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Examining the Features of NaCl Activated Kaolinite Nano-layers for Use in Excipients

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Abstract

Successful application of 1:1 layered phyllosilicates as excipients of drugs and agrochemicals depends on the efficiency and effectiveness of activation reactions carried out prior to their usage. Reluctance of kaolinite to direct reactions involving interlayer spaces created a challenge which requires a sustainable search for optimum activation agents. This study investigated the features of cyclone based wet beneficiated kaolinite with kaolinite sheets activated using solid dispersion of NaCl. Starting materials and the resulting activated counterparts were characterized for their chemistry, functionalities (as per mineral phases present), and variation of crystal sizes upon each treatment cycle along with lattice contraction and expansion in the interlayer spaces and orientation of layers (as per their morphological changes) as well as molecular vibration. It was observed that, upon successful activation with NaCl, there was a significant change in the orientation of kaolinite sheets from euhedral pseudohexagonal platelets into vermiform whose pattern offer a maximum orientation for reactions involving interlayer spaces. The formation of vermiform which may be due to packing of nano-layers was noted to be associated with the contraction of interlayer spaces of about 0.018 nm from $2\theta = 12.543^{\circ}$ to 12.552° as revealed in the x-ray diffraction trials. Therefore, the ability of NaCl activation reactions to orient kaolinite layers into well-ordered vermiform pattern makes NaCl a suitable activation agent for use when kaolinite is to be used for design of excipients for drugs and agrochemicals.

Keywords: Excipients; Kaolinite; Intercalation; Drug delivery systems; Controlled release fertilizers; Controlled Release systems; Vermiform; Kaolinite activation; Nano layers

Introduction

Kaolinite is clay of kaolin group of minerals; it is among the layered phyllosilicates meaning that it is organized into sheets whose interaction forms a 1:1 layered configuration [1-20]. As 1:1 phyllosilicate clay, it is comprised of crystal lattice units formed by one alumina octahedral sheet sandwiched with one tetrahedral sheet of silica molecules [21,22]. The pattern in which tetrahedral [T] and octahedral [O] sheets of kaolinite are arranged provides a room for intercalation reactions to be carried out. Nevertheless, kaolinite O-T sheets are arranged in a 1:1 pattern as compared to other kind of layered phyllosilicates such as smectites whose layer arrangement consist of T-O-T repetition units giving a 2:1 layered pattern [23,24].

Owing to that, the interlayer spaces between O-T sheets of kaolinite are considered less reactive towards most reactions involving the interlayer spaces [25-29]. As stated elsewhere, the difficulty of kaolinite in undergoing intercalation reactions is due to its asymmetric configuration which is associated with little substitution in the structural lattices [25-29]. In other words, having an asymmetric configuration, kaolinite can form hydrogen bonds between consecutive layers thereby forming a fixed structure with no internal surfaces and little isomorphous substitution thereby providing a larger cohesive energy which in turn must be overcome in order for any reaction involving interlayer spaces to proceed. This reluctance for undergoing intercalation reactions distinguishes kaolinite from many 2:1 layered minerals in undergoing intercalation reaction.

Essentially, studies have demonstrated the need for activating kaolinite prior to reactions or any chemical transformation on the layered sheets [1,6,10,11,14,16,30,31]. In view of that, this study was set to investigate the effects of NaCl on the effectiveness of kaolinite intercalation reactions focusing on the comparative analysis of wet beneficiated as well as NaCl activated kaolinite mineral. The hypothesis is that, it is possible to arrive at suitably activated kaolinite nano-layers for use as excipient of drugs and agrochemicals.

Materials and Methods

Materials

Kaolinite was collected at Pugu hills in the Coast region Kisarawe Tanzania by using quartering sampling technique described by Sempeho et al. [23]. Sodium chloride (Extra pure, ≥ 99.0%) was supplied by Samchun pure chemicals Co. Ltd, Gyonggi-do, Korea, Silver chloride (ACS reagent, 99.0%) was supplied by Sigma Aldrich.

Methods

Raw Pugu kaolinite labeled C1 was used as starting material. Cyclone based size separation technique was employed by using classifier. By virtue of variations in setting velocities associated with particle size as per Stockes's law, it was possible to separate kaolinite from coarse quartz, feldspar, mica and other impurities. The procedure involved mixing distilled water with the starting material at a ratio of 1 part of clay to 10 parts of treated water in a high velocity cyclone. Thereafter, suspended mist was carefully decanted and left to settle for three weeks. The fine cake was dried in a vacuum oven at 105°C to dryness. The powdered sample was labeled C2. Subsequently, about 10 g of C2 was dispersed in 100 mL of 0.1M NaCl and treated ultrasonically at 50°C for 6 h and then magnetically stirred at 90°C for 24 h. Suspension obtained was filtered under vacuum and washed with excess water and tested for chloride with $AgNO_3$. The washed sample was dried in a vacuum oven at 60°C and labeled C3.

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Characterization

The FTIR-ATR analyses were carried out using a Bruker Optic GmbH (alpha model, Laser class 1) Spectrometer with attenuated total reflectance [ATR] at the University of Dar es Salaam. XRD measurement were performed on Rigaku Coorperation, D/MAX-2500/PC X-ray Diffractometer equipped with a back monochromator operating at 40 kV and 100 mA at the scanning range of 5° – 80° with a step size of 0.1° and a time/step of 1 s using copper cathode [Cu Kα1] as the X-ray source [λ] 1.54056 Å) at Hanyang University. The X-ray diffraction patterns were indexed by using mathematical method by first determining the unit cell parameter from the peak position and then miller indices; the estimations of the crystallite size was performed by using X-ray diffraction pattern basing on Scherrer equation. SEM images of the samples were taken with Field Emission Scanning Electron Microscopy (SEM-Hitachi-s-4800, Japan) at Hanyang University; the accelerated voltage was 15 kV. Analysis oxide composition was performed using X-ray Fluorescence (Siemens SRS 3000 XRF, Rhodium anode, 8 analyzer crystals with beryllium window 125 μm) using Semi Quantitative XRF analysis technique at AMGC in Dar es Salaam, Tanzania.

Results and Discussion

Principally, raw kaolinite was sampled as described before and purified by using wet beneficiation technique which involves the application of Stokes' law due to settling of particles under cyclone [7,22] with intention of removing ferrous impurities contained in the sample (Figure 1). In view of our recent publication [23], the building blocks for kaolins include Silicon, Aluminium, Oxygen and Hydrogen. The chemistry of the kaolin used in this study (Table 1) revealed that almost more than 90% of the oxides present in the sample contained the four elements; this is necessary in this study because the presence of these elements speaks a lot about the nature of the interlayer spaces available for intercalations which in turn is critical in the preparation of excipient molecules or rather nano-devices for use in the controlled release systems of drugs [DDSs] and agrochemicals [CRFSs].

Figure 1: Raw kaolin containing Fe^{3+} stains.

Oxide composition	Sample	
SiO_2	63.64	54.99
Al_2O_3	31.43	40.20
Na_2O	0.43	0.09
MgO	0.16	0.13
SO_3	0.25	0.08
Cl	0.76	0.04
K_2O	1.39	0.96
CaO	0.06	0.04
TiO_2	0.80	1.02
Cr_2O_3	0.03	0.04
MnO	0.01	0.01
Fe_2O_3	1.01	2.00
LOI	0.03	0.40

Table 1: Chemistry of the samples.

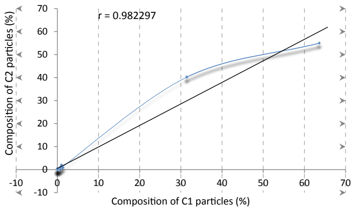

Figure 2: Correlation between C1 and C2 particles.

Phases	Sample	
	C1	C2
Major phases	$Al_2Si_2O_5(OH)_4$	$Al_2Si_2O_5(OH)_4$
Minor phases	SiO_2	$Mg_5Al(Si,Al)_4O_{10}(OH)_8$
	$KAlSi_3O_8$	$KAl_2(Si_3AlO_{10})(OH)_2$

Table 2: Determination of mineral phases presents the samples.

The robustness of the relationship between C1 and C2 particles (Figure 2) indicate a positive relationship meaning that the variables move in the same direction and magnitude. Besides, despite a strong linear relationship between the two, the percentage of chemical composition of SiO_2 and Al_2O_3 behaved like outliers as clearly seen in Figure 2. Nevertheless, these are not outliers; instead they indicate a strong relationship between alumina and silica species necessary in the kaolinite reactions involving interlayer spaces of the functional nano layers. Typically, these results showed that, wet beneficiation can modify the chemistry of the kaolins particularly in the alteration of alumina and silica contents where in the raw kaolin their amounts were 31.34% and 63.64% whereas in beneficiated kaolin were 40.20% and 54.99% respectively and this could account for the observed outliers.

The phases present were determined and found to be kaolinite $[Al_2Si_2O_5[OH]_4]$ as a major phase in both raw and purified kaolin samples. The minor phases were Quartz $[SiO_{2]}$, Microcline $[KAlSi_3O_8]$, Clinochlore $[Mg_5Al[Si,Al]_4O_{10}[OH]_8]$, and Illite $[KAl_2[Si_3AlO_{10}][OH]_2]$ (Table 2). The fact that this study capitalizes on the application of kaolinite, the findings were found to be viable since kaolinite was in fact the major phases present before and after beneficiation trials.

As stated before, kaolinite [which is the major phase in both extremes] is reluctant to most direct reactions [29]. Like any other layered phyllosilicate, it possesses interlayer spaces made of silica tetrahedral and alumina octahedral forming sheets whose interlayer spaces may be activated for the purpose of carrying out a number of ion substitution reactions. The presence of functional nano-sheets makes it possible to use kaolinite as a carrier molecule in the engineering design of controlled release systems of drugs [DDSs] and agrochemicals [CRFs]. The chemistry and the phases present so far described are such that, the starting material used in this study is suitable for use in conducting intercalation reactions which are critical for preparation of excipients that involves interlayer spaces.

Owing to the fact that kaolinite 1:1 layered pattern makes it difficult to intercalate foreign molecules by a way of replacing interstitial water present within the layers, activation of the interlayer spaces was needed and so, NaCl was used as an activation agent in order to obtain kaolinite [C3] whose nano-layers have been activated ready for use as a carrier. The characteristics of the NaCl activated kaolinite and its wet beneficiated counterpart [C2] was compared and the results are hereto provided.

Comparative analysis of x-ray diffraction patterns

Both C2 and C3 were subjected though x-ray diffraction experiments; data were indexed and summarized (Table 3). The findings revealed that, the crystal structure was FCC crystal Bravais lattices as reflected in the Miller indices (Table 3). This showed that neither wet beneficiation nor NaCl activation affected the natural order of FCC lattices of the starting raw materials. In other words, the experiments geared at utilizing 1:1 layered phyllosilicates such as kaolinite as excipients have this confidence level pertaining stability of crystal lattices during wet beneficiation as well as NaCl activation. That is to say, if an activation agent used can either change or disrupt the natural 1:1 pattern or alter the structure of crystal lattices, such activator may be considered as unfit for use if one needs to mobilize 1:1 layered phyllosilicate into excipients.

Parameters	Sample	
2θ	12.0607	12.3597
$Sin^2θ$	0.011036	0.011588
FWHM	0.2982	0.3169
$h^2 + k^2 + l^2$	3	3
hkl	111	111

Table 3: Analysis of X-ray diffraction data.

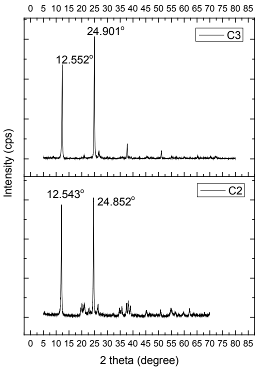

Figure 3: X-ray diffraction peak for C2 and C3.

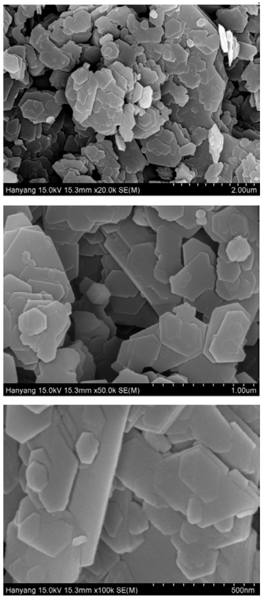

Figure 4: SEM micrographs for C2.

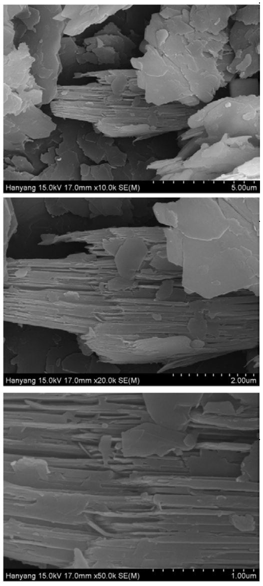

Figure 5: SEM micrographs for C3.

Similarly, Table 3 revealed a contrasting property which showed a contraction of about 0.018 nm of the interlayer spaces after NaCl activation thereby leading to a reduced size of the resulting nanoparticles from 32.92 nm of C2 to 30.98 nm of C3. A plot of x-ray diffraction data (Figure 3) revealed that, such contraction was associated with a shift in diffraction peak positioning from $2\theta = 12.543°$ of C2 to 12.552° of C3. In most cases, when kaolinite interlayer spaces are reacted, it is expected that the incoming group will intercalate the interlayer spaces and so expansion is expected and not contraction. The outcome of this study has revealed the opposite; instead of lattice expansion, contraction took place as measured by x-ray diffraction technique. The reason behind this phenomenon may not be available at the moment but a glimpse of fact may be obtained in the study conducted by Greathouse et al. [12] regarding the molecular dynamics simulation of both, diffusion and electrical conductivity in the interlayer spaces. According to [12], the trend in cation and water diffusion in the interlayer spaces can be attributed to the effect of layer charge, interlayer cation and cation charge [sodium of calcium], water content and temperature. That said, the need to carry molecular simulation studies in order to investigate the present phenomena of layer contraction instead of expansion is called for.

Comparative analysis of scanning electron micrographs

Curiosity over the un-explained phenomena so far described led to conducting further investigation of C2 and C3 with scanning electron microscope. Comparative analysis of SEM micrographs as seen in Figures 4 and 5 revealed that, originally both C2 and C3 particles were dominated with euhedral pseudo-hexagonal platelets whose orientation got changed upon NaCl agitation. A change of orientation was not associated with disruption of crystal lattice structures and that is evident due to retaining of FCC crystal Bravais system after activation with NaCl (Table 3). On the contrary, a change of orientation may be

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attributed to packing of crystal lattices. In other words, NaCl helped to orient the packing of crystal lattices into vermiform morphology appearing in Figure 5.

Comparatively, the pattern observed in Figure 4 of euhedral pseudo-hexagonal platelets and that of Figure 5 of vermiform speaks a lot about the likelihood of intercalation reactions to proceed. Vermiform orientation is preferred over the former in order to achieve maximum intercalation of drug molecules and agrochemicals into the interlayer spaces. There is a close packing of layers as seen in Figure 5 as compared to Figure 4; this may be attributed to the contraction of interlayer spaces described earlier. Nevertheless, the reason as why NaCl causes contraction of layers needs a further investigation particularly molecular dynamics simulation studies. Essentially, it may be set clear to say, when kaolinite or any other 1:1 layered phyllosilicate is to be used as a carrier molecule, activation with NaCl is necessary in order to attain orientation of layers into vermiform whose pattern offers maximum site and suitable for reactions involving interlayer spaces to take place.

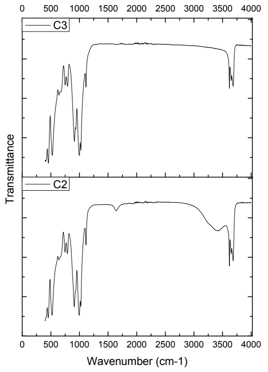

Figure 6: FTIR/ATR vibrational spectra for C2 and C3.

Wavelength (cm^{-1})	C2	C3	Description	References
3683		✓	In-phase OH stretching of the inner surface hydroxyl of 1:1 kaolinite sheets	[3, 9, 17, 19]
3684	✓			
3650	✓	✓	Out-phase OH stretching vibrations of the inner surface hydroxyl groups	
3618	✓	✓	Inner layer OH stretching due to Al- O-H stretching vibrations of alumina of the kaolinite in the octahedral configuration	
3412	✓		Wide O-H stretching vibration (broad shoulder) due to hydrogen bonding upon wetting	[5, 21, 30]
1113	✓	✓	Apical Si-O stretching	[4]
1023		✓	In-plane Si-O planar stretching	[3, 8, 9, 17]
997		✓	Out-phase Si-O planar stretching	[13]
995	✓			
910		✓	OH deformation of inner hydroxyl groups due to Al-OH bending	[9, 13, 15, 17]
909	✓			
788	✓	✓	Al-O-Si asymmetric bending of the bonds	[9]
749		✓	Si-O-Si symmetrical stretching	[13, 19]
525		✓	Si-O-Al (VI) ; Al^{3+} is in octahedral coordination	[13, 15, 28]
520	✓			

Table 4: FTIR vibration spectra analysis for C2 and C3.

Comparative analysis with vibration spectra

Vibrational spectral analysis of C2 and C3 has revealed a pattern observed in Figure 6 whose description is given in Table 4. The characteristic peak for C2 at 3412 indicated the reason for an increased size attributable to the diffusion of water molecules into the interlayer spaces as a result of cyclone applied during wet beneficiation process.

Presumably, NaCl activation may have led to adsorption of water molecules by the salt particles followed by their removal during drying procedure which was carried in a vacuum oven as explained earlier thereby causing a size reduction observed in Table 4. Indeed, the differences in peak position (Figure 6) explain the characteristics features of kaolinite as a carrier substance upon activation. Furthermore, another characteristics band observed at 1113 in C2 signify a change of layer orientation as indicated in Figures 4 and 5.

Overall, the results depict that, NaCl as used in this study is suitable activator of the kaolinite 1:1 nano-sheets thereby making it suitable carrier materials for use in the design of drug delivery systems and controlled release formulations of agrochemicals.

Conclusion

Fundamentally, kaolinite is one of the layered phyllosilicates characterized by 1:1 arrangement of nano-layers comprised of silica tetrahedral and alumina octahedral as opposed to 2:1 layered silicates such as Montmorillonite. By virtue of being 1:1 layered, kaolinite is known to be reluctant to direct reaction involving the interlayer spaces. Since such reaction involving the interlayer spaces are useful in design of controlled release systems of drugs [DDSs] and agrochemicals [CRFs], the need to find out a way to activate the interlayer spaces was necessary and this the aim of this study. Typically, researches pertaining using NaCl as activation agent are known but the record of the contrasting features between NaCl kaolinite and wet beneficiated counterpart is worth reporting owing to its significance in the current nanotechnological initiatives of using layered materials as carrier molecules. The findings indicated that NaCl is a suitable activator of 1:1 interlayer spaces as per the conditions/assumptions stated in this study. Outstandingly, the ability of NaCl activation process to change the orientation kaolinite nano-sheets from euhedral pseudohexagonal platelets into vermiform provide a room for more advanced application of the mineral in the designs of DDSs and CRFs because the resultant vermiform orientation portray a maximized molecules insertion points needed in these studies.

References

1. Abou-El-Sherbini KS, Elzahany EA, Wahba MA, Youssef N (2017) Evaluation of some intercalation methods of dimethylsulphoxide onto HCl-treated and untreated Egyptian kaolinite. Appl Clay Sci 137: 33-42.
2. Ani TA, Sarapää O (2013) Geochemistry and mineral phases of REE in Jammi carbonatite veins and fenites, southern end of the Sokli complex, NE Finland. Geochem Explor Env A 13: 217-224.
3. Aroke U, El-Nafaty U (2014) XRF, XRD and FTIR properties and characterization of HDTMA-Br surface modified organokaolinite clay. IJETAE 4: 817-825.
4. Balan E, Saitta AM, Mauri F, Calas G (2001) First-principles modeling of the infrared spectrum of kaolinite. Am Mineral 86: 1321-1330.
5. Banwell C, McCash EM (1994) Fundamentals of molecular spectroscopy. Tata McGraw Hill, New Delhi, India.
6. Bhattacharyya KG, Sen Gupta S (2007) Influence of acid activation of kaolinite and montmorillonite on adsorptive removal of Cd (II) from water. Ind Eng Chem Res 46: 3734-3742.
7. Bond W (1927) LXXXII. Bubbles and drops and Stokes' law. Philos. Mag 4: 889-898.
8. Dang TH, Chen BH, Lee DJ (2013) Application of kaolin-based catalysts in biodiesel production via transesterification of vegetable oils in excess methanol. Bioresour Technol 145: 175-181.
9. Dawley MM, Scott AM, Hill FC, Leszczynski J, Orlando TM (2012) Adsorption of formamide on kaolinite surfaces: A combined infrared experimental and theoretical study. J Phys Chem C 116: 23981-23991.
10. DudkinI BN, Loukhina IV, Isupov VP, Avvakumov EG (2005) Mechanical activation of kaolinite in the presence of concentrated sulfuric acid. Russ J Appl Chem 78: 33-37.
11. Frost RL, Makó É, Kristóf J, Horváth E, Kloprogge JT (2001) Mechanochemical treatment of kaolinite. J Colloid Interface Sci 239: 458-466.
12. Greathouse JA, Cygan RT, Fredrich JT, Jerauld GR (2016) Molecular dynamics simulation of diffusion and electrical conductivity in montmorillonite interlayers. J Phys Chem C 120: 1640-1649.
13. Heah CY, Kamarudin H, Mustafa AM, Bakri AL, Bnhussain M, et al. (2012) Study on solids-to-liquid and alkaline activator ratios on kaolin-based geopolymers. Constr Build Mater 35: 912-922.
14. Khalifa A, Pontikes YY (2017) Alkali activation of pure calcined montmorillonite.
15. Liew YM, Kamarudin H, Mustafa Al-Bakri AM, Luqman M, Nizar IK (2012) Processing and characterization of calcined kaolin cement powder. CONSTR BUILD MATER 30: 794-802.
16. Makó E, Frost RL, Kristóf J, Horváth E (2001) The effect of quartz content on the mechanochemical activation of kaolinite. J Colloid Interface Sci 244: 359-364.
17. Mgbemena CO, Ibekwe NO, Sukumar R, Ravindranatha Menon AR (2013) Characterization of kaolin intercalates of oleochemicals derived from rubber seed (*Hevea brasiliensis)* and tea seed (*Camelia sinensis)* oils. JKSUS 25: 149-155.
18. Nakamoto K (1977) Infrared and Raman spectra of inorganic and coordination compounds, Wiley, NY, USA.
19. Olejnik S, Aylmore LA, Posner AM, Quirk JP (1968) Infrared spectra of kaolin mineral-dimethyl sulfoxide complexes. J Phys Chem A 72: 241-249.
20. Parolo ME, Fernández LG, Zajonkovsky I, Sánchez MP, Baschini M (2011) Antibacterial activity of materials synthesized from clay minerals. Science against microbial pathogens: Communicating current research and technological advances. Formatex, Microbiology series 3: 144-151.
21. Pope RM, Fry ES (1997) Absorption spectrum (380–700 nm) of pure water. II. Integrating cavity measurements. Appl Opt 36: 8710-8723.
22. Rubey WW (1933) Settling velocity of gravel, sand, and silt particles. Am J Sci 148: 325-338.
23. Sempeho SI, Kim HT, Mubofu E, Hilonga A (2014) Meticulous overview on the controlled release fertilizers. Advances in Chemistry 2014.
24. Siafu SI (2017) The prospects of layered alumino-silicates in the synthesis of nano-excipients for controlled release systems. J Nanomed Res 5: 00128.
25. Soils A (2015) Soil colloids and the surface chemistry of soils.
26. Sposito G (1984) The surface chemistry of soils, Oxford University Press, UK.
27. Sposito G (2008) The chemistry of soils, Oxford University Press, UK.
28. Tironi A, Trezza A,Irassar EF, Scian AN (2012) Thermal treatment of kaolin: effect on the pozzolanic activity. Procedia Materials Science 1: 343-350.
29. Unalan IU, Cerri G, Marcuzzo E, Cozzolinoa CA, Farris S (2014) Nanocomposite films and coatings using inorganic nanobuilding blocks (NBB): current applications and future opportunities in the food packaging sector. RSC Adv 4: 29393-29428.
30. Venyaminov SY, Prendergast FG (1997) Water (H_2O and D_2O) Molar absorptivity in the 1000–4000 cm^{-1} range and quantitative infrared spectroscopy of aqueous solutions. Anal Biochem 248: 234-245.
31. Zhang C, Zhang Z, Tan Y, Zhong M (2017) The effect of citric acid on the kaolin activation and mullite formation. Ceram Int 43: 1466-1471.