The influence of using Jordanian natural zeolite on the adsorption, physical, and mechanical properties of geopolymers products

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ABSTRACT

Geopolymers consist of an amorphous, three-dimensional structure resulting from the polymerization of aluminosilicate monomers that result from dissolution of kaolin in an alkaline solution at temperatures around 80 °C. One potential use of geopolymers is as Portland cement replacement. It will be of great importance to provide a geopolymer with suitable mechanical properties for the purpose of water storage and high adsorption capacity towards pollutants. The aim of this work is to investigate the effect of using Jordanian zeolitic tuff as filler on the mechanical performance and on the adsorption capacity of the geopolymers products. Jordanian zeolitic tuff is inexpensive and is known to have high adsorption capacity. The results confirmed that this natural zeolitic tuff can be used as a filler of stable geopolymers with high mechanical properties and high adsorption capacity towards methylene blue and Cu(II) ions. The XRD measurements showed that the phillipsite peaks (major mineral constituent of Jordanian zeolite) were disappeared upon geopolymerization. The zeolite-based geopolymers revealed high compressive strength compared to reference geopolymers that employ sand as filler. Adsorption experiments showed that among different geopolymers prepared, the zeolite-based geopolymers have the highest adsorption capacity towards methylene blue and copper(II) ions.

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1. Introduction

Geomaterials are the most commonly used construction materials worldwide since earth or soil is readily available almost anywhere on the planet. Stabilization of soil can be achieved by mechanical, physical, and chemical techniques. Mechanical stabilization compacts the soil, changes its density, mechanical strength, compressibility, permeability, and porosity. Physical stabilization changes the properties of the soil by acting on its texture, which can be done by controlling the mixture of different grain fractions. Chemical stabilization changes the properties of the soil through adding other materials or chemicals. This happens by creating a matrix which binds or coats the grains of soil and filler [1].

It has been observed [1] that through chemical polymerization reactions, the aluminosilicates such as clay (kaolinite) could be hardened and transformed into aluminosilicate polymers, also known as geopolymers, which are useful construction materials [2]. Geopolymers consist of an amorphous, three-dimensional structure resulting from the polymerization of aluminosilicate monomers in an alkaline solution [3].

The exact mechanism of the geopolymerization is not known precisely until now. There is a good possibility for Na$^+$ from alkaline NaOH to exchange the hydrogen ions on the broken edges of the clay. As a result of this ion exchange, repulsion between the Na$^+$ ions will dissolute some clay particles into other grains of the soil and binds them together [4]. Davidovits [5] has proposed a reaction pathway for geopolymerization involving the polycondensation of hypothetical monomers, i.e. the orthosialate ions, as shown below. As a result of these reactions, solid, hard, and stable materials with hydroxysodalite, feldspatiod, or zeolite like materials are formed [2].

$$Al_2O_3 \cdot 2SiO_2 + 2nH_2O \xrightarrow{\text{NaOH}} n(OH)_3-Si-O-Al^{(-)}-(OH)_3$$
$$\textbf{orthosialate}$$

$$n(OH)_3-Si-O-Al^{(-)}-(OH)_3 \xrightarrow{\text{NaOH}}$$

$$Na^{(+)} - \left(\begin{matrix} | \\ Si \\ | \\ O \end{matrix} -O- \begin{matrix} | \\ Al^{(-)} \\ | \\ O \end{matrix} -O- \right)_n + 3nH_2O$$
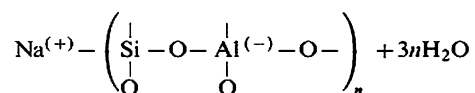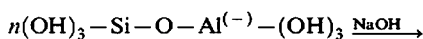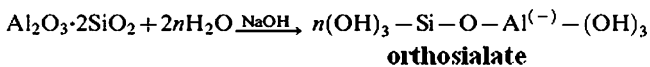
When aluminum is four coordinated to oxygen atoms, a negative charge is created and therefore the presence of cations such as Na$^+$ is essential to maintain electric neutrality in the geopolymeric matrix (hydroxysodalite). Hydroxysodalite, which ranges from amorphous to microcrystalline material, consists of SiO$_4$ and AlO$_4$ tetrahedra linked alternately by sharing all the oxygen atoms [6]. Positive ions (Na$^+$, K$^+$, Li$^+$, Ca^{2+}, Ba^{2+}, NH$_4^+$, and H$_3$O$^+$) must be present in the framework cavities to balance the negative charge of Al in the four-fold coordination.

Fillers, like silica sand (SS), could be used in different amounts in kaolin-based geopolymers depending on the workability of the overall mixture and the physical stability of the end products. These materials are usually the least expensive of the major ingredients of geopolymers. However, fillers may participate in geopoloymerization process (functional fillers) and thus are very important in establishing the performance of geopolymers.

Little work was found in the literature on the adsorption behaviour of geopolymers. Li et al. [7] 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 (5.61 × 10^{-3} mmol MB/g adsorbent). Wang et al. [8] reported an amorphous aluminosilicate geopolymer resulted from solid-state conversion of fly ash. The synthesized geopolymer was found to have higher adsorption capacity towards Cu^{2+} ion (92 mg Cu/g adsorbent) than the fly ash itself (0.1 mg Cu/g adsorbent).

There is a large-scale pollution in many areas around the world by micropollutants, an example is Zarka basin (in Jordan) [9]. For treatment of this pollution, low cost solid materials with high adsorption capacity are needed. The materials required may also be used for constructing water storage (e.g. pools and dams) and transportation channels. They can be utilized to construct large filters to be employed in a large-scale reduction of pollution in large bonds and basins. Geopolymers are potential materials for this purpose.

This research focuses on the influence of using natural Jordanian zeolitic tuff (ZT) as a filler on the adsorption, physical, and mechanical properties of kaolin-based geopolymers products. The target of zeolite addition is to provide a material with suitable mechanical properties for the purpose of water storage and high adsorption capacity for water purification. The zeolitic tuff is characterized by its availability, high adsorption capacity, and stability. The influence of silica sand as an inert filler on geopolymers was studied

as a reference material in order to evaluate the effect of zeolitic tuff on geopolymers. The adsorption of the produced kaolin-based geopolymers as well as their starting materials, i.e. zeolitic tuff and kaolin, towards methylene blue and Cu^{2+} ion was investigated. The methylene blue was chosen as a colored pollutant in waste water from different industries [7], while the Cu^{2+} ion was chosen as an example of a heavy metal pollutant.

2. Materials and methods

2.1. Materials used for geopolymerization

2.1.1. Reference kaolin (RK)
Kaolin from Ukraine (purchased by Jordan international modern trade co.) with a purity of 95% was used as a reference for Jordanian kaolin (JK) to prepare geopolymers specimens.

2.1.2. Jordanian kaolin (JK)
Jordanian kaolin with a purity of 60% [10] was from El-Hiswa deposit, which is located in the south of Jordan about 45 km to the east of Al-Quweira town [11]. The elevation of the upper surface deposit ranges between 850 and 950 m above sea level. Thirty-two individual samples were collected from different layers of an outcrop, weighing in total 32 kg. These samples represent 8 m of the upper layers of this outcrop.

Preparation of the Jordanian kaolin samples involved crushing (using Jaw crusher, RETCH-BB1A) of an oven dried clay (at 105 °C) with a grain size less than 425 μm. Then the samples were mixed in 50 L plastic drum for several times to make them more homogenous.

For a better understanding of the geotechnical properties of the samples and for optimizing the filler/clay/water/NaOH ratios, which should be used in the fabrication of geopolymers, kaolin clay samples were tested for plasticity limit. The plasticity limits are important to optimize the amount of water needed for the specimens' preparation. The plasticity limits, according to the ASTM D4318 [12], for the Jordanian kaolin and reference kaolin (RK) were found to be 22% and 38%, respectively.

2.1.3. Jordanian zeolitic tuff (ZT)
The zeolitic tuff was from North–East Jordan deposits (Aritayn area) located around 50 km to the east from Amman. The mineral composition of this tuff belongs mainly to phillipsite type of zeolites [13–15].

2.1.4. Jordanian silica sand (SS)
Silica sand is one of the most well-known inert fillers which are used in cement-based materials. It is characterized by its low price, high stability, and high resistance to chemical attack [16–18]. This filler should be well crystalline and should not include impurities such as organic matter or swilling/shrinking minerals to be utilized as an inert filler. Organic matter dissolves easily in the presence of chemical solutions, while the swelling/shrinking minerals experience dramatic changes in their dimensions in presence of water. Therefore, these impurities cause disintegration of the end geopolymeric products even if they represent a small percentage. However, the silica sand employed in the present work was washed with distilled water and sieved at 100 and 400 μm [19].

2.2. Fabrication of geopolymers' specimens

Four different series of geopolymers' specimens with different compositions were prepared from kaolinitic soil, filler, and alkali solution as shown in Table 1.

Table 1
Composition of geopolymers used in the study.

Series	Clay			Filler			NaOH		Water	
ID	Type	Ratio	%	Type	Ratio	%	Ratio	%	Ratio	%
M-RS	RK	100	28.1	SS	200	56.2	18	5.1	38	10.7
M-RZ	RK	100	48.3	ZT	50	24.2	18	8.7	39	18.8
M-JS	JK	100	29.8	SS	200	59.5	14	4.2	22	6.5
M-JZ	JK	100	41.7	ZT	100	41.7	14	5.8	26	10.8

M-RS and M-RZ geopolymers produced from geopolymerization of reference kaolin (RK) using silica sand (SS) and zeolitic tuff (ZT), respectively. M-JS and M-JZ geopolymers produced from geopolymerization of Jordanian kaolin using silica sand (SS) and zeolitic tuff (ZT), respectively.

The first two series of produced geopolymers (Table 1), i.e. M-RS and M-RZ, are based on Ukrainian kaolin (reference kaolin) and differ in the filler type (silica sand or zeolitic tuff). Silica sand was used as a filler material to prepare M-RS geopolymer while the zeolitic tuff was used in M-RZ geopolymer. The other two series, i.e. M-JS and M-JZ, are based on local Jordanian kaolin, again the sand (SS) was used as a filler in M-JS geopolymer while zeolite (ZT) was used in the preparation of M-JZ geopolymer.

The role of employing the above ingredients in the fabrication of geopolymers is as follows. Kaolinitic soil (JK and RK) was used as a source of aluminumsilicate. Silica sand was used as a filler to provide high mechanical properties. NaOH was used as an alkaline activator for dissolution of aluminoslicate. Water was the reaction medium. The zeolitic tuff was employed as a filler proposed by the present study.

It has been reported [20] that the optimum water content for high quality construction was found to be close to the plasticity limit of the solid ingredients mixture (i.e. the clay and the filler). Sodium hydroxide should be used in small amounts 15–20% of the kaolin to avoid any residual alkali in the material and for economical reasons [10]. The ratio of clay/filler was determined based on the workability of the mixture and the compaction of the ingredients.

The weighed filler (silica sand or zeolitic tuff) and kaolinitic soil were mixed (KitchenAid, heavy duty 5K5SSS) first and then the sodium hydroxide (GCC, 96%) solution was added. Mixing was done at two different speeds; the first speed at ~107 rpm for 2 min and the second speed at ~198 rpm for 10 min. Good mixing is important to obtain homogeneous and comparable specimens and to avoid the agglomeration of the mixture.

The procedure of specimens' fabrication and tests made on specimens are illustrated in Fig. 1. Each mixture (series) was divided into eight specimens (50 g each). The paste was molded immediately after weighing to avoid drying and decrease of the workability of the mixture. The paste was molded in a stainless steel cylinder (diameter of 25 mm and height of 45 mm) at a pressure of about 15 MPa (Carver hydraulic laboratory press). The eight molded specimens of each series were cured by placing them in a ventilated oven (Binder-ED115) at 80 °C for 24 h. After this curing time, the specimens were removed and let to cool at room temperature.

Eight specimens of each series were divided into three groups. Three specimens (Group-1) were further dried in an oven at 40 °C for 7 days. Other three specimens (Group-2) were immersed in plastic containers filled with tap water at room temperature for 7 days. The remaining two specimens (Group-3) were used for X-ray diffraction (XRD) measurements and adsorption experiments.

2.3. Mechanical and physical characterization of geopolymers

The fabricated specimens for each series were tested for the water absorption, the density, and the compression strength. Water absorption of the immersed specimens (Group-2) was calculated for each series according to Eq. (1), where $W\%$ is the absorption of water expressed as percentage; W_w and W_d are the weights of the immersed specimen and of specimen after drying (g), respectively.

$$W\% = ((W_w - W_d)/W_d) \times 100 \qquad (1)$$

For density measurements, the eight specimens (see Fig. 1) were weighed using an electronic balance (SPE2001, Scout Pro) and their dimensions were measured using a digital micrometer (electronic digital calibre, 0.155 mm).

Compression test was performed using CONTROLS testing machine (Model T106 modified to suit with standard testing), where the load was applied and increased by a displacement rate
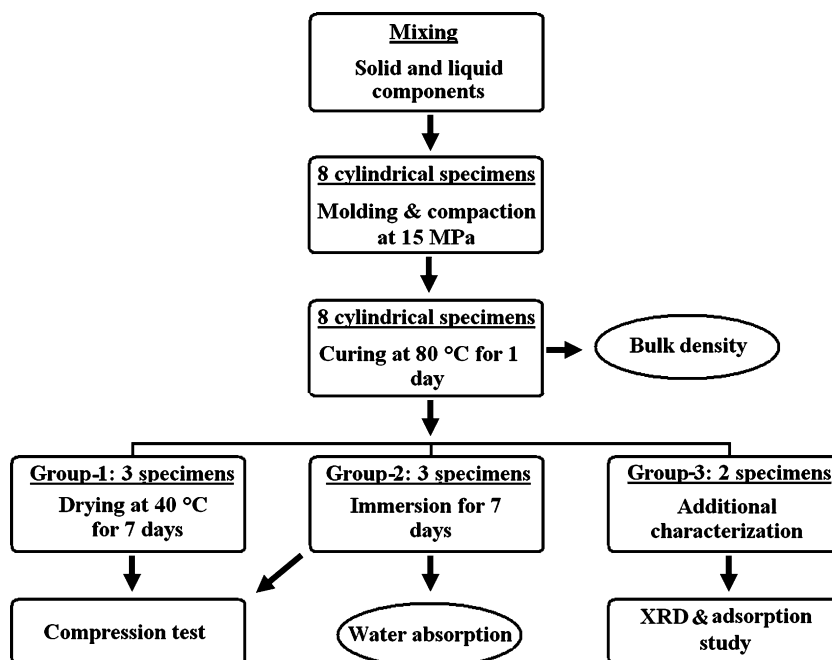

Fig. 1. Experimental design of fabricating and testing the prepared geopolymers.

of (2 mm/min). The compression test was applied to calculate the unconfined compressive strength from the following relationship shown in Eq. (2), where S is the compressive strength (N/mm^2 or MPa), F is the maximum load applied before failure (N), and A is the cross section area of the specimens (mm^2).

$$S = F/A \qquad (2)$$

2.4. X-ray diffraction (XRD)

The X-ray diffraction measurements were carried out (X-ray diffractometer-6000, Shimadzu) on powdered samples of geopolymer (M-JZ), Jordanian zeolitic tuff, and Jordanian kaolin to identify the dominant crystalline phases. The XRD patterns were measured from 5° to 80° 2θ at a scan rate of 2°/min. The crystalline phases were identified by analyzing the positions of the peaks using the software package supplied with the instrument.

2.5. Adsorption properties of geopolymers and their starting materials

2.5.1. Sample preparation

About 100 g sample (the two specimens of Group-3) of each geopolymer M-RS, M-JS, M-RZ, and M-JZ were crushed using Retsch RM 100-crusher. The crushed samples as well as the filler (zeolitic tuff) and the clay materials (Jordanian kaolin, reference kaolin) were sieved (Fema-SAIZGITTER) at different meshes (<250, 250–500, and >500 μm). The portion with a particle size of 250–500 μm was washed seven times with distilled water (100 mL each) to ensure complete removal of excess NaOH (by measuring pH). The washed sample was dried in the oven overnight at 105 °C and kept in a dessiccator over anhydrous CaCl$_2$.

2.5.2. Adsorption of methylene blue (MB)

Ten methylene blue (Acros organics, pure) standard solutions (8×10^{-6} to 4×10^{-5} M) were prepared. The absorbances of these solutions were measured using UV–vis spectrophotometer (Spectroscan-80DV) at λ_{max} = 665 nm in order to draw the calibration curve.

2.5.2.1. Time-dependence experiments.
A 0.04 g sample of zeolite-based geopolymers (M-JZ, M-RZ) and the clays (RK, JK) was independently placed in a 500 mL stoppered reagent bottle to which 250 mL of 1×10^{-5} M MB standard solution was added. The stoppered bottles were shaken in a shaker water bath (Clifton-11268) at 25 °C and 320 rpm for 48 h. A 1.0 mL sample of adsorbate was withdrawn at different contact times (0–48 h) and diluted to 5 mL with distilled water and then its concentration was measured spectrophotometrically.

2.5.2.2. Batch experiments.
A series of 50 mL glass bottles were employed. Each bottle was filled with 100 mL of methylene blue solution of varying concentrations (8×10^{-6} to 4×10^{-5} M, ten standards) and 0.02 g of adsorbent (JK, RK, ZT, M-RS, M-JS, M-RZ, and M-JZ). The stoppered bottles were shaken at 25 °C and 320 rpm for 48 h. A 3.0 mL portion of each solution was withdrawn after 48 h and centrifuged (ANNITA.III, 6500 rpm, 10 min). The MB concentrations were determined spectrophotometrically.

2.5.3. Adsorption of Cu^{2+} cations

Ten standard solutions (10–100 ppm) of cupric acetate (98%, Hopkin and Williams) in 0.1 M NaClO$_4$ solution (98%, Eurostar Scientific LTD) at two pH values, i.e. 4 and 6, were prepared (pH adjustment using NaOH/HClO$_4$). In order to draw the calibration curve, the absorbances of several standard solutions (10, 30, 50, 70,
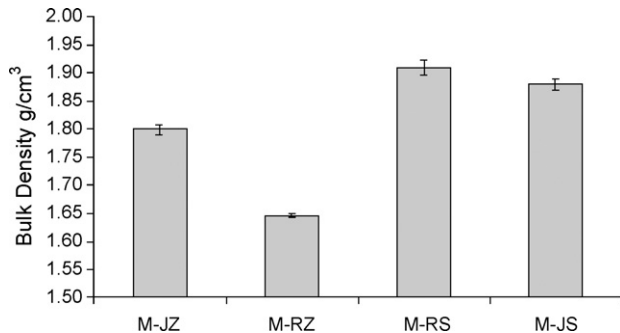

Fig. 2. Bulk density (average of eight cured samples, see Fig. 1) of geopolymers with different compositions.

and 100 ppm) were measured using atomic absorption spectrometer (Varian, AA-250 plus).

For isotherm studies, a 100-mL polyethylene bottle was filled with 50 mL of Cu^{2+} solution of varying concentrations (10–100 ppm, ten standards) and 0.05 g of adsorbent (JK, RK, ZT, M-RS, M-JS, M-RZ, and M-JZ). A 10.0 mL portions from each reagent bottle were withdrawn after 24 h of shaking, filtered by microfilters (0.45 μm Nylon), and centrifuged. The metal concentrations were determined using the atomic absorption spectrometer.

3. Results and discussion

3.1. Mechanical and physical properties of geopolymers

3.1.1. Density

As shown in Fig. 2, geopolymers based on zeolitic tuff filler have lower bulk density (1.65 g/cm^3 in M-RZ and 1.80 g/cm^3 in M-JZ) than those based on silica sand filler (2.16 g/cm^3 in M-RS and 1.93 g/cm^3 in M-JS). Thus, using Jordanian zeolitic tuff as a filler material in the geopolymers decreases the bulk density of the end products. This is due to the fact that the Jordanian zeolitic tuff is a porous material with low bulk density.

3.1.2. Water absorption

The water absorption data of the four series with different fillers and clays are shown in Fig. 3. It was observed that water absorption is higher in the geopolymers based on zeolitic tuff filler (23.2% in M-RZ and 17.6% in M-JZ) than those based on silica sand filler (11.0% in M-RS and 13.0% in M-JS). Again this behaviour is due to the fact that incorporation of zeolitic tuff into the geopolymer increases the porosity of the product, which increases the water absorption capability.
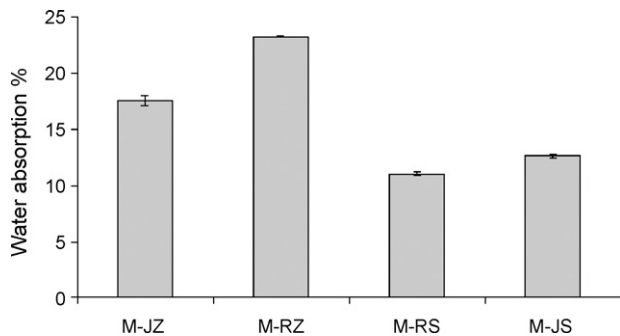

Fig. 3. Water absorption percentages of geopolymers with different compositions (Group-2 samples).
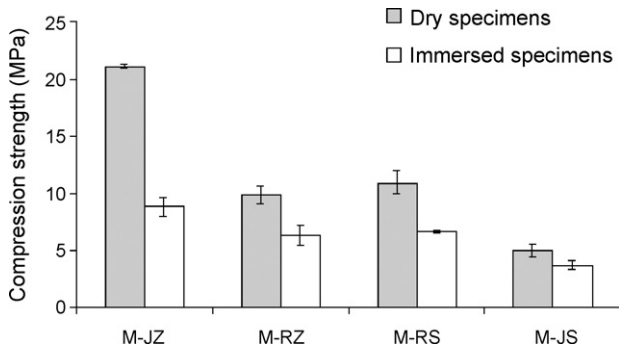
Fig. 4. Compression strengths of geopolymers with different compositions under dry conditions (Group-1 samples) and under immersed conditions (Group-2 samples).

3.1.3. Compression strength

The compression strengths of the four series of synthesized geopolymers are shown in Fig. 4. Although they did not show disintegration, the immersed specimens showed much less strength than the same dry specimens of all series. The strength of M-RS specimen (used reference kaolin) is almost twice as high as M-JS specimen (used Jordanian kaolin). This is due to the higher kaolin content of the former (95%) compared to the latter (60%) as mentioned in Sections 2.1.1 and 2.1.2. Higher kaolin content leads to more amount of hard geopolymeric products (feldspatiod or hydroxysodalite) and thus shows an increase in strength.

In spite of their low density and high water absorption as shown in Figs. 2 and 3, it was observed that M-JZ specimen (used Jordanian kaolin as a clay and Jordanian zeolitic tuff as a filler) expresses a very high strength compared to the rest of geopolymers series. The higher compressive strength of M-JZ is associated with the high surface area of zeolite compared to silica sand. The higher surface area of zeolite gives it more opportunity to interact with the geopolymeric phase.

3.2. X-ray diffraction patterns for M-JZ geopolymer and its constituents

The XRD patterns of Jordanian kaolin, Jordanian zeolitic tuff, and the geopolymer (M-JZ) are shown in Fig. 5. The Jordanian kaolin spectrum showed silica accompanied with kaolinite. The XRD spectrum of Jordanian zeolitic tuff showed the characteristic peaks of phillipsite-K. Upon geopolymerization, these peaks were disappeared due to dissolution as shown in the XRD pattern of M-JZ.
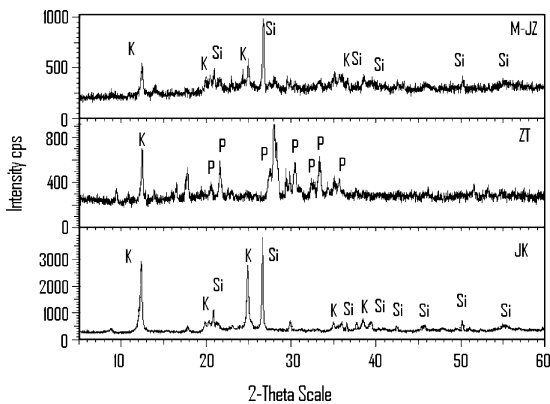

Fig. 5. X-ray diffraction spectra of geopolymer (M-JZ), Jordanian zeolitic tuff (ZT), and Jordanian kaolin (JK). Si: silica; K: kaolinite; P: plillipsite-K.
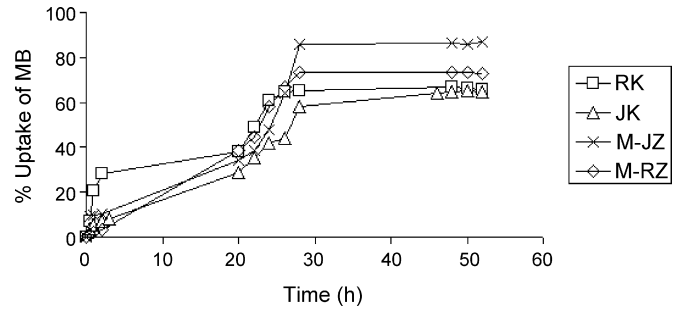

Fig. 6. The effect of contact time on the amount of MB adsorbed on RK, JK, M-RZ, and M-JZ samples.

3.3. Adsorption behavior of geopolymers

3.3.1. Adsorption of methylene blue (MB)

The effect of contact time on the amount of MB adsorbed on selected samples, i.e. RK, JK, M-RZ, and M-JZ, is shown in Fig. 6. It is obvious that adsorbents need about 30 h to reach MB adsorption saturation equilibrium. Thus, all the adsorption isotherms were studied at a contact time more than 30 h (about 48 h) to ensure reaching equilibrium.

The adsorption isotherms of methylene blue onto synthesized geopolymers (M-RS, M-JS, M-RZ, M-JZ) at 25 °C were determined. In order to compare the adsorption properties of the geopolymers with the materials from which they are made, adsorption isotherms of MB on Jordanian zeolitic tuff, Jordanian kaolin, and reference kaolin were also determined. Jordanian silica sand was found to have a negligible adsorption.

Two methods can be followed to obtain the Langmuir parameters Q_m and K. The first method employs the nonlinear regression of the Langmuir equation (Eq. (3)), where Q is the amount of MB adsorbed (mmol MB/g adsorbent), Q_m is the monolayer adsorption capacity (mmol MB/g adsorbent), K is the affinity constant (L/mmol MB), and C is the equilibrium concentration of MB (mmol/L). The resultant plots of nonlinear fitting of the adsorption isotherms of MB on ZT, JK, RK, M-RS, M-JS, M-RZ, and M-JZ specimens are shown in Fig. 7a.

$$Q = Q_m KC/(1 + KC) \tag{3}$$

The second method employs the linearized form of the Langmuir equation (Eq. (4)).

$$C/Q = C/Q_m + 1/Q_m K \tag{4}$$

A plot of C/Q against C gives a straight line with a slope equal to $1/Q_m$ and an intercept equals to $1/Q_m K$ as shown in Fig. 7b. The Langmuir parameters calculated form the linearized plots were very close to those obtained from nonlinear regression and are given in Table 2.

Table 2
Langmuir adsorption parameters for the adsorption of methylene blue onto ZT, JK, RK, M-RS, M-JS, M-RZ, and M-JZ specimens.

Specimen	Q_m (mmol/g)	K (L/mmol)	R^2
ZT	0.0612	3248	0.9980
JK	0.0662	3200	0.9931
RK	0.0638	2632	0.9905
M-RS	0.0077	[a]	0.8463
M-JS	0.0024	[a]	0.9050
M-RZ	0.0707	1668	0.9454
M-JZ	0.0806	662	0.9680

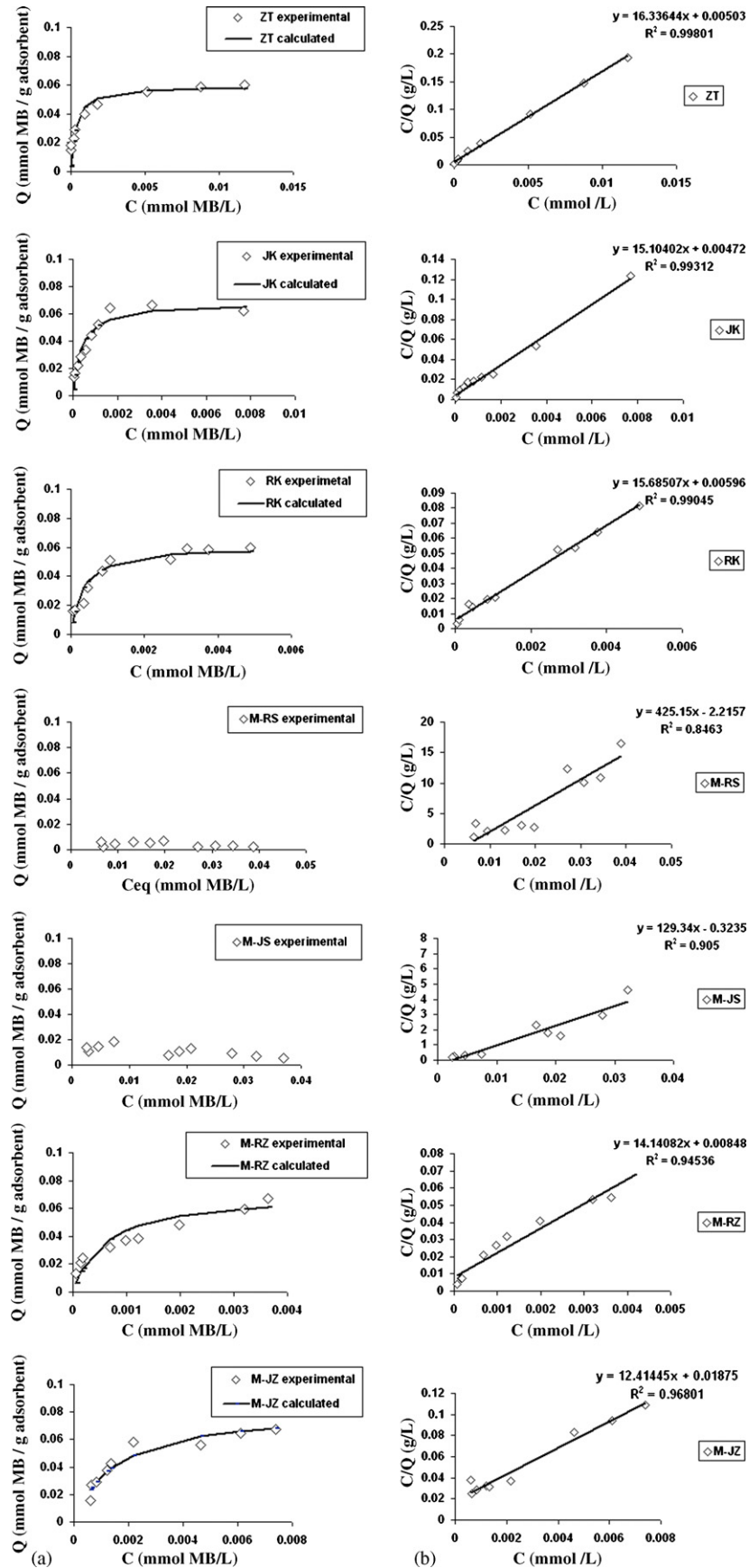[a] Negative intercept was obtained for the lines.

Fig. 7. (a) Adsorption isotherms of methylene blue. (b) Linearized Langmuir plots for the adsorption isotherms of methylene blue on ZT, JK, RK, M-RS, M-JS, M-RZ, and M-JZ specimens.
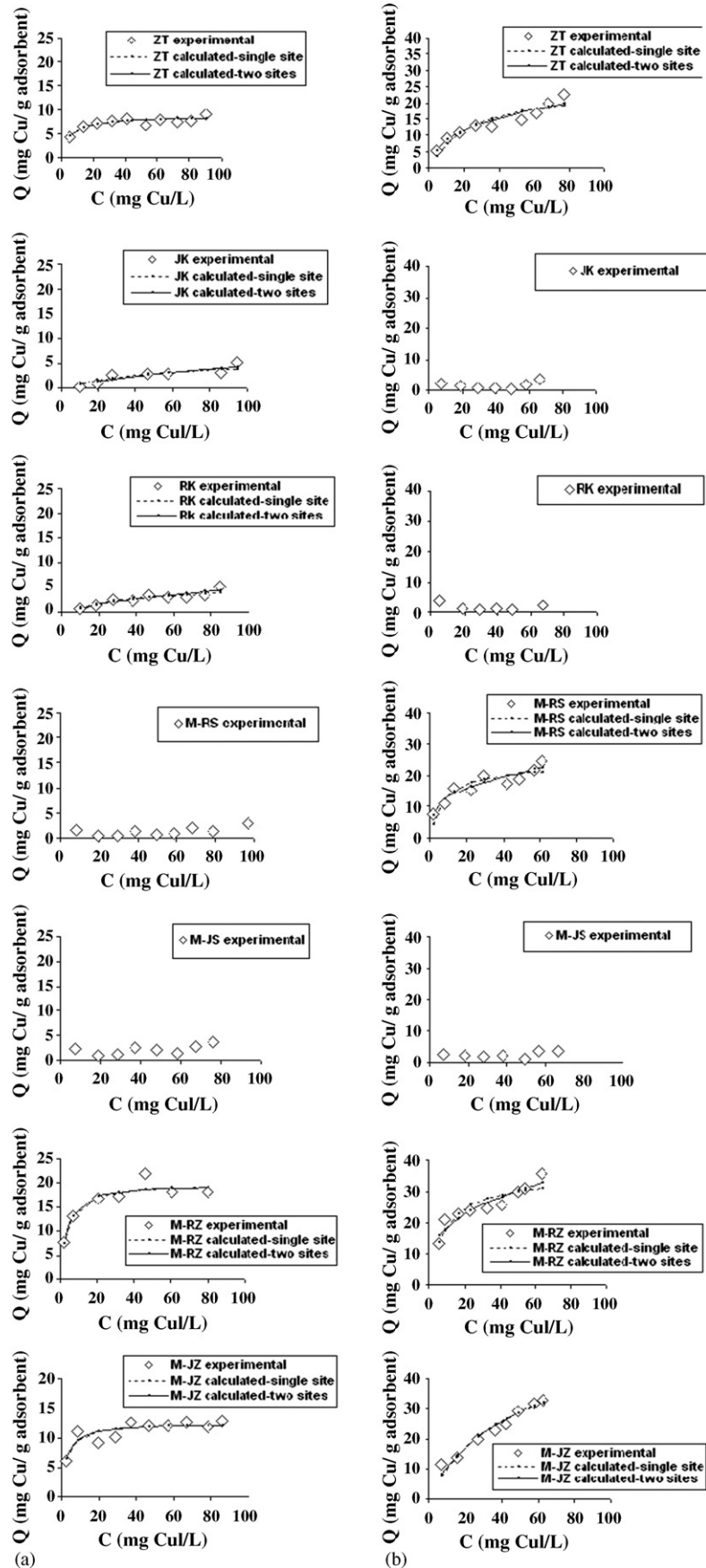
Fig. 8. Adsorption isotherms of Cu(II) onto ZT, JK, RK, M-RS, M-JS, M-RZ, and M-JZ specimens at (a) pH 4 and (b) pH 6.

Table 3
Single and two-site Langmuir adsorption parameters for the adsorption of Cu(II) ion onto ZT, JK, RK, M-RS, M-JS, M-RZ, and M-JZ specimens at pH 4 and 6.

	pH 4.0						pH 6.0					
	Q_m (mg Cu/g adsorbent)		K (L/mg)		Standard error[a]		Q_m (mg Cu/g adsorbent)		K (L/mg)		Standard error[a]	
	Single	Two-site	Single	Two-site	Single	Two-site	Single	Two-site	Single	Two-site	Single	Two-site
ZT	8.46	$Q_{m1}=8.47$ $Q_{m2}=10.0$	0.196	$K_1=0.194$ $K_2=0.007$	0.63	0.64	25.7	$Q_{m1}=9.77$ $Q_{m2}=38.7$	0.039	$K_1=0.202$ $K_2=0.005$	2.17	1.69
JK	5.98	$Q_{m1}=11.0$ $Q_{m2}=10.0$	0.020	$K_1=0.007$ $K_2=0.005$	0.86	0.76		n.d.		n.d.		
RK	5.97	$Q_{m1}=9.76$ $Q_{m2}=9.98$	0.021	$K_1=0.009$ $K_2=0.007$	0.70	0.69		n.d.		n.d.		
M-RS		n.d.		n.d.			23.6	$Q_{m1}=12.3$ $Q_{m2}=37.0$	0.133	$K_1=0.731$ $K_2=0.006$	2.51	1.96
M-JS		n.d.		n.d.				n.d.		n.d.		
M-RZ	20.1	$Q_{m1}=20.1$ $Q_{m2}=10.1$	0.284	$K_1=0.284$ $K_2=0.008$	1.59	1.59	35.2	$Q_{m1}=18.8$ $Q_{m2}=61.0$	0.112	$K_1=0.496$ $K_2=0.005$	2.90	2.20
M-JZ	12.4	$Q_{m1}=12.4$ $Q_{m2}=9.90$	0.413	$K_1=0.413$ $K_2=0.008$	1.11	1.11	52.7	$Q_{m1}=16.3$ $Q_{m2}=70.7$	0.024	$K_1=0.076$ $K_2=0.006$	2.07	1.65

n.d.: No detectable adsorption was observed.

[a] Standard error = $\{\Sigma(y_i - \hat{y}_i)^2/(n-2)\}^{0.5}$, y_i: experimental, $\hat{y}_i$: predicted.

As shown in Table 2, Jordanian zeolitic tuff, Jordanian kaolin, and Ukranian kaolin (RK) have almost the same MB adsorption capacity ($Q_m = \sim0.06$ mmol/g). Geopolymers M-RS and M-JS (based on kaolin and silica sand) have relatively very low adsorption capacity ($Q_m = \sim0.008$ and 0.002 mmol/g, respectively), which indicates that the surface area of kaolin decreased upon geopolymerization. On the other hand, geopolymers M-RZ and M-JZ (based on kaolin and Jordanian zeolite) have the highest adsorption capacity among the specimens studied ($Q_m = 0.07$ and 0.08 mmol/g, respectively). This indicates that the three-dimensional crystalline zeolite transformed into a new form of higher surface area upon geopolymerization and thus enhanced its adsorption capability.

3.3.2. Adsorption of Cu^{2+} cation

The adsorption isotherms of Cu^{2+} ion onto geopolymers (M-RS, M-JS, M-RZ, and M-JZ) were investigated. In order to compare the adsorption properties of the geopolymers with the minerals from which they are made, the adsorption isotherms of Cu^{2+} on Jordanian zeolitic tuff, Jordanian kaolin, and reference kaolin were also investigated. The best fit curves for the adsorption isotherms at pH 4.0 and 6.0 are shown in Fig. 8a and b, respectively. The resultant Langmuir parameters determined from these nonlinear plots are given in Table 3. Nonlinear regression was employed for Cu^{2+} isotherms because of the poor correlation coefficients of the linear curves of Langmuir equations. However, the aim of the adsorption study was a comparison between the adsorption capacities of specimens rather than exact fitting of the isotherms.

As shown in Fig. 8 and Table 3, Jordanian zeolite (ZT) exhibits much higher adsorption towards Cu^{2+} than both kaolin clays JK and RK. This is in agreement with several reported studies in literature [21–25], given in Table 4, for the adsorption of Cu^{2+} on different natural kaolin and zeolite.

Kaolin possesses two kinds of charges. The first is the permanent negative charge which is produced from isomorphic replacement of Si^{4+} with Al^{3+} in the silica tetrahedral sheet or of trivalent metal ions (such as Al^{3+}) by divalent ions such as Fe^{2+} and Mg^{2+} in the alumina octahedral sheet. The second is the pH dependent charge on the edge surfaces resulting from surface hydroxyl groups (aluminol and silanol) [21,22,26]. Many workers reported that the adsorption of Cu(II) and other heavy metal ions takes place at surface hydroxyl groups at the edge of sheets rather than in the layers [23,24]. Thus, upon participation in geopolymerization process, many of kaolin's hydroxyl groups at the edges surface were involved and thus kaolin- and sand-based geopolymers M-RS and M-JS showed lower adsorption capacity (at pH 4) than kaolin itself (Fig. 8 and Table 3).

On the other hand, zeolite has different sites available for adsorption of heavy metal ions. Zeolite has a cage-like structure suitable for ion exchange [27]. However, the adsorption of metal ions onto zeolite particles is a complex process because of their porous structure, inner and outer charged surfaces, mineralogical heterogeneity, crystal edges, and other imperfections on the surface [25,28]. The incorporation of zeolite with kaolin revealed that the produced geopolymers M-RZ and M-JZ show a high adsorption capacity (Fig. 8 and Table 3). The XRD pattern of M-JZ showed that all the phillipsite peaks of zeolitic tuff were disappeared upon geopolymerization (see Fig. 5). Thus, geopolymerization destructs crystals of zeolite leading to more open amorphous structure which leads to an increase of the number of adsorption sites. The adsorption mechanism of Cu^{2+} can be proposed as cation exchange of Na^+ with Cu^{2+}. This is justified since the geopolymerization process was made under highly alkaline solution of NaOH, the dispersion of aluminosilicate particles is due to Na^+ exchange with the hydrogen ions of the broken edges of aluminosilicate, and the Na-ions

Table 4
The reported adsorption capacity (Q_m) of Cu(II) ion on natural kaolin and zeolite.

Specimen	Q_m (mg Cu/g adsorbent)	Conditions	Ref.
Kaolin (Clay Mineral Repository, USA)	3.9	pH 5.7, without inert electrolyte	[17]
Three samples of Kaoline (Kalemaden Ceramic Factory at Omerli, Istanbul)	0.6–1.3	unbuffered solutions, 0.1 NaCl inert electrolyte	[18]
Kaolin (Usak, Turkey)	10.8	unbuffered solutions, without inert electrolyte	[19]
Kaolin (Ajax Chemicals, Sydney)	1.9	pH 6.0, 0.01 M NaClO₄ inert electrolyte	[20]
Zeolite (Croatian deposit, Donje Jesenje)	25.4	pH 5.5, without inert electrolyte	[21]

play an important role in electrical neutralization of the resultant geopolymeric matrix.

As shown in Fig. 8 and Table 3, the adsorption capacity of the specimens towards Cu(II) metal ion increases significantly with increase of pH, due to the decrease of competition between H$^+$ and Cu^{2+}.

In order to improve the fitting of the adsorption isotherms of Cu^{2+}, the two-site Langmuir model (Eq. (5)) was also employed, where K_1 and K_2 are the affinity constants (L/mmol Cu^{2+}) using two-site Langmuir equation. Q_{m1} and Q_{m2} are the monolayer adsorption capacities (mmol Cu^{2+}/g adsorbent) using two-site Langmuir equation.

$$Q = Q_{m1}K_1C/(1 + K_1C) + Q_{m2}K_2C/(1 + K_2C) \tag{5}$$

The results of the best fitting parameters obtained from nonlinear regression are given in Fig. 8 and Table 3. The two-site Langmuir model showed lower standard errors than the single model for the Cu^{2+} isotherms obtained at pH 6.0. This indicates that there is some heterogeneity on the surface. However, at pH 4.0, both models gave almost the same standard errors.

4. Conclusions

Using natural Jordanian zeolitic tuff filler instead of silica sand filler showed that the end geopolymer product provides lower density and higher water absorption. This can be attributed to the porous nature of zeolitic tuff. The higher mechanical strength of zeolite-based geopolymer is associated with the high surface of zeolite compared to silica sand filler.

Geopolymers based on kaolin and silica sand revealed very low adsorption capacities towards methylene blue and Cu(II) ions. On the other hand, the geopolymers based on kaolin and Jordanian zeolitic tuff showed the highest adsorption capacity among the specimens studied.

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