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Microstructural characteristics and adsorption potential of a zeolitic tuff–metakaolin geopolymer

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ABSTRACT

The aim of this work is to investigate the microstructural characteristics and the adsorption potential of zeolitic tuff–metakaolin (ZM) geopolymers. For the identification of microstructure, X-ray diffraction (XRD) and scanning electron microscope (SEM) analyses were used. XRD showed that mordenite, a major zeolite mineral, disappeared upon geopolymerization, while SEM showed that ZM-geopolymers exhibit a uniform porous matrix consisting of nanoparticles (~40 nm). The adsorption efficiency of ZM-geopolymers was assessed using solutions containing 250 mg/L copper. The experimental results show that the maximum adsorption efficiency (7.8 mg Cu^{2+}/g of adsorbent) is observed at an initial zeolitic tuff/metakaolin ratio of 0.5 which indicates that ZM-geopolymers can be used in environmental applications including the clean-up of industrial effluents and wastewaters.

Keywords: Geopolymers; Zeolitic tuff; Metakaolinite; Adsorption

1. Introduction

It is known that through chemical polymerization, aluminosilicates, such as clays, can be hardened and transformed into aluminosilicate polymers, also known as geopolymers [1,2]. Geopolymers consist of an amorphous, three-dimensional structure resulting from the polymerization of aluminosilicate monomers in an alkaline solution [3,4]. The exact mechanism of geopolymerization is not known precisely and several studies have been carried out to elucidate kinetics and solution chemistry [5–7]. Most relevant studies propose a reaction pathway for geopolymerization involving polycondensation of hypothetical monomers, i.e. orthosialate ions. These reactions result in the production of a stable material similar to hydroxysodalite, feldspatiod or zeolite [8]. Geopolymers, which may be amorphous or microcrystalline, consist of SiO_4 and AlO_4 tetrahedra linked alternately by sharing all the oxygen atoms. When aluminum is four coordinated to oxygen atoms, a negative charge is created and therefore the presence of cations such as Na^+, K^+, Li^+, Ca^{2+}, Ba^{2+}, NH_4^+, and H_3O^+ is essential to balance the negative charge of Al in the fourfold coordination [9–11].

Limited references have been traced in literature on the adsorption potential of geopolymers, mainly synthesized by using fly ash. Li et al. [12] have studied the

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adsorption of methylene blue (MB) dye on fly ash-based geopolymer, which exhibited much higher adsorption potential towards MB than fly ash itself. Wang et al. [13] prepared an amorphous aluminosilicate geopolymer through solid-state conversion of fly ash. The synthesized geopolymer was also found to have higher adsorption potential towards Cu^{2+} ions (92 mg Cu/g of adsorbent) than fly ash (0.1 mg Cu/g of adsorbent). Zhang et al. [14,15] studied immobilization of heavy metals, namely Cr^{6+}, Cd^{2+}, and Pb^{2+} using fly ash-based geopolymers, while Yousef et al. [16] investigated the effect of zeolitic tuff, used as filler, on the mechanical performance and the adsorption potential of kaolinite-based geopolymers. Chen et al. [17] investigated the behavior and mechanisms of metakaolin-fly ash geopolymers during adsorption of Sr, Co, and Cs and mentioned that the adsorption efficiency is controlled by pH and initial heavy metal ion concentration. Finally, Mužek et al. [18] carried out a kinetic study on the adsorption of copper ions by fly ash-based geopolymers.

In order to minimize large-scale impacts caused by micropollutants on the environment, low-cost materials with adequate adsorption potential and suitable mechanical properties need to be developed. Geopolymers may be considered as candidate materials for this purpose [19–21]. Geopolymers may also be used for the construction of water storage or transport facilities (e.g. pools, dams, channels) and as liners in landfills to improve leachates quality and thus minimize the risk for groundwater and soil contamination [22].

The present paper investigates the microstructural characteristics and the adsorption potential of zeolitic tuff–metakaolin (ZM)-geopolymers when used for the clean-up of industrial effluents and wastewaters.

2. Materials and methods

2.1. Materials

Geopolymers were synthesized using zeolitic tuff and metakaolinite as starting raw materials while sodium silicate (Na_2SiO_3) and sodium hydroxide were used as alkaline activators. The zeolitic tuff, which is characterized by high content of mordenite that is mainly associated with calcite and dolomite was obtained from Kimolos Island, Greece. The tuff was pulverized, sieved through an 880 μm sieve, and exhibited a median grain size (d_{50}) of 40 μm. Kaolinite (Fluka, Germany, natural purum) was heated at 750°C for 4 h in a laboratory furnace (Optic Ivymen System, model SNOL 8.2/1100, Lithuania) to obtain metakaolinite. The chemical analysis of zeolitic tuff was determined by X-ray fluorescence (Bruker-AXS type S2 range energy dispersive spectrometer) and is given in Table 1. Na_2SiO_3 and NaOH solutions were used as alkaline activators for the dissolution of aluminosilicate phases. The sodium silicate solution (Merck, Germany) contained 25.5–28.5% SiO_2 and 7.5–8.5% Na_2O. The hydroxide solution with a concentration of 6.0 M was prepared by dissolving sodium hydroxide (NaOH) flakes of 98% purity (Merck) in distilled water. This concentration was used based on previous optimization studies.

Table 1
Chemical analysis of zeolitic tuff

Compound	Composition, %
MnO	0.04
Na_2O	0.77
CaO	14.66
K_2O	3.42
MgO	2.76
P_2O_5	0.05
Fe_2O_3	1.36
Al_2O_3	11.04
SiO_2	58.35
LOI	7.55

2.2. Production of geopolymers

The activating solution of Na_2SiO_3, NaOH, and H_2O, after overnight cooling was mechanically stirred for 1 min prior to use. Zeolitic tuff and metakaolinite were dry-mixed first and then added to the aqueous activating solution. All reagents were mixed for 15 min. Based on the results of previous studies carried out by the authors, the molar ratios of SiO_2 (in sodium silicate solution)/Al_2O_3 (in metakaolinite) and Na_2O (in sodium silicate and NaOH solution)/Al_2O_3 (in metakaolinite) were maintained at one, while the molar ratio H_2O/Na_2O at 13. The resulting pulp was poured into rectangular molds (11 cm × 1.5 cm × 4 cm each) and cured in a ventilated oven (ON-02G JEIO TECH, Korea) at 40°C for 24 h. After curing, the specimens were removed from the molds and cooled at room temperature. In addition, nine discs (2 cm × 2 cm × 1 cm) were prepared from each mixture and used for mineralogical studies using X-ray diffraction (XRD) and scanning electron microscope (SEM) as well as for the determination of their adsorption potential.

Four series of tests were carried out (Table 2). In the first series, G1, geopolymers were produced using only metakaolinite as raw material. Three different ratios of zeolitic tuff to metakaolinite, varying between 0.25 and 0.75, were used in the other three series G2, G3, and G4 for the production of geopolymers, the

Table 2
Weight ratios used for the production of ZM-geopolymers

Series	Zeolitic tuff/metakaolinite weight ratio
G1	0
G2	0.25
G3	0.50
G4	0.75

characterization of their microstructure, and the determination of their adsorption potential. Metakaolinite was used as a source of aluminum and silicon. Zeolitic tuff was used in the present study as a second precursor aiming to improve both adsorption potential and mechanical properties of the produced geopolymers. During geopolymerization, the zeolitic tuff can also act as a source of essential ions such as Al^{+3}, Si^{+2}, and Na^{+}.

2.3. Mineralogical analyses

XRD analyses were carried out on powdered samples to identify major crystalline and potentially, newly-formed phases using a Siemens D500 diffractometer (Germany) with a Co tube and a scanning range from 3° to 70° 2θ with a step 0.03° and 4° s/step measuring time. Qualitative analysis was carried out using the $\mathrm{Diffrac_{plus}}$ Software (Bruker AXS) and the PDF database.

The morphology of the specimens was studied using an Inspect F50 SEM (Netherlands). The samples were precoated with platinum under an argon atmosphere. Energy-dispersive X-ray spectroscopy (EDX) was used for elemental analysis.

2.4. Adsorption potential

In order to assess the adsorption potential of the produced geopolymers, a solution containing 250 mg/L of Cu was prepared using a standard solution of cupric acetate (98%, Hopkin and Williams). The geopolymeric discs produced were first immersed for one day in distilled water to remove any residual water-soluble salts formed on the surface of the specimens. This process was repeated four times. Discs were then immersed in the copper-containing solution and pH was adjusted from almost 7 to 3 using a solution of 0.1 N HCl. The glass beakers containing the geopolymeric discs and the solution were agitated for 24 h at 200 rpm in a water bath at room temperature. Ten milliliters of liquid samples were withdrawn from each solution, filtered through microfilters (0.45 μm Nylon) and centrifuged prior to the determination of Cu^{2+} concentration using atomic absorption spectrometer (Spectroscan-80DV, UK).

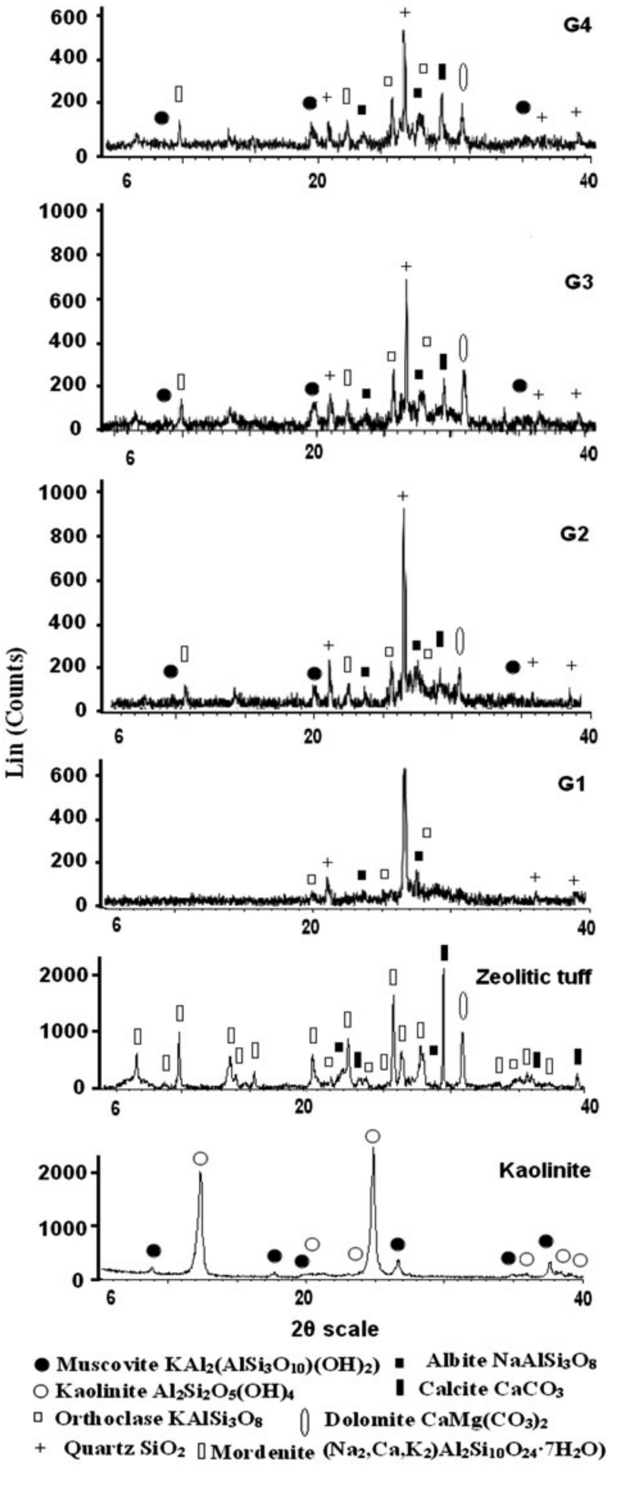

Fig. 1. XRD patterns of kaolinite, zeolitic tuff, and geopolymers (G1–G4).

3. Results and discussion

3.1. Microstructural characteristics

Fig. 1 shows the XRD patterns of kaolinite, zeolitic tuff (ZK), and the geopolymers produced (G1–G4). The patterns show that kaolinite contains also some muscovite, $KAl_2(AlSi_3O_{10})(F,OH)_2$, while the zeolitic tuff (ZK) contains mainly mordenite as well as calcite, dolomite, and orthoclase. During metakaolinite, geopolymerization muscovite partially disappears due its dissolution in the alkaline environment. Metakaolinite geopolymers (G1) show only some minor phases associated with muscovite, which were initially present in metakaolinite.

It is observed that the addition of zeolitic tuff resulted in an increase of residual muscovite, in all ZM-geopolymers (G2, G3, and G4). Besides muscovite, some phases present in G1, i.e. quartz, albite, and orthoclase, are also present in G2, G3, and G4 geopolymers. The high background seen between 26° and 32° in the XRD patterns of the produced geopolymers indicates the presence of amorphous phases [23].

As shown in Fig. 2, SEM analysis of metakaolinite-based geopolymers (G1) indicates that their microstructure is characterized by the coexistence of a geopolymer matrix (point A) and partially unreacted metakaolinite layers (point MK).

Fig. 3 shows selected SEM images of ZM-geopolymers. All geopolymers exhibit a well-ordered porous geopolymeric matrix where nanoparticles (~40 nm) are present (Fig. 3(A)). Fig. 3(B) shows that coarser particles (~250 nm) are distributed randomly in the microstructure. These coarser particles contain high Si/Al ratio, 3.7, compared with the finer particles where the Si/Al ratio is 2.2. Coarse particles were not observed in metakaolinite-based geopolymer (G1), due to the absence of zeolitic tuff in the starting mixture.

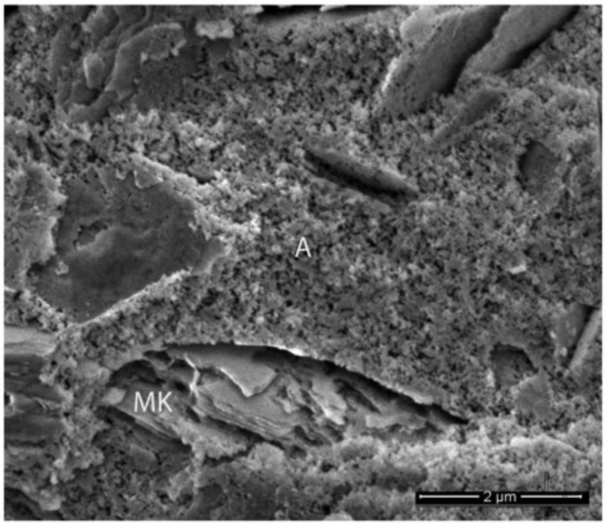

Fig. 2. SEM image of G1 geopolymers (reference metakaolinite geopolymers); MK: partially transformed metakaolinite; and A: sodium aluminum silicate phase.

The zeolitic tuff, which is used as precursor in this study, was attacked by the alkaline solution during geopolymerization and reacted partially as shown in Fig. 3(C). The residual zeolitic tuff was mainly amorphous. Due to the alkaline attack, macropores filled with newly-formed Na-aluminosilicates are widely scattered in the residual zeolitic tuff aggregate. Broad fiber zones, containing mainly quartz, were observed in Fig. 3(D), where a crystal growth zone is also shown. Finally, Fig. 3(E) and (F) shows the formation of new crystalline phases on the surface of the residual amorphous zeolitic tuff.

Microstructural observations, through EDX and SEM analyses (Fig. 4), reveal phase inhomogeneities in regions of high silicon concentration. Although the residual metakaolinite shows similar morphology to the initial one, its chemical composition is different. This is because the alkaline solution attacks mainly the surface of metakaolinite layers without altering their overall structure. Upon geopolymerization, the Si/Al ratio increased in metakaolinite from 1.1 to 1.9. According to elemental analysis, the average Si/Al ratio in the geopolymeric matrix is 2.3, whereas in regions when coarse particles are abundant, the Si/Al ratio is much higher (~3.7). Regions with high silica content are frequently observed in ZM-geopolymers, as seen in Fig. 3(B). They are easily spotted because of their microstructure, which is distinctively less porous than that of a typical geopolymer matrix. The inhomogeneities in the matrix are probably caused by the different release rates of silicon and aluminum from zeolitic tuff aggregates as indicated by EDX analysis (Table 3). These release rates are affected by reaction temperature and silicate concentration. It is likely that good homogenization cannot be achieved before extensive dissolution of the reactive materials takes place. At the onset of gelation (polycondensation), species transferred into solution react locally, viscosity increases rapidly, and hence the gel formed prevents further homogenization [24].

According to EDX elemental analysis, the average Si/Al ratio in the geopolymeric gel was 2.3, while the respective ratio in the partially transformed metakaolinite was lower (~1.9). SEM analysis also reveals that due to geopolymeric reactions, the area between the partially reacted metakaolinite layers has been filled with formed sodium aluminosilicate nanoparticles with a size of ~40 nm as shown in Fig. 2. This finding is in agreement with the results reported by Rahier et al. [25], who produced partially amorphous sodium aluminosilicates after the activation of metakaolinite with sodium silicate.

The metakaolinite-based geopolymer resembles the structure of porous nano-channels formed by aluminosilicate particles [26]. The size of the aluminosilicate particles (~40 nm), which are encapsulated in the geopolymeric matrix determines the pore pattern observed in their microstructure. The formation of a uniform pore structure in aluminosilicate particles through sol–gel chemistry is also commonly observed. The particle size can then be easily modified by changing the reaction temperature, curing time, and silicate content, as has also been observed in metakaolinite-based geopolymer gels [27].

3.2. Adsorption potential of geopolymers

The adsorption rate of Cu on geopolymers increased with increasing zeolitic tuff/metakaolin ratios (Fig. 5) and reached 8 mg Cu/g for specimens G3 and G4. Actually, no further increase is noticed for zeolitic tuff/metakaolin ratios higher than 0.50. It is important to mention that when the zeolitic tuff/metakaolin ratio doubles, from 0.25 to 0.50, the adsorption rate also doubles, from 3.8 to 7.8 mg/g. Although the surface area of ZM-geopolymers is lower compared with the respective powdered samples, the adsorption rate determined is comparable to that of a powdered zeolitic tuff used in a previous work (8.5 mg/g, at pH 4) [16,28]. Although the pH in this study was adjusted at 3, value in which the adsorption potential of zeolites is normally low compared to neutral pH, adsorption of copper ions on ZM-geopolymers still remains high. Cheng et al. [29]

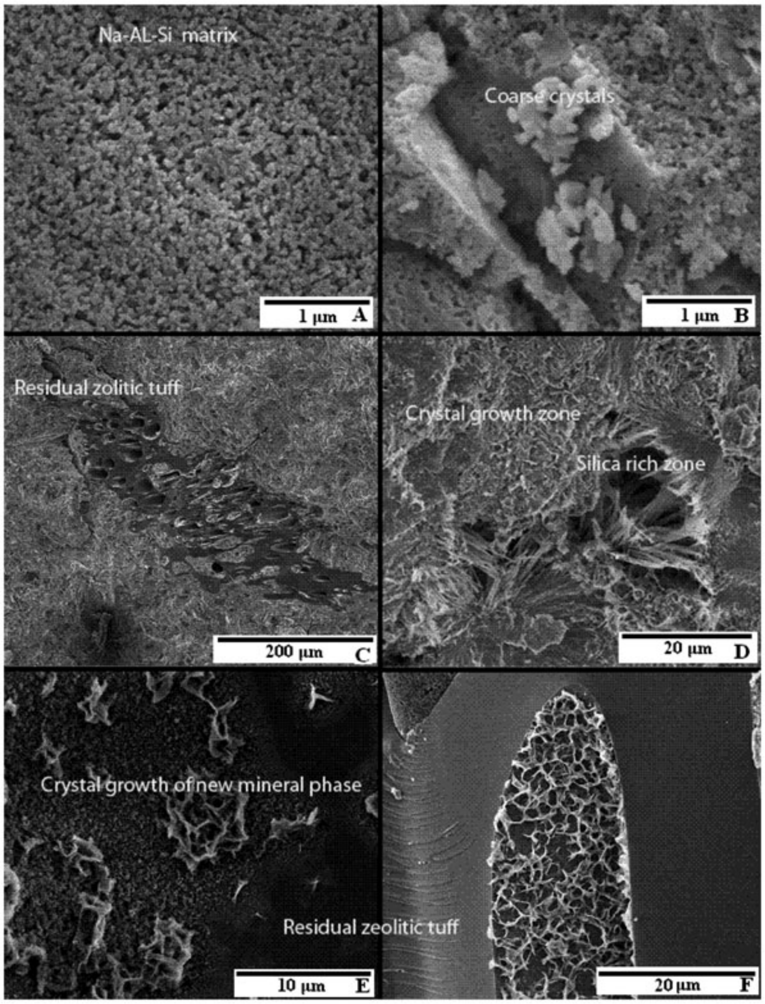

Fig. 3. SEM images of ZM-geopolymers.

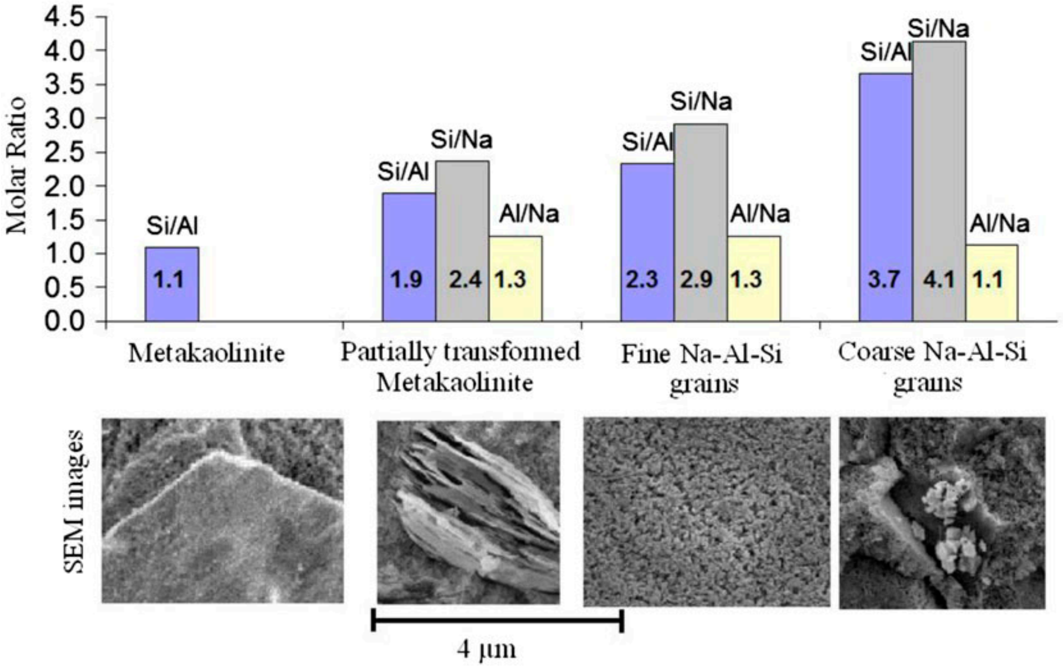

Fig. 4. Si/Al and Na/Al ratios in different geopolymeric regions.

also mention that the adsorption potential of metakaolinite-based geopolymers increases substantially when pH increases from 2 to 4. These findings indicate that geopolymers can be used for the adsorption of copper and potentially other heavy metal ions even under acidic conditions and the subsequent clean-up of wastewaters and industrial effluents [30].

Other studies also indicate that geopolymers produced from metakaolinite and zeolitic tuff exhibit high adsorption potential for Cu(II) ions when compared to other adsorbents such as natural zeolites, fly ash [12], and muscovite [31].

By summarizing the experimental results in this study, we can conclude that the formation of a nanoporous mineral matrix during geopolymerization, as indicated in the present study and shown in Figs. 2 and 3(A), results in higher surface area, and thus increased adsorption rates. The presence of muscovite (Fig. 1) in geopolymers G2, G3, and G4 is beneficial for the removal of heavy metals from solutions. It is known that zeolite has a cage-like structure which is suitable for ion exchange [32]. However, adsorption of metal ions onto zeolite particles is a complex process due to their porous structure, inner and outer charged surfaces, mineralogical heterogeneity, crystal edges, and other surface imperfections [33,34]. Mixing of zeolite tuff with metakaolinite revealed that the produced geopolymers (G2, G3, and G4) show a relatively high

Table 3
Changes in matrix molar ratios compared to Al present in the zeolitic tuff

	Precursor	After geopolymerization
Al	1.00	1.00
Si	4.50	3.40
Na	0.12	0.00
Ca	1.21	0.73
K	0.34	0.25

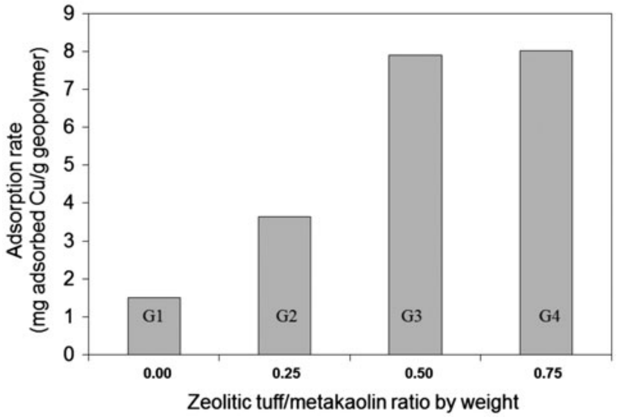

Fig. 5. Adsorption of Cu(II) by ZM-geopolymers (Cu^{2+} concentration: 250 mg/L, period: 24 h).

adsorption potential (Fig. 5). The XRD patterns of ZM-geopolymers (G2, G3, and G4) showed that all mordenite peaks of zeolitic tuff disappeared upon geopolymerization (Fig. 1). Thus, geopolymerization results in decrease of crystallinity for zeolite and the development of a more amorphous structure, as seen in Fig. 3(C), which increases the number of adsorption sites. Adsorption of Cu^{2+} ions is carried out through cation exchange between Na^+ and Cu^{2+}. This is well justified since geopolymerization of the starting materials involved the use of a very alkaline solution. Na^+ ions present in the alkali solution play an important role in electrical neutralization of the resulting geopolymeric matrix, by replacing hydrogen ions present at the broken edges of the aluminosilicate layers. Subsequently, Na-aluminosilicate particles are formed and dispersed in the geopolymeric matrix.

4. Conclusions

Metakaolinite–zeolitic tuff geopolymers have been successfully produced by alkali activation. The products contain phases such as residual muscovite, feldspar, and quartz. The present study shows clearly the beneficial influence of the use of zeolitic tuff in the starting mixture on microstructure and adsorption potential of geopolymers.

An important finding of the present study is that the microstructure of ZM-geopolymers, as defined through SEM analyses, consists of a nanoparticle matrix with nanosized pores. EDX analysis also defines the ratio of Si/Al in the aluminosilicate matrix of ZM-geopolymers, which ranges between 1.82 and 3.52 and results in different morphologies and properties.

The adsorption rate of copper for the geopolymers produced with an initial optimum zeolitic tuff: metakaolinite ratio of 0.5 is considered quite high and reaches 8 mg Cu/g indicating that ZM-geopolymers can be used in several environmental applications, such as the clean-up of wastewaters or mild industrial effluents from electroplating and galvanizing operations. Further studies are required to assess the adsorption efficiency of these materials towards other hazardous heavy metal ions, such as chromium, arsenic, and lead.

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