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Adsorption of Cu(II), Ni(II), Zn(II), Cd(II) and Pb(II) onto Kaolin/Zeolite Based- Geopolymers

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ABSTRACT

This work deals with geopolymers based on local Jordanian resources, namely, kaolin and zeoltitic (phillipsite) tuff. The geopolymers were prepared from these two materials by a reaction with an alkali solution at 80ºC. The research group of the present work has demonstrated in previous work that addition of zeolitic tuff to kaolin based-geopolymers increases the adsorption capacity toward Cu(II) metal ion compared to zeolite-free geopolymers, while retaining high mechanical strength. The aim of the present work is to extend our work and to study the effect of changing geopolymers components (zeolitic tuff and kaolin) on their adsorption properties toward Cu(II), Ni(II), Zn(II), Cd(II) and Pb(II) metal ions. Both isothermal and kinetic studies revealed that increasing the zeolitic tuff: kaolin ratio improves the adsorption capacity of geopolymer toward metal ions. The adsorption capacity of the geopolymers of 150: 50 zeolites: kaolin content was found to be higher than that of the raw materials themselves. The rate of adsorption of geopolymers was found to be lower than that of raw materials due to kinetic limitations imposed by the formation of geopolymerization network. The selectivity of geopolymers toward adsorption of metal ions was found to be distinct from raw zeolite and kaolin where the adsorption onto geopolymers was found to be more preferential for small size metal ions (Cu(II), Ni(II), Zn(II)) than for large size metal ions (Pb(II), Cd(II)). The adsorption of Cu(II) and Pb(II) onto geopolymers did not decrease with competition with other metal ions, which indicates cooperative adsorption. The adsorption process of metal ions onto geopolymers was found to be reversible that indicates that metal ions are bound by physical cation exchange to the exchangeable sites of unreacted phillipsite and new amorphous geopolymer sites. Leaching of metal ions from raw kaolin was much more effective than geopolymers and zeolite because of compact structure of geopolymers.

Keywords: Geopolymers; Kaolin; Zeolitic Tuff; Adsorption; Heavy Metal Ions

1. Introduction

Several methods have evolved over the years on the removal of heavy metal ions present in industrial wastewaters and soils. These are chemical precipitations, conventional coagulation, reverse osmosis, ion exchange, and adsorption. Out of these methods, adsorption appears to be the most widely used for the removal of heavy metals [1]. Substances like kaolin and zeolites have assumed a wide application in this regard [2-4].

This work deals with geopolymers based on local Jordanian resources, namely, kaolin and zeoltitic (phillipsite) tuff. The geopolymers were prepared previously from 1:1 mass ratio of these two materials by a reaction with an alkali solution at 80ºC. The research group of the present work has demonstrated in previous work that addition of zeolitic tuff to kaolin based-geopolymers increases the adsorption capacity toward Cu(II) metal ions compared to zeolite-free geopolymers, while retaining high mechanical strength [5,6]. These geoplymers can be used as construction materials for water treatment, storage and transportation. The process used in the present work is of much lower cost than the most popular metakaolin based geopolymers which, involves calcination of kaolin at 600ºC which requires large amounts of energy and complete dissolution of metakolin which requires large amount of base [7].

The exact mechanism of the geopolymerization is not known precisely. It was suggested that Na^+ or K^+ from alkaline solution to exchange the hydrogen ions on the broken edges of the clay. Because of this ion exchange, repulsion between the Na^+ ions will dissolute some clay particles [8]. The breakdown of the solid aluminosilicate into smaller ‘monomers’ where Al is already tetrahedrally coordinated is followed by polycondensation of these monomers into the geopolymer [9,10]. Because of these reactions, solid, hard, and stable materials with hydroxysodalite, feldspatiod, or zeolite like structure are formed [11].

When aluminum is four coordinated to oxygen atoms, a negative charge is created and therefore the presence of cations such as Na^+ is essential to maintain electric neutrality in the geopolymeric matrix (hydroxysodalite). Hydroxysodalite, which ranges from amorphous to microcrystalline material, consists of SiO_4 and AlO_4 tetrahedral linked alternately by sharing all the oxygen atoms [11]. Positive ions (Na^+, K^+, Li^+, Ca^{2+}, Ba^{2+}, NH_4^+, and H_3O^+) must be present in the framework cavities to balance the negative charge of Al in the four-fold coordination.

Little work was found in the literature on the adsorption behavior of geopolymers. Li et al. [12] studied the adsorption of methylene blue (MB) dye onto geopolymeric adsorbent based on fly ash. The synthesized geopolymer was found to have much higher adsorption capacity towards MB (0.12 mmol MB/g adsorbent) than fly ash itself (5.6 x 10^{-3} mmol MB/g adsorbent). Wang et al. [13] reported an amorphous aluminosilicate geopolymer resulting from solid-state conversion of fly ash. The synthesized geopolymer was found to have a higher adsorption capacity towards Cu^{2+} ion (1.4 mmol Cu/g adsorbent) than the fly ash it self (1.6x10^{-3} mmol Cu/g adsorbent). A Geopolymer of Jordanian kaolin and zeolitic tuff prepared by the research group of the present article was found in previous works to have adsorption capacity of 8.06 mmol MB/g adsorbent and 0.83 mmol Cu/ g adsorbent [6] and 0.36 mmol Pb/ g adsorbent (at pH 6) [14]. Cheng et al. [15] demonstrates that at pH 4, the adsorption capacity of meta-kaolin based geopolymer toward Pb(II), Cu(II), Cr(III) and Cd(II) was 0.71, 0.77, 0.38, 0.60 mmol/g adsorbent. The aim of the present work is to extend previous studies and to study different kaolin: zeolitic tuff geopolymeric samples in order determine the best ratio of the geopolymer that gives the highest adsorption capacity toward Cu(II), Ni(II), Zn(II), Cd(II) and Pb(II). The main concern is determining the optimum zeolitic content in the geopolymer that will provide a material with high efficiency for water purification.

2. Materials and Methods

2.1. Materials

Preparation and characterization of Jordanian kaolinite and zeolitic (phillipsite) tuff were discussed in our previous works [6,14, 16].

2.2. Fabrication of Geopolymeric Samples

Seven geopolymeric samples with different zeolitic content were prepared from kaolinitic Jordanian soil (K), functional reactive filler (zeolitic tuff, Z), and alkali solution as shown in **Table 1**.

The zeolitic tuff and kaolinitic soil were mixed in different ratios (**Table 1**), and then the sodium hydroxide solution was added. After mixing, a semi-dry mixture was formed. After molding, compacting, curing at 80ºC, the samples were ground and sieved into aggregate size between 250-500 μm. Then the product was washed with excess amount of distilled water (to remove unreacted alkali), dried at 100ºC and kept in a desiccator.

Table 1. Composition of synthesized geopolymers in grams.

Geopolymer	K	Z	NaOH	Water
G1	200	0	14	44
G2	175	25	14	40
G3	150	50	14	36
G4	125	75	14	32
G5	100	100	14	28
G6	75	125	14	24
G7	50	150	14	20

2.3. Characterization of Geopolymers

XRD pattern and SEM pictures were obtained for geopoplymers G5 and G7 in order to determine the fate of kaolinite and phillipsite in the geopolymers sample.

2.4. Kinetics of Adsorption of Metal Ions onto Geopolymers and Raw Materials

A 0.5000 g sample of geopolymers (G1-G7) and raw materials (Z and K) were independently placed in a 500 mL-conical flask, to which 250 mL of 100 ppm of a standard solution of a metal ion (Cu(II), Ni(II), Zn(II), Cd(II), Pb(II)) prepared in 0.1 M NaCl was added . The solution was adjusted to pH 4 and shaken in the shaker water bath at 25°C and 320 rpm. A 1.0 mL sample of the solution was withdrawn at different contact times (0 - 72 h) and diluted to 5 mL with distilled water, then filtered by microfilter and centrifuged. The concentrations of metal ions were measured using the atomic absorption spectrometer (Varian, AA-250 plus).

2.5. Adsorption Isotherms of Metal Ions onto Geopolymers and Raw Materials

Adsorption of single metal ions: Standard solutions (10–100 ppm) of metal (Cu(II), Ni(II), Zn(II), Cd(II, Pb(II)) in 0.1M NaCl at pH 4 were prepared (pH adjustment using NaOH/HCl). Conical flasks were filled with 50 ml of the prepared standard solutions of metal ions and 0.05 g of geopolymer (G1- G7) or raw materials (K, Z). A 10.0 mL portions from each conical flask were withdrawn after 24 h of shaking in water bath at 25ºC and 320 rpm and filtered by microfilters (0.45μm Nylon). The concentrations of metal ions were determined using the atomic absorption spectrometer.

Adsorption of multiple metal ions: The same procedure above was followed, but using standards prepared from combination of metal ions (Cu(II), Ni(II), Zn(II), Cd(II, Pb(II)). Analysis using atomic absorption was made for the four elements in each sample.

2.6. Desorption of Metal Ions

A 0.5 g of geoplymers or raw materials was shaken with 250 mL of 1000-ppm solution of metal ions at pH 4 and 0.1 M NaCl ionic strength for 24 h. The solution was then filtered and dried in an oven at 100 C. The solid was then leached with 250 mL of 0.1 M NaCl solution at different contact times ranging from 0.25-72 h, where 1.00 mL was pipetted at each time, and diluted to 5.00 ml and analyzed for metal ions concentration using atomic absorption spectrometer.

3. Results and Discussion

3.1. Characterization of Geopolymers

The XRD patterns of geopolymers G5, G7, raw materials zeolite, and kaolin are presented in **Figure 1**.

The phillipsite peaks were more noticeable in the patterns of G7, which is of higher zeolitic content. The kaolin peaks were observed in the case of G5 and G7, indicating incomplete dissolution of kaolin. The new phase of geopolymer was not detected because this new phase is amorphous.

The SEM graphs (**Figure 2**) of geopolymers G5 and G7 indicates the presence of crystalline phillipsite immersed in amorphous geopolymeric material.

3.2. Adsorption Kinetics

The effect of contact time on the amount of metal ions (Pb(II), Cd(II), Cu(II), Ni(II), Zn(II)) adsorbed onto geopolymers and raw materials was investigated. A sample of this data is given in **Figure 3** for Ni(II). Among several kinetic models employed (first order, pseudo-second order, intraparticle diffusion, film diffusion) to fit Q_t - t data, the pseudo-second order model was selected depending on the correlation coefficient values of the models. Thus, pseudo-second order kinetics model (eq. 1) [17] was used to fit the kinetics data of adsorption of metal ions onto geopolymers and raw materials. The linear form of the pseudo-second order kinetics model is:

$$t/Q_t = 1/\left(kQ_e^2\right) + t/Q_e \qquad (1)$$

where Q_e is the amount of metal ion adsorbed at equilibrium (mmol metal ion/g adsorbent); t is the time (min); Q_t is the amount of metal ion adsorbed (mmol metal ion/g adsorbent) at time t; k is the rate constant of pseudo-second order adsorption (g adsorbent/ mmol metal ion.min). By plotting t/Q_t versus t (**Figure 4**, for Ni(II)), the value of the slope $1/Q_e$ and the intercept $1/(kQ_e^2)$ can be used for determination of Q_e and k.

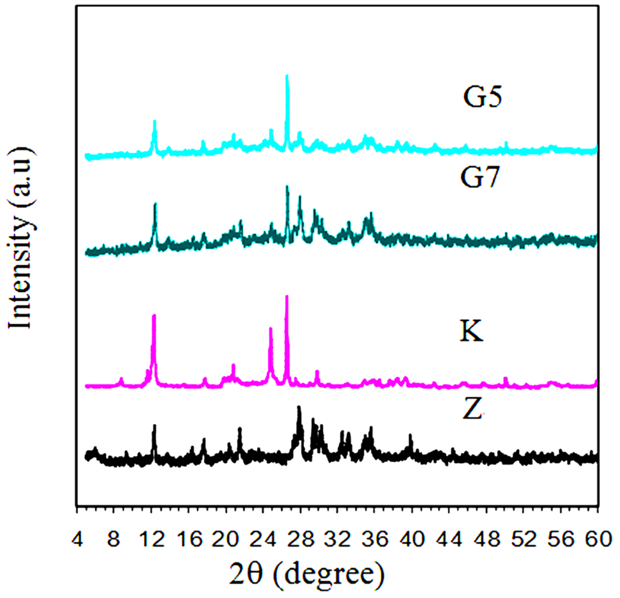

Figure 1. XRD patterns of geopolymers G5, G7, and raw materials K and Z.

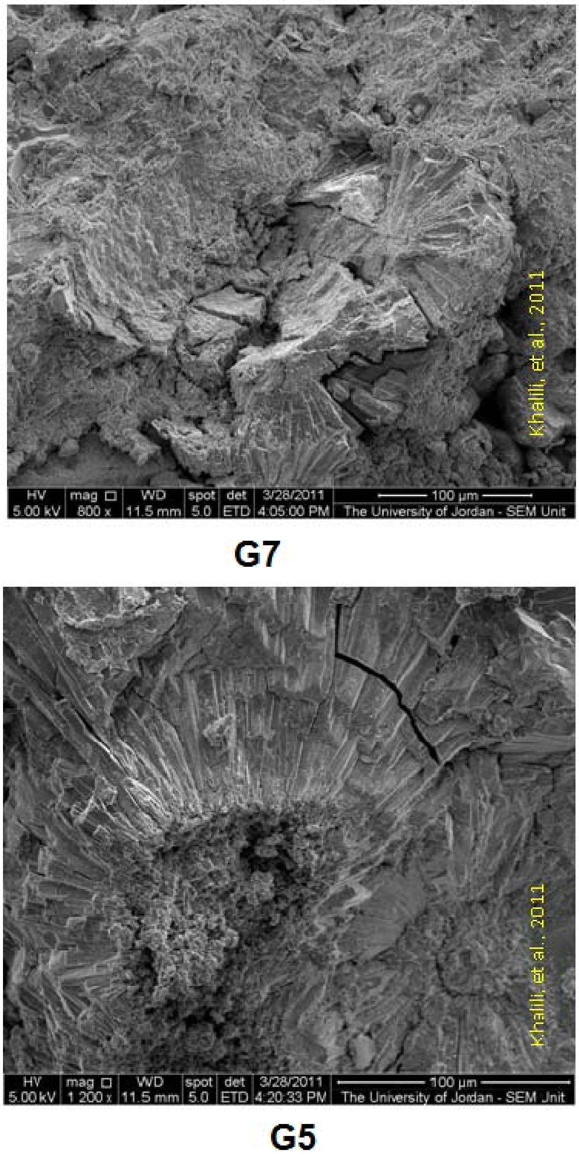

Figure 2. SEM of geopolymers G5 and G7, respectively.

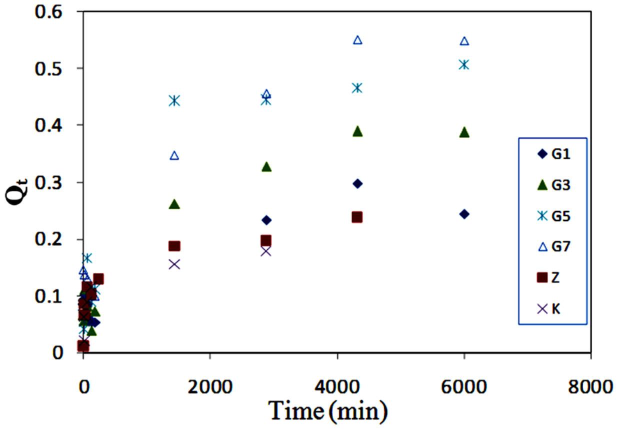

Figure 3. Plots of Q_t (mmol/g adsorbent) versus t (min) for kinetic study of adsorption of Ni(II) onto geopolymers G1, G3, G5, G7 and raw materials Z and K.

The results of Q_e and k obtained for Cu(II), Ni(II), Zn(II), Cd(II) and Pb(II) are presented in **Figure 5**. It is clear from **Figure 5**, that the amount of adsorption of metal ions onto geopolymers (Q_e) is higher than that of raw materials.

Thus, the geopolymerization process that resulted from dissolution of aluminosilicate monomers followed by polymerization of theses monomers creates new cation exchange sites. The amount of equilibrium adsorption capacity (Q_e) of metal ions onto the geopolymers increases with increasing zeolitic content of the geopolymers. This may be due to the increasing phillipsite content, which increases adsorption efficiency. Nevertheless, the rate constant of adsorption (k) of kaolinite is higher than that of geopolymer and zeolite, which indicates that the sheet structure of kaolinite imposed less kinetic limitations than zeolite and geopolymers. It seems that the three dimensional structure of geopolymer is similar to zeolite.

When comparing the amount metal ions adsorbed, the obtained trends of Q_e are:

For G1-G7: Ni, Cu, Zn > Cd, Pb

For Z: Cu > Cd > Ni > Zn > Pb

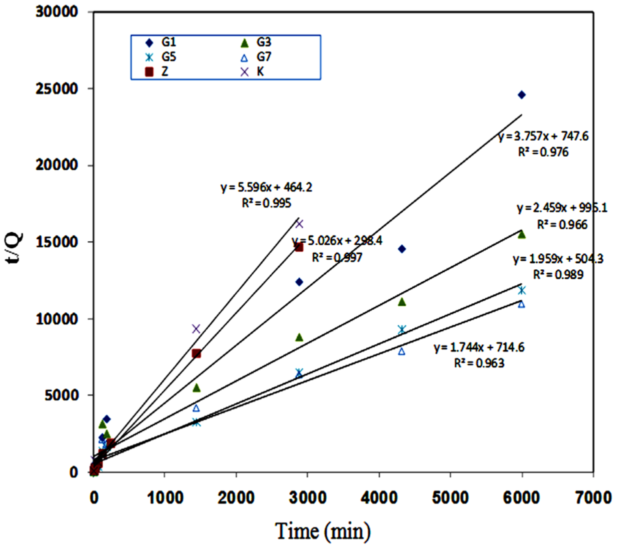

Figure 4. Plots of t/Q (min. mmol^{-1}. g adsorbent) versus t (min) for kinetic study of adsorption of Ni(II) onto geopolymers G1, G3, G5, G7 and raw materials Z and K.

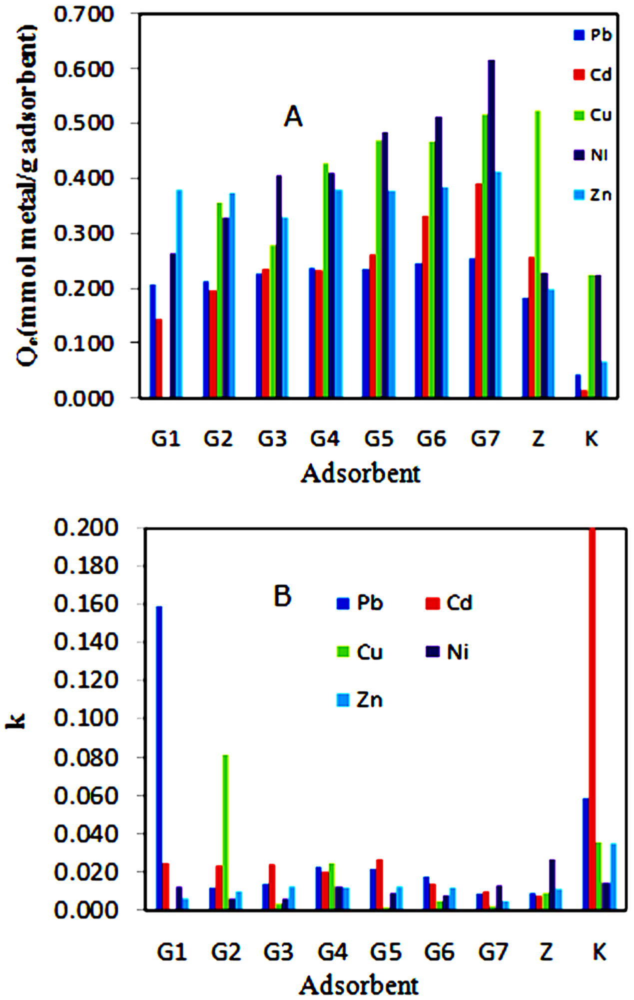

Figure 5. Variation of (A) equilibrium adsorption capacity Q_e and (B) rate constant k calculated from pseudo-second order kinetic model with change of composition of geopolymer.

For K: Cu= Ni > Zn > Pb > Cd

The difference in behavior of zeolite, kaolinite and geopolymers indicates the unique structure of the geopolymers. The structure of geopolymer may be so condense that it is more accessible for small size metal ions like Cu, Ni, Zn than large one like Cd and Pb.

3.3. Adsorption Isotherms

The adsorption isotherms of metal ions (Pb(II), Cd(II), Cu(II), Ni(II), Zn(II)) onto synthesized geopolymers and raw materials were investigated. The Langmuir equation (eq. 2) is the most popular equation for modeling adsorption isotherms [18]:

$$Q = Q_m KC / (1 + KC) \qquad (2)$$

where, Q is the amount of metal ions adsorbed (mmol metal/g adsorbent), Q_m is the adsorption capacity (mmol metal/g adsorbent), K is the affinity constant (L/mmol metal), and C is the equilibrium concentration of metal ions (mmol metal/L). Langmuir equation can be linearized in the form (eq. 3) [18]:

$$C/Q = (1/Q_m)C + 1/(Q_m K) \qquad (3)$$

The values of adsorption capacity (Q_m) and affinity constants K were determined from the slope and intercepts of the plots of C/Q versus C. The values of Q_m are presented in Figure 6 for the metal ions investigated. Geopolymer G7, which has the highest zeolitic content, has higher adsorption capacity toward metal ions than raw materials K and Z. The adsorption capacity of small size metal ions like Cu and Zn is higher than those of large size one like Cd and Pb. These results are similar to those obtained from the kinetic study.

It is obvious from **Figure 6** that increasing the zeolitic tuff content of geopolymers (moving from G1 to G7) leads to an increase of adsorption capacity of geopolymers toward.

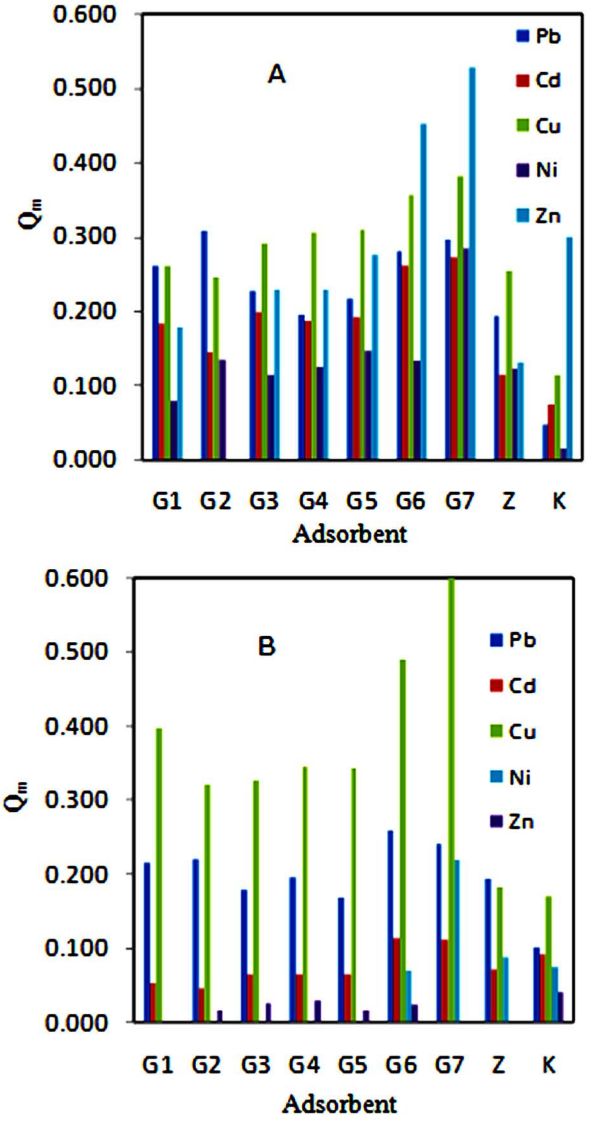

Figure 6. Langmuir adsorption capacity (Q_m, mmol metal/g adsorbent) for geopolymers and raw materials at pH 4, (A) single and (B) multiple metal adsorption.

3.4. Multiple Adsorption

In the case the multiple metal ions adsorption (**Figure 6**), one should expect a decrease of adsorption capacity of geopolymers compared to single metal ions adsorption due to competition between metal ions. This was observed in the case of raw zeolite. On the other hand, in the case of kaolinite, a reverse trend was observed, where adsorption capacity Q_m increases with competition, which indicate cooperative adsorption. The adsorption capacity of Cd(II), Ni(II), Zn(II) onto geopolymers decreases with competition in a similar manner to the adsorption of metal ions onto zeolite. However, the adsorption of Cu(II) onto geopolymers increases with competition like adsorption of metal ions onto kaolinite. The adsorption of Pb(II) onto geopolymers was not affected significantly by competition. Thus, the adsorption sites of geopolymers are unique and different from that of zeolite and kaolinite. The cooperative adsorption is evident in the case of adsorption of Cu(II) onto geopolymers and in the case of adsorption of metal ions onto kaolinite.

3.5. Desorption Study

The adsorption process of metal ions onto geopolymers was found to be reversible. After 24 h leaching with 0.1M NaCl solution, about 60% of the adsorbed metal ions were desorbed from geopolymer loaded with metal ions solution. This indicates that metal ions are bound by physical cation exchange and could be exchanges with Na^+. The results of leaching geopolymer loaded with Cu(II) ions are shown in **Figure 7**. Leaching of metal ions from raw kaolin was much more effective than geo polymers and zeolite because of compact structure of geopolymers.

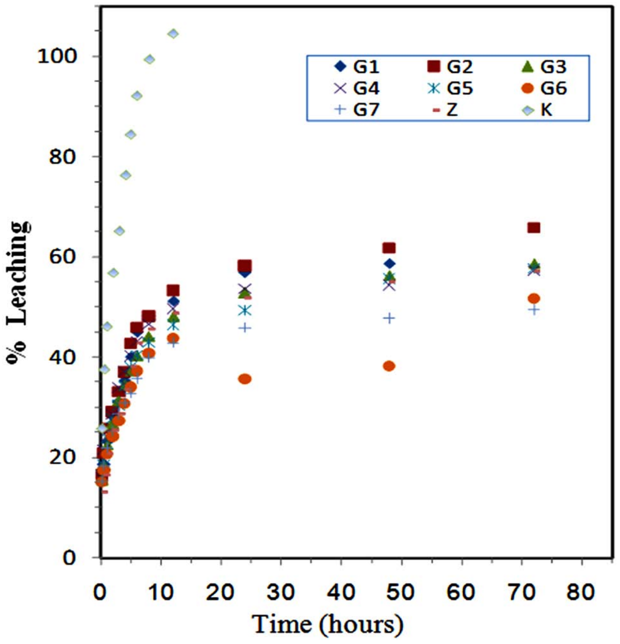

Figure 7. The %leaching of Cu(II) from geopolymers and raw materials loaded with Cu(II) as a function of time. Leaching was carried out using 0.1 M NaCl solution.

4. Conclusion

Both isothermal and kinetic studies revealed that increasing the zeolitic tuff: kaolin ratio improves the adsorption capacity of geopolymer toward metal ions. The adsorption capacity of the geopolymers of 150:50 zeolites: kaolin content was found to be higher than that of the raw materials themselves. The rate of adsorption of geopolymers was found to be lower than that of raw materials due to kinetic limitations imposed by formation of geopolymerization network. The selectivity of geopolymers toward adsorption of metal ions was found to be distinct from raw zeolite and kaolin where the adsorption onto geopolymers was found to be more preferential for small size metal ions (Cu(II), Ni(II), Zn(II)) than for large size metal ions (Pb(II), Cd(II)). The adsorption of Cu(II) and Pb(II) onto geopolymers did not decrease with competition with other metal ions that indicates cooperative adsorption. The adsorption process of metal ions onto geopolymers was found to be reversible, which indicates that metal ions are bound by physical cation exchange to the exchangeable sites of unreacted phillipsite and new amorphous geopolymer sites. Leaching of metal ions from raw kaolin was much more effective than geopolymers and zeolite because of compact structure of geopolymers.

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