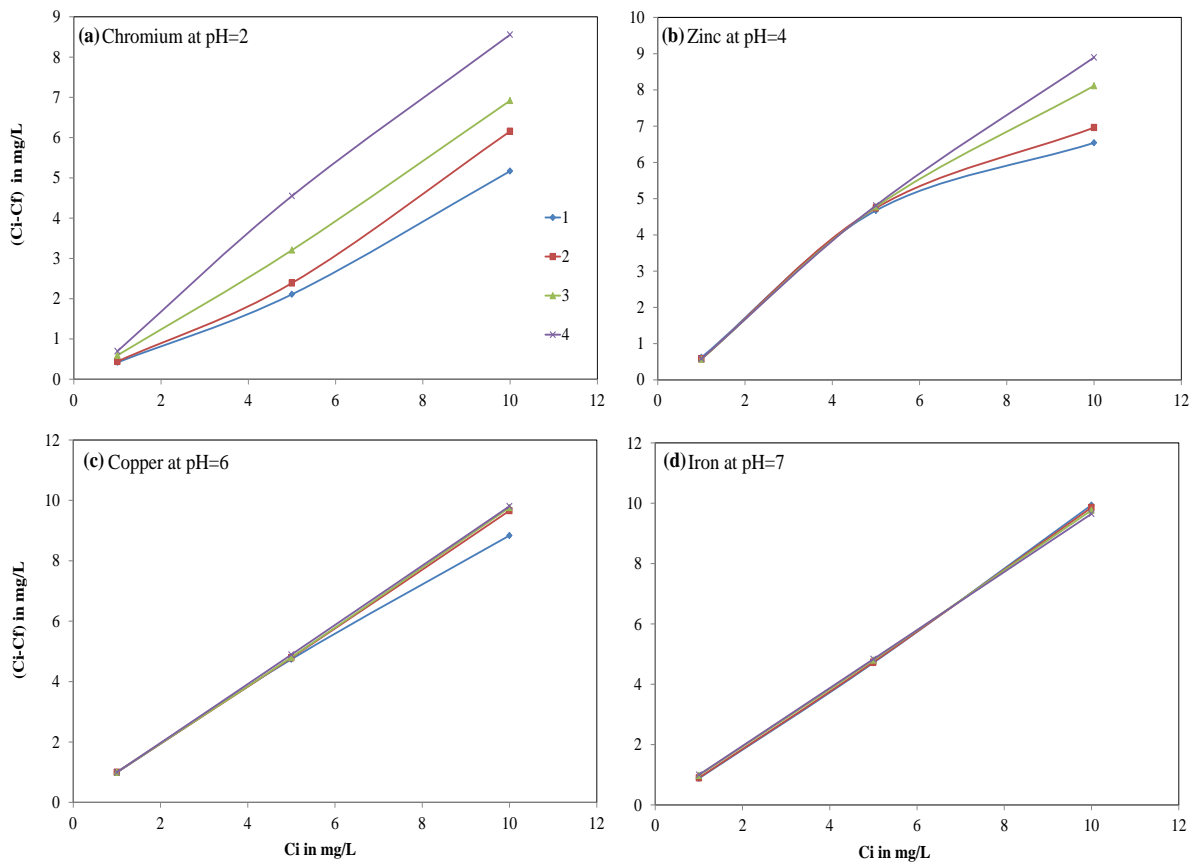


Figure 3. Uptake of metal ions in relation to initial concentration; (a) Chromium at pH=2, (b) Zinc at pH=4, (c) Copper at pH=6, and Iron at pH=7

Results of concentration decrease within the fixed bed can be taken to represent the uptake capacity of the fixed bed material. The concentration decrease in dependence of the initial concentration of the aqueous solution is presented in Figure 3. Figure 3 represents 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 can be concluded that the uptake capacity of the material has followed the linear adsorption model.

3.3 THE UPTAKE CAPACITY OF VOLCANIC TUFF

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 with respect to the initial concentration and fixed pH value. The plots in Figure 4 show the uptake degree of each heavy metal ion as a function of the initial concentration. The uptake degree measured in mg/L/g can be defined as in the equation (3).

$$\alpha = (C_i - C_e / \text{g tuff}) \quad (3)$$

Where C_i and C_e are the initial and final concentrations, respectively, of the particular ion. It is to emphasize that the volume of all solutions considered was 40 ml for each application.

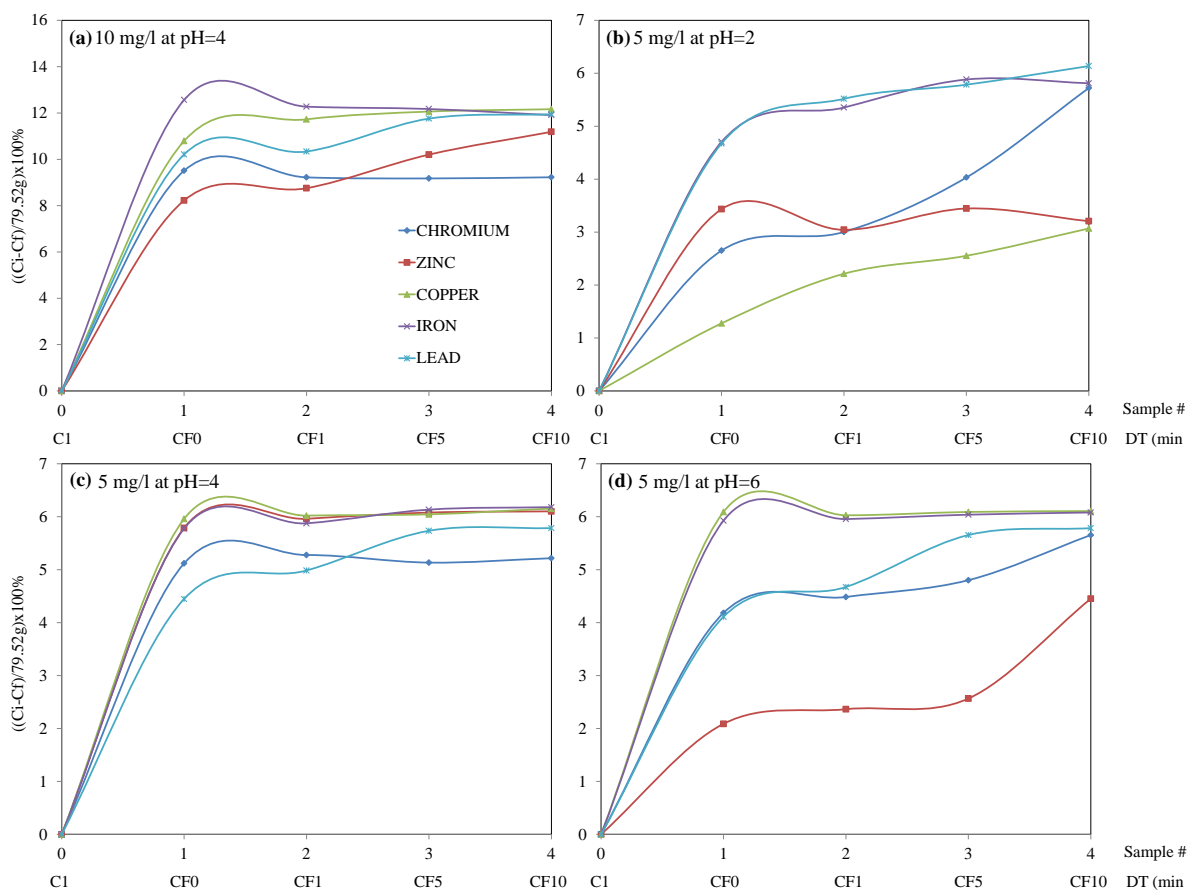


Figure 4. Binding of metals on fixed bed material at different pH values as a function of initial concentration applied; (a) initial concentrations of 10mg/l at pH=4, and initial concentrations of 5 mg/l at; (b) pH=2, (c) pH=6, and (d) pH=7

Analysis of final effluents shows that applying solutions containing low concentrations of heavy metal ions is an efficient method of removal of heavy metal ions from wastewater and is highly efficient. In addition, the metal uptake was also shown to be selective. The quantity of particular ionic species (Cu^{2+} , Pb^{2+} , Cr^{2+} , Fe^{2+} , Zn^{2+}), which is absorbed by tuff in dependence of the initial concentrations, indicates that the removal efficiency from the liquid phase follows the sequence $\text{Pb}^{2+} > \text{Fe}^{2+} > \text{Cr}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$ when keeping the pH at 4 and follows the sequence $\text{Zn}^{2+} > \text{Cu}^{2+}$ if the initial concentration is 5 mg/L and when keeping the pH at 2. In comparison, the removal efficiency sequence can be written as $\text{Fe}^{2+} > \text{Pb}^{2+} > \text{Cr}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+}$ when metal ions flow through the fixed bed with an initial concentration = 10 mg/L and keeping the pH at 2.

Several selectivity sequences have been reported in the literature (mainly conducted in a single solution) for natural zeolites (Alvarez-Ayuso et al., 2003; Inglezakis et al., 2003; Hui et al., 2005), such as $\text{Ba}^{2+} > \text{Pb}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+}$, $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Cr}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+}$, $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cr}^{2+}$, $\text{Pb}^{2+} > \text{Cr}^{2+} > \text{Fe}^{2+} > \text{Cu}^{2+}$, and $\text{Pb}^{2+} > \text{Fe}^{2+} > \text{Cu}^{2+} > \text{Cr}^{2+}$. 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.

3.3.1 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), in order to examine the elimination of these ions at different acidic conditions. The experiments and obtained results clearly indicate the decrease in initial concentrations of metal ions as a direct function of pH.

In Figure 5 (a), zinc shows little ability to be absorbed by bed material by applying an aqueous solution at pH=2 and pH=7 when compared to its 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 5 (b).

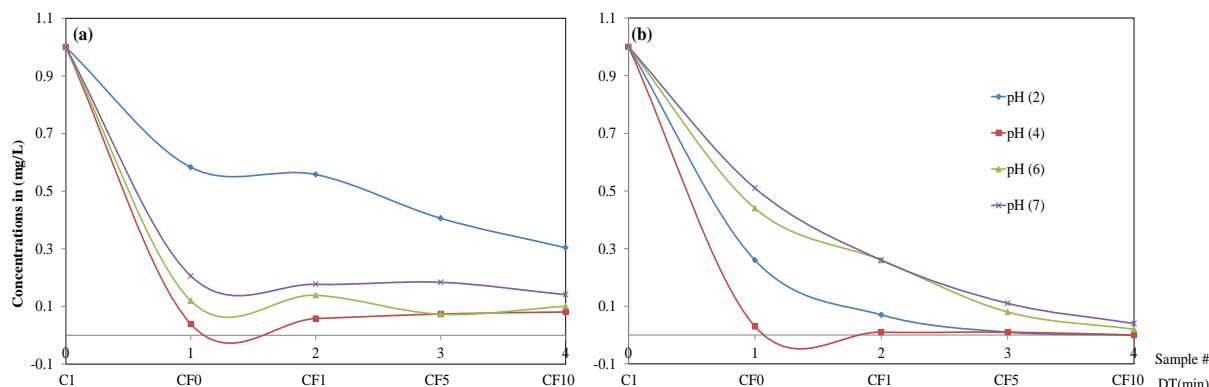


Figure 5. (a) Zink, and (b) Lead ions uptake behavior at different pH

3.3.2 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:

$$UP = (V/m) \times (C_i - C_f) \tag{4}$$

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, 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 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 was completely absorbed by the 79.52 g bed material before reaching the saturation point. The calculation for the uptake capacity (UC) factor for both iron and copper are presented in Table 4. 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 UP_{Fe}/UP_{Cu} ratio was found as much as 2.76.

Table 4. The uptake capacity factor calculations for both iron and copper based on total added loading

Metal ion	Loading mg	UC factor mg/g
Fe^{+2}	$35 \times 0.040 \text{ L} \times 10 \text{ mg/L} + 24 \times 0.040 \text{ L} \times 20 \text{ mg/L} = 33.2$	$33.2/79.52 \text{ g} = 70.08$
Cu^{+2}	$30 \times 0.04 \text{ L} \times 10 \text{ mg/L} = 12$	$12.0 \text{ mg}/79.52 \text{ g} = 0.151$

3.4 BREAKTHROUGH CURVES

The experiment for the breakthrough curve 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) were 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. Nearly 40 ml of this solution was applied to the column containing 10 g of bed material every 10 minutes. The discharge was taken and analyzed and after exactly 335 minutes of the analysis, it was revealed that the final concentration of iron in samples was still low, which means that the adsorption capacity of material is high. In order to fasten the saturation of the bed material, the experiment was then continued with an initial concentration of iron = 20 mg/l with 10 minutes tact. After exactly 580 minutes, the final concentration stabilized and started to increase, this gave an indication that the material was saturated with iron and reached its ultimate absorbing capacity.

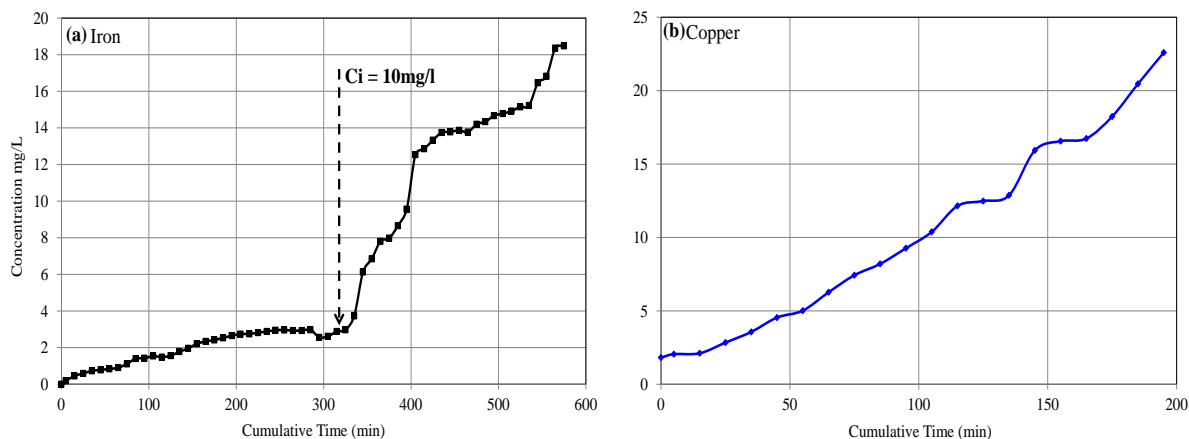


Figure 6. Breakthrough curves for (a) Iron, and (b) Copper

Figures 6 (a) and 6 (b) show the breakthrough curves for both iron and copper, respectively. The experiment was 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 was observed that after exactly 192 minutes the material was completely saturated with copper ions. It is to emphasize that iron was selected with the concept that since iron is a major component of the natural material; 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 can be concluded 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.

4. CONCLUSIONS

The research work carried out in this study has showed that the natural volcanic tuff possesses a retention capacity for heavy metal ions, in particular copper [Cu^{+2}], zinc [Zn^{+2}], chromium [Cr^{+3}], lead [Pb^{+2}] and iron [Fe^{+2}], with selectivity behavior which depends strongly on prevailing pH condition i.e. the initial pH of the solution. Other factors for effective removal of heavy metal ions from aqueous solutions were the initial concentrations of heavy metal ions, the time to first breakthrough, the retardation factors, the volume of water treated and the amount of contaminant bounded on the ion exchangers.

Results of experimental analysis indicated that natural volcanic tuff possesses a high potential for absorbing heavy metals found in aqueous solutions. Observations showed that at pH = 6, the tuff has a huge affinity to absorb, Fe^{2+} , Zn^{2+} and Cu^{2+} , but to a lesser extent to bound Cr^{2+} and Pb^{2+} . Using breakthrough curves and equilibrium modeling of heavy metals removal showed that the adsorption behavior of the metal ions followed the linear adsorption isotherm. It can be concluded that natural volcanic tuff can be used with high efficiency for the elimination of metal ions from water and wastewater. This naturally occurring material provides an alternative for the use of high cost activated carbon as adsorbent due to its availability and its low cost.

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