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Degree of reactivity of two kaolinitic minerals in alkali solution using zeolitic tuff or silica sand filler

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Abstract

Four geopolymers were synthesized by NaOH-activation of a mixture of kaolinite (Jordanian kaolinite or Ukrainian kaolinite) and a filler (zeolitic tuff or silica sand). X-ray powder diffraction (XRD), Fourier-transform infrared spectrometry (FTIR), and solid-state magic angle spinning nuclear magnetic resonance (MAS-NMR) were employed to monitor the extent of reaction and to characterize the phases in the geopolymer. Remaining kaolinite in all produced geopolymer specimens unambiguously indicated an incomplete reaction. The ^{29}Si MAS-NMR spectra of the geopolymers revealed the presence of tetrahedral-SiO$_4$ whereas the ^{27}Al MAS-NMR spectra revealed the presence of both tetrahedral-AlO$_4$ and octahedral-AlO$_6$. The XRD patterns of geopolymers showed the formation of a new feldspar mineral. Replacing silica sand filler by zeolitic tuff enhanced markedly the specific surface area of the corresponding geopolymers.

Keywords: Geopolymers; Inorganic polymers; Kaolinite; Zeolitic tuff

1. Introduction

Geopolymers are a class of mostly X-ray amorphous aluminosilicate materials, generally synthesized at ambient or slightly elevated temperature by reaction of a solid aluminosilicate powder with a concentrated alkali metal silicate or hydroxide solution [1–6]. Due to the fact that aluminosilicates are the compounds most abundant in the earth's crust, there exist a large number of raw material sources rich in alumina and silicon with the potential for producing geopolymers. Among the materials with which have been used for procuring geopolymers predominates flying ash [7,8] and include calcined clays [9], tailings [10], kaolin [11,12], and puzzolans [13]. These works have shown that geopolymerization with calcined materials promote quick dissolution and gelation and at the same time develop high mechanical strength in short time [14]. In this work kaolinite and zeolitic tuff will be used without a thermal treatment. In doing so less energy is needed for the production of this material, helping in reducing the amount of CO$_2$ emitted. A drawback is the lower reactivity and hence lower reaction rate at room temperature. As such, pure NaOH or KOH solutions have to be used to alkali activate the kaolinite and heating to about 60–80 °C is necessary to reduce the curing time [15].

The effects of high pH on the stability of clay minerals have been extensively studied on clay rocks [16–19]. Some of the earlier investigations focused on the stability of the kaolinites under highly alkaline conditions [20]. Numerous investigations have been carried out to understand the interaction between high pH alkaline solutions and natural clay barriers [21–24].

Abbreviations: JK, Jordanian kaolinite; RK, reference kaolinite; Z, Jordanian zeolitic tuff; S, Jordanian silica sand; RKS, geopolymer prepared from reference kaolinite and silica sand; RKZ, geopolymer prepared from reference kaolinite and zeolitic tuff; JKS, geopolymer prepared from Jordanian kaolinite and silica sand; JKZ, geopolymer prepared from Jordanian kaolinite and zeolitic tuff; MB, methylene blue; *C*, equilibrium concentration of MB (mmol/L); *Q*, amount of MB adsorbed (mmol/g adsorbent); Q_m, monolayer adsorption capacity of MB (mmol/g adsorbent); *K*, affinity constant of MB (L/mmol MB); *SSA*, specific surface area (m^2/g); *CSA*, cross sectional area occupied by one molecule (Å^2); *N*, Avogadro's number (mol^{-1}).

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Geopolymers can be considered amorphous equivalents of certain synthetic zeolites. The polymerization reaction route can be classified as an inorganic polycondensation reaction and can be compared with zeolite formation. Most zeolite syntheses are carried out under basic conditions by using OH^- as a mineralizing agent. According to Van Jaarsveld [25] an alkaline metal is necessary for silicon and aluminum dissolution to occur. This is also true for catalyzing the condensation reaction [26]. Geopolymers are formed by individual co-polymerization of the aluminum and silicate species, which in turn are formed from silicon and aluminum dissolution contained in materials with high pH in the presence of soluble silicates [27].

The exact chemical mechanisms responsible for the dissolution and gel formation reactions in geopolymeric systems are still unknown. However, it is apparent that in many cases where materials such as fly ash and clays are used, the dissolution of the starting materials is not completed before the final hardened structure is formed [28].

The alkali activation of Jordanian kaolinite has already been described [29]. The maximum compression strength of kaolinite/NaOH samples was obtained for a mixture of 100kaolinite/16NaOH/22H_2O (wt%). The amount of water used is close to the plasticity limit of the kaolinite. The alkali activation of kaolinite with NaOH leads to the formation of a mainly amorphous matrix with some sodium zeolite phases and feldspathoids. At the composition used, not all of the kaolinite is reacted, so remaining flakes of unreacted kaolinite can be retrieved after the hardening.

A selection of multiple source materials may also be used to manipulate the geopolymeric reaction by exploiting their respective structural and surface properties and elemental compositions [30]. Using a low cost mineral, namely zeolitic tuff, in combination with kaolinite has been reported by our group [31–33]. In an attempt to shed some light on the reaction mechanism of the geopolymer formation under the employed conditions, in this work the X-ray diffraction (XRD), Fourier-transform infrared spectrometry (FTIR), solid-state magic angle spinning nuclear magnetic resonance (^{27}Al and ^{29}Si MAS-NMR), and the surface area for the synthesized geopolymers and their raw materials were investigated.

2. Materials and methods

2.1. Materials

Jordanian Kaolinite (*JK*) with a purity of 60 wt%, and about 40 wt% of α-quartz [31] was obtained from El-Hiswa deposit, which is located in the south of Jordan about 45 km to the east of Al-Quweira town. Preparation of the Jordanian kaolinite samples involved crushing (using Jaw crusher RETCH-BB1A) of an oven dried clay (at 105 °C) to a grain size less than 425 μm. *Reference Kaolinite* (*RK*) from Ukraine (purchased from Jordan International Modern Trade Company) with a purity of 95 wt% was used as a reference mineral. *Jordanian Zeolitic Tuff* (*Z*) was obtained from North–East Jordan deposits (Aritayn area) located around 50 km to the east from Amman, which belongs to the phillipsite type of zeolites ($(Ca,Na_2,K_2)_3Al_6Si_{10}O_{32}\cdot 12H_2O$) [34–36]. *Jordanian Silica Sand* (*S*) of high quality was processed by washing with distilled water and sieved at 100 micron and 400 micron to satisfy the needs of using it as a filler material [37]. *Sodium hydroxide* pellets (96 wt%) were purchased from GCC (Gainland Chemical Company, UK).

2.2. Geopolymers synthesis

Four geopolymers (RKS, RKZ, JKS, and JKZ) with different compositions were prepared from kaolinite (Jordanian kaolinite JK, reference kaolinite RK), filler (zeolitic tuff Z, silica sand S), and sodium hydroxide solution similar to our previous work [31], Table 1. The weighed filler (S or Z) and kaolinite (JK or RK) were mixed first and then sodium hydroxide solution was added. After mixing, the paste was molded in a stainless steel cylinder at a pressure of 15 MPa and cured at 80 °C for 24 h. The specimens were aged for around one month at room temperature before subjected to different characterization techniques.

2.3. Characterization

2.3.1. X-ray diffraction (XRD)

The X-ray diffraction (XRD) measurements were carried out with an X-ray diffractometer-6000, Shimadzu, on powdered samples of geopolymers RKS, RKZ, JKS, and JKZ and their starting materials, i.e. zeolitic tuff (Z), kaolinite (JK and RK) 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.

2.3.2. Fourier-transform infrared spectrometry (FTIR)

The FTIR spectra for geopolymers RKS, RKZ, JKS, and JKZ as well as zeolitic tuff (Z), kaolinite (JK, RK), and silica sand (S) were collected using a Nexus 870 FTIR spectrophotometer in transmittance mode from 400 to 4000 cm^{-1}

Table 1
Composition (wt%) of geopolymers used in this work [31].

Geopolymer	Jordanian kaolinite (JK)	Reference kaolinite (RK)	Zeolitic tuff (Z)	Silica sand (S)	NaOH	Water
JKS	29.8	–	–	59.5	4.2	6.5
JKZ	41.7	–	41.7	–	5.8	10.8
RKS	–	28.1	–	56.2	5.1	10.7
RKZ	–	48.3	24.2	–	8.7	18.8

using standard KBr technique (1.0 mg sample with 100 mg KBr). All spectra were obtained with a sensitivity of 4 cm^{-1} and 64 scans per spectrum taken.

2.3.3. MAS-NMR measurements

The ^{29}Si and ^{27}Al magic angle spinning nuclear magnetic resonance spectra were obtained on a Bruker AC250 spectrometer operating at 49.70 MHz and 65.18 MHz for the ^{29}Si and ^{27}Al resonance frequencies, respectively. The spectrometer was interfaced with an Aspect-3000 computer and equipped with a MAS broad-band probe. For solid state NMR rotors of 4 mm diameter and a spinning rate of 5 kHz were used. The ^{29}Si spectra were obtained over a spectral width of 9.9 kHz (acquisition time: 0.2 s), with 1000 scans and a relaxation delay of 5 s. The ^{27}Al spectra were acquired over a spectral width of 167 kHz (acquisition time: 0.04 s), with 400 scans and a relaxation delay of 0.5 s. More details are described elsewhere [38].

2.3.4. Surface area estimation

The specific surface areas for the produced geopolymers (RKS, RKZ, JKS, JKZ) and their starting materials (JK, RK, and Z) were determined by the method of methylene blue (MB) [31]. The adsorption capacity of MB was obtained from batch adsorption experiments. A series of 50 mL bottles were employed. Each bottle was filled with 50 mL of MB (Acros organics, pure) solution of varying concentrations and 0.02 g of adsorbent. The stoppered bottles were shaken (water bath shaker, Clifton-11268) at 25 °C and 320 rpm for 48 h. The MB concentrations were determined spectrophotometrically using UV-Vis spectrophotometer (Spectroscan-80DV) at λ = 665 nm.

3. Results and discussion

3.1. X-ray diffraction analyses

The XRD patterns of the synthesized geopolymers (JKS, JKZ, RKS, RKZ), zeolitic tuff (Z), Jordanian kaolinite (JK), and reference kaolinite (RK) are shown in Fig. 1.

The Jordanian kaolinite (JK) spectrum shows the presence of kaolinite ($Al_2Si_2O_5(OH)_4$) accompanied with α-quartz. The difference between the reference kaolinite (RK) (purity = 95%) and the local Jordanian kaolinite (purity = 60%) is that the latter contains α-quartz as an impurity, Fig. 1. This is reflected in the presence of α-quartz peaks in the corresponding geopolymer JKZ spectrum, where Jordanian kaolinite was used as a clay source.

Geopolymers RKS and JKS showed nearly identical spectra. The new feldspar mineral plagioclase ($NaAlSi_3O_8$) was observed in these two specimens as a result of reaction.

The XRD spectrum of local zeolitic tuff (Z) showed the characteristic peaks of phillipsite ($(Ca,Na_2,K_2)_3Al_6Si_{10}O_{32}\cdot 12H_2O$). Upon reaction, phillipsite ($(Ca,Na_2,K_2)_3Al_6Si_{10}O_{32}\cdot 12H_2O$) peaks disappeared as shown in the XRD patterns of zeolite-containing geopolymers, i.e. JKZ and RKZ, which is in agreement with MAS-NMR results presented in Section 3.3. This can be attributed to transformation of phillipsite ($(Ca,Na_2,K_2)_3Al_6Si_{10}O_{32}\cdot 12H_2O$) due to alkali treatment with NaOH. The RKZ specimen (geopolymer from reference kaolinite and zeolitic tuff) shows more intense peaks of the new feldspar mineral plagioclase ($NaAlSi_3O_8$). Thus, it is clear that the use of reference kaolinite (purity of 95%) leads to a higher amount of crystalline reaction products compared to local Jordanian kaolinite (purity of 60%).

However, the presence of kaolinite ($Al_2Si_2O_5(OH)_4$) peaks in all geopolymers' spectra is a clear indication of incomplete reaction.

3.2. Fourier-transform infrared spectrometry (FTIR)

A part of the IR spectra (3800–3600 cm^{-1}) of the prepared geopolymers (JKS, JKZ, RKS, RKZ) and their starting materials, i.e. reference kaolinite (RK), Jordanian kaolinite (JK), zeolitic tuff (Z), and silica sand (S) is shown in Fig. 2a. The characteristic bands of the hydroxyl stretch of kaolinite appear at 3696, 3652, and 3620 cm^{-1} are observed in the

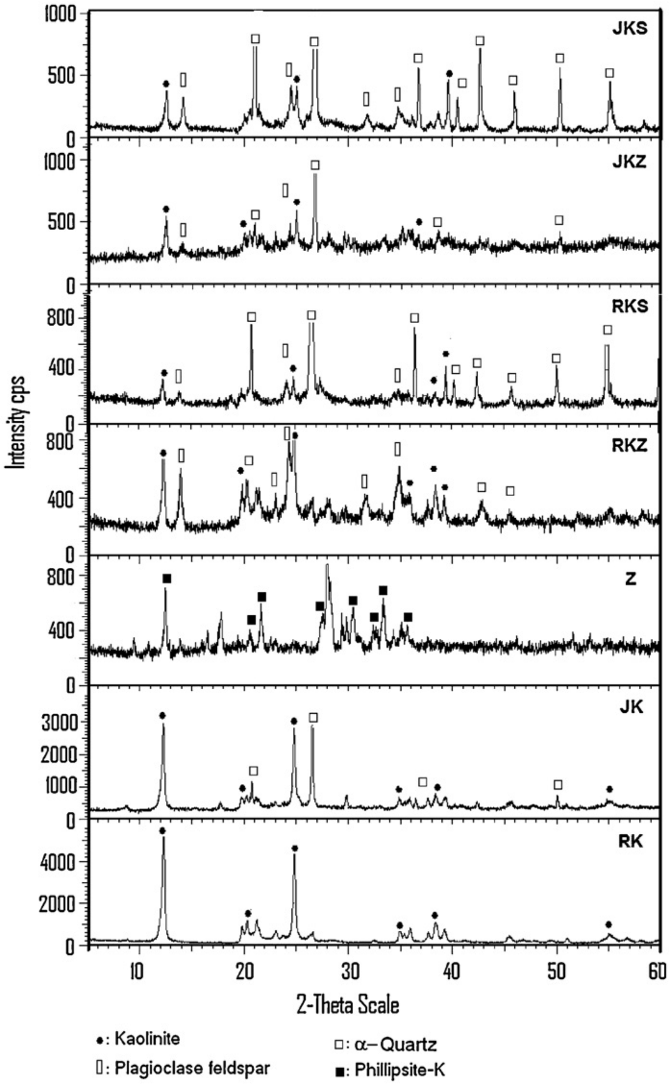

Fig. 1. X-ray diffraction spectra of geopolymers (JKS, JKZ, RKS, RKZ), zeolitic tuff (Z), Jordanian kaolinite (JK), and reference kaolinite (RK).

spectra of all produced geopolymers. The presence of the kaolinite OH-bands is a clear indication of incomplete reaction. Investigation of partial geopolymerization using infrared spectrometry was reported in the literature [39]. Fig. 2b shows nonsymmetric bands (antisymmetric T–O vibration in TO_4 unit) at 1010 and 1030 cm^{-1} and shoulders ascribed as a low-frequency band at 915 cm^{-1} and a high-frequency band at 1100 cm^{-1}.

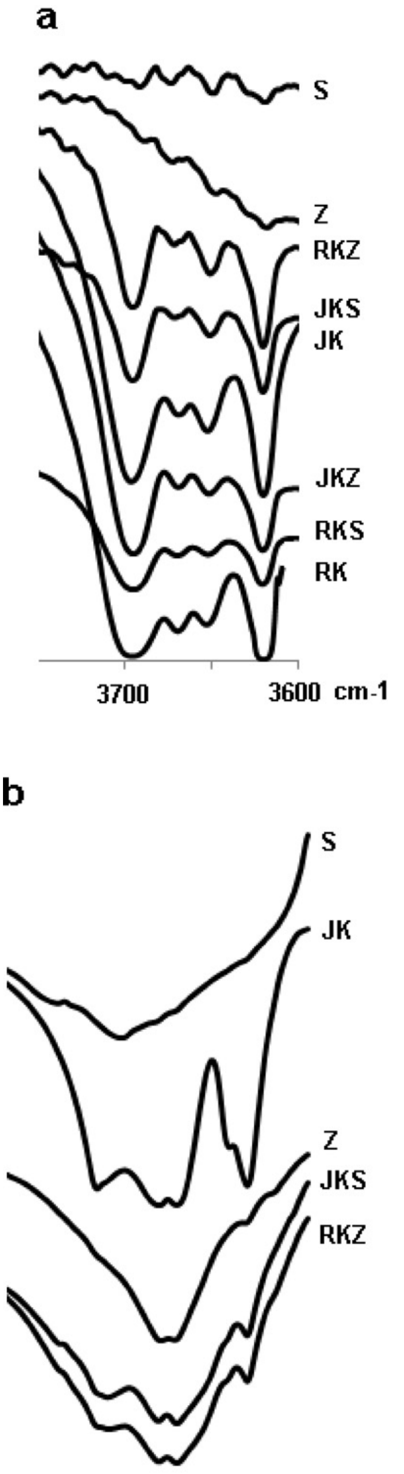

Fig. 2. Parts of the IR-spectra of the prepared geopolymers and their starting materials: (a) (3800–3600 cm^{-1}), (b) (1200–800 cm^{-1}).

3.3. ^{27}Al and ^{29}Si MAS-NMR measurements

The ^{29}Si MAS-NMR and ^{27}Al MAS-NMR measured spectra for geopolymers RKS, RKZ, JKS, and JKZ as well as zeolitic tuff (Z) and Jordanian kaolinite (JK) are shown in Figs. 3 and 4, respectively. The main peak positions in these spectra are tabulated in Table 2.

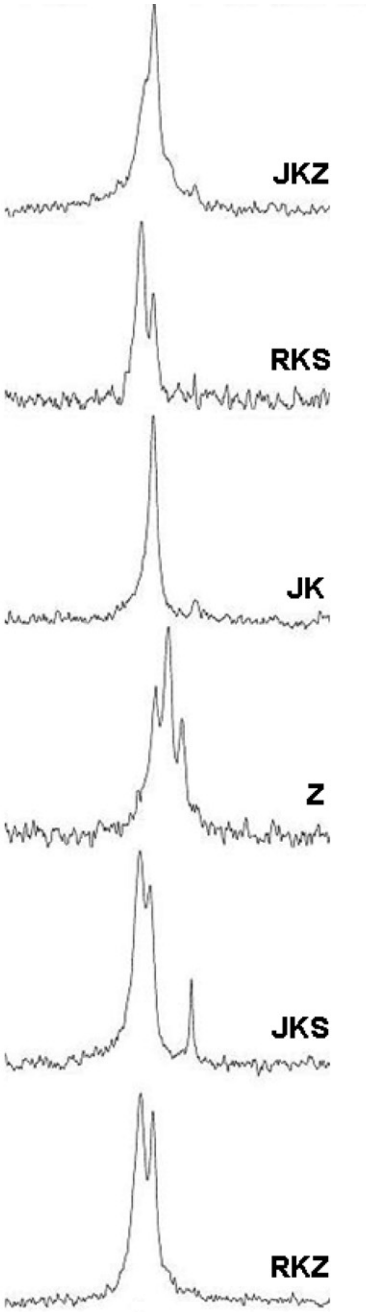

Fig. 3. The ^{29}Si MAS-NMR spectra of geopolymers (JKZ, RKS, JKS, RKZ), kaolinite (JK), and zeolitic tuff (Z).

Table 2
Main ^{29}Si and ^{27}Al MAS-NMR resonances for JK, Z, RKS, RKZ, JKS, and JKZ samples.

	JK	Z	RKS	RKZ	JKS	JKZ	Assignment
δ_{Al}	–	59.1	59.4	60.3	60.6	60.1	AlO_4-tetrahedral
	−5.5	–	−6.1	−5.7	−5.7	−5.7	AlO_6-octahedral
δ_{Si}	–	–	−87.1	−86.6	−87.5	−87.0	Si (different coord. no.)
	−91.6	−93.1	−91.5	−91.4	−91.5	−91.3	SiO_4-tetrahedral
	–	−98.2		–	–	–	Si (coord. with Al or OH)
		−103.4		–	–	–	Si (coord. with Al or OH) SiQ^4(1 Al)[a]

[a] Ref. [40].

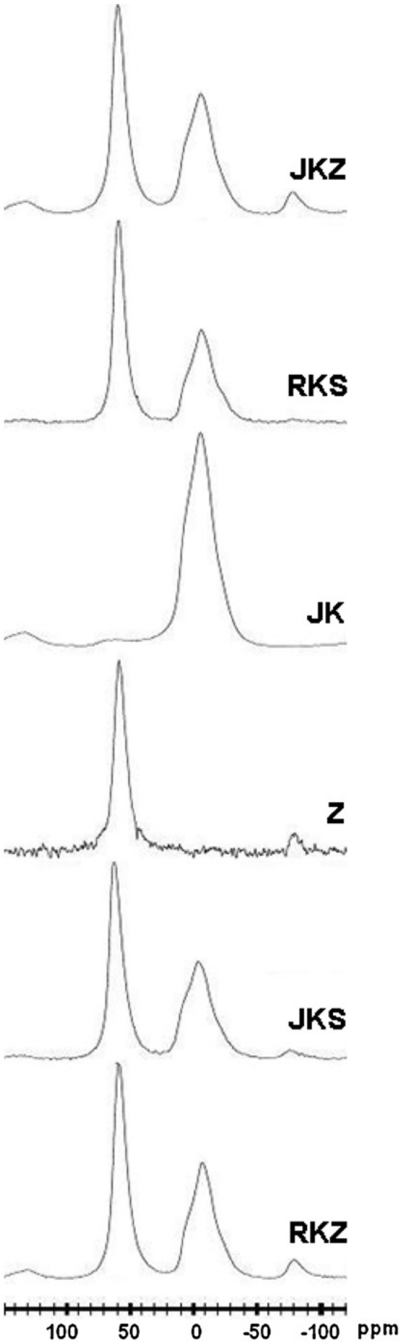

Fig. 4. The ^{27}Al MAS-NMR spectra of geopolymers (JKZ, RKS, JKS, RKZ), kaolinite (JK), and zeolitic tuff (Z).

The ^{29}Si MAS-NMR spectra showed that kaolinite (JK) has a single sharp ^{29}Si NMR peak centered at −91.6 ppm corresponding to Q^3 as expected. The spectra of the four synthesized geopolymers (RKS, RKZ, JKS, JKZ) retained this peak at (−91.5 to −91.3) ppm. New resonances ranging from −87.5 to −86.6 ppm, which correspond to different Si surroundings were observed. This downfield shift from the kaolinite signal is consistent with the occurrence of Al into the coordination environment of Si [41].

The zeolitic tuff resonances observed in the ^{29}Si MAS-NMR spectrum at −98.2 and −103.4 ppm, which assigned to different environments of SiO_4-tetrahedron in aluminosilicate structure due to different amount of Al or OH linked to Si, disappeared upon reaction.

The ^{27}Al MAS-NMR for kaolinite (JK) showed a peak centered at −5.5 ppm indicating that Al in kaolinite is in the 6-coordinate state (Al^{VI}). Zeolitic tuff (Z) shows a main peak at 59.1 ppm assigned to tetrahedral Al. The spectra of the four synthesized geopolymers (RKS, RKZ, JKS, JKZ) all exhibit two peaks, one at ~60 ppm and the other at ~−6 ppm, corresponding to tetrahedral and to octahedral Al, respectively. Unambiguously, a part of the original octahedral Al (at δ_{Al} −5.5 ppm) has been converted to tetrahedral coordination (at δ_{Al} 60 ppm).

The presence of octahedral Al, again points to unreacted kaolinite, reveal the incomplete polymerization. The intensities of such peaks that appeared at $\delta_{Al} \sim -6$ ppm reflect the degree of reaction that occurred. An estimation of a degree of geopolymerization using ^{27}Al-MAS NMR technique was reported in the literature [39]. Consequently, the reactivity decreases in the order (relative intensities $\delta_{AlO_6} : \delta_{AlO_4}$) JKZ (0.57) > RKZ (0.53) > JKS (0.50) > RKS (0.45). Despite the close ratios, the trend may show that zeolitic tuff filler (Z) is more effective than silica sand (S) for geopolymerization process.

As shown in Table 2, both the ^{27}Al and ^{29}Si MAS-NMR resonances clearly indicate that the four synthesized geopolymers specimens have a similar tetrahedral Al and Si environment, which is in agreement with literature [41,42].

3.4. Surface area estimation

The adsorption isotherms of methylene blue (MB) onto synthesized geopolymers (RKS, JKS, RKZ, JKZ), zeolitic tuff

Table 3
Langmuir adsorption parameters for the adsorption of methylene blue (MB) onto zeolitic tuff (Z), Jordanian kaolinite (JK), reference kaolinite (RK), and geopolymers (RKS, JKS, RKZ, JKZ).

Specimen	Q_m (mmol/g)	Specific surface area (m^2/g)
Z	0.0612	47.9
JK	0.0662	51.8
RK	0.0638	50.0
RKS	0.0077	6.0
JKS	0.0024	1.9
RKZ	0.0707	55.4
JKZ	0.0806	63.1

(Z), Jordanian kaolinite (JK), and reference kaolinite (RK) were determined. The linearized form of the Langmuir equation ($C/Q = C/Q_m + 1/Q_m K$) [43] was employed to obtain the Langmuir parameter Q_m. 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 values of Q_m calculated from the linearized plots (C/Q vs C) are given in Table 3.

Depending on Q_m values, the specific surface area (*SSA*) of geopolymers (RKS, JKS, RKZ, JKZ), zeolitic tuff (Z), kaolinite (JK), and reference kaolinite (RK) were calculated from Eq. (1) [44,45] and tabulated in Table 3. Where *CSA* is the cross sectional area occupied by the MB molecule (130 Å^2) and N_A is Avogadro's number (mol^{-1}).

$$SSA = Q_m \cdot CSA \cdot N_A \tag{1}$$

As shown in Table 3, the specific surface area of zeolitic tuff and kaolinite are nearly the same (48–52 m^2/g). The specific surface areas of the geopolymers JKZ and RKZ, which showed high extent of geoploymerization (Section 3.3), were slightly increased to 63 and 55 m^2/g, respectively. On the other hand, the specific surface area of geopolymers RKS and JKS (based on kaolinite and silica sand) was markedly decreased to 6 and 2 m^2/g, respectively. Similar to the surface area of some reported geopolymers synthesized from metakaolinite [39], these extraordinarily small surfaces may be explained by the presence of the silica sand which has a small specific surface and which fills the mesopores of the geopolymers.

4. Conclusions

Semi crystalline geopolymers can be formed from the reaction of kaolinite with NaOH solution. The XRD patterns of geopolymers showed clearly the presence of a feldspar mineral, plagioclase. The disappearance of phillipsite in synthesized geopolymers is a consequence of a transformation of zeolite upon reaction. The AlO_6-octahedral peak may be considered as a characteristic peak for the extent of reaction process occurred. The specific surface areas of geopolymers formed from kaolinite/zeolite were found higher than those formed from kaolinite/silica sand.

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