Materials Science
ISSN: 0974-7486

Material Science: An Indian Journal

Research | Vol 17 Iss 1

Kaolinite Intercalation Reactions Induced by Naturally Occurring Fe^{3+} Oligomers

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Received date: January 23, 2019; **Accepted date:** February 01, 2019; **Published date:** February 10, 2019

Abstract

Kaolinite is one of the layered aluminosilicates capable of undergoing intercalation by virtue of ion substitution reaction taking place in the interlayer spaces which in turn creates site vacancies whose compensation give rise to sorption reaction thereby smoothening the progress of intercalation reactions. Nevertheless, the fact that kaolinite is a 1:1 layered silicate and so, hard to intercalate spontaneously, opened up experiments pertaining the application of intermediate intercalation reactions utilizing powerful organic and inorganic intercalants. This study was therefore set to investigate the effect of both laboratories synthesized and naturally oligomer zed cationic Fe^{3+} oligomers in inducing kaolinite intercalation as intermediate intercalation compounds. The kaolinite nanomaterial were characterized for particle size using Andreasen pipette sedimentation technique, chemical composition using XRF, molecular absorption spectroscopy using ATR/FTIR, thermo-properties using TG/DTG and mineralogical analysis as well as intercalation ratios using XRD techniques. The X-ray diffraction pattern revealed the existence of FCC Crystal Bravais for both kaolinite intercalated with laboratory synthesized and naturally oligomerized cationic Fe^{3+} oligomers whose crystallite sizes as per the Scherer equation were between 80.01 and 23.85 nm and between 64.58 and 19.25 nm respectively. Similarly, intercalation ratios were respectively 70.41% (associated with lattice expansion along the c-plane of about 3.62 Å) and 37.53% (associated with lattice expansion along the c-plane of about 3.61 Å) indicating that laboratory synthesized cationic Fe^{3+} oligomers (under controlled experimental condition and enough aging) intercalate twice as compared to naturally oligomerized one but in general the findings revealed that it is possible to use Fe^{3+} cationic oligomers as intermediate intercalation compounds. Analysis of kaolin phases indicated that kaolinite phase was the major kaolin phase whereas illite was the minor phase. The structure of kaolinite was seen to be maintained in both extremes as revealed in the molecular vibrational studies. Thermal stability between 0°C to 800°C revealed that both kaolinite nanomaterial intercalated with laboratory synthesized and naturally oligomerized cationic Fe^{3+} oligomers exhibited three degradation phases in common namely; 25°C-375°C, 425°C-450°C and the 475°C-800°C phases.

Keywords: ***Intercalation; Beneficiation; Oligomer; Controlled release systems; Kaolin; Beneficiation; Pugu; FCC***

Citation: Sempeho Ibahati Siafu. Kaolinite Intercalation Reactions Induced by Naturally Occurring Fe^{3+} Oligomers. Mat Sci Ind J. 2019;17(1):143.

Introduction

Kaolinite intercalation reactions are kind of topochemical reactions (merely the following physisorption as opposed to chemisorption kinetics) which entail insertion of guest molecules into interlayer nano-spaces found between kaolinite aluminosilicate functional sheets. In other words, in the context of layered aluminosilicates intercalation could mean the process whereby guest molecules (in most cases organic species or rather intercalants) insinuate into the lattices of the host species and that the guest-host hybrid (intercalation compound) is somewhat perturbed from the host structure and that the reaction is reversible [1,2]. Studies show that kaolinite intercalation can be induced by a number of organic and inorganic based intercalants such as DMSO, methanol, chlorhydrol [1,3,4] etc. However, most of these intercalation agents are synthetic. To date, the literature is silent regarding the ability of cationic Fe^{3+} in the ferrous contaminated kaolinite to intercalate kaolinite and be used in the controlled release systems. This study, therefore, is set to investigate this phenomenon along with the effect of laboratory synthesized cationic Fe^{3+} oligomers in the kaolinite intercalations. The study is anticipated to open a global discussion on the naturally occurring kaolinite intercalation in ferrous sullied kaolins.

By virtue of being a layered phyllosilicate mineral, kaolinite is known to be a 1:1 layered aluminosilicate mineral with its crystal lattice unit formed by one alumina octahedral sheet sandwiched between one silica tetrahedral sheets [3]. The occurrence of ion substitution or the site vacancies at the tetrahedral and/or octahedral sheets gives rise to a negatively charged surface; the exchangeable cations between the layers compensate the negative charge and may be easily exchanged by other metal cations giving rise to sorption reactions which in turn facilitate intercalation reaction [5]. Owing to that, surface modifications occur [6] and as a result, large surface areas and reactivity of nanolayers form on the surfaces and interfaces of nano-layers which act as substrate for chemical reactions thereby making kaolinite nano-layers suitable excipients for use in different controlled release systems [7], such as Drug Delivery systems (DDs), Controlled Release Fertilizers (CRFs) etc. These properties influence researches to investigate the suitability of intercalated kaolinites as excipients [8], particularly in the nano-dimensions.

PLATE 1. **Satellite map around Kazimzumbwi forest reserve.**

According Bhatachary and Gupta [9], “Oligomerization is a chemical process that links monomeric compounds (e.g., amino acids, nucleotides, or monosaccharides) to form dimers, trimers, tetramers, or longer chain molecules (oligomers). Examples are the conversion of nucleotides to oligonucleotides and amino acids to peptides”. In our context oligomerization may mean the ability of inorganic cations to associate into macromolecular species [10] which can penetrate the interlayer spaces by a way of overcoming the associated electrostatic forces. The definition may not be exhaustive but further investigations on the subject could lead to a better description.

Study Area

Sampling spot was carefully selected within Kazimzumbwi forest at Kisarawe in the Coast region of Tanzania (**PLATE 1**). The forest hosts Pugu kaolin hills found at around 43.9 km from the Dar es Salaam city centre. This forest is historically known for kaolin mining since the period of German colonialism in Tanganyika. Currently, the kaolin in the Pugu hills is being researched for various applications including its suitability for use as that, it was worth investigating the natural intercalation tendency which was seen to occur, a phenomenon that may open the door for further research on the application of ferrous contaminated kaolins in the kaolinite-based intercalation reactions.

Methodology

Kaolinite was collected at Pugu hills in the Coast region Kisarawe Tanzania by using quartering sampling technique. Sodium chloride (Extra pure, ≥ 99.0%) was purched from Samchun pure chemicals Co. Ltd, Korea, Silver chloride (ACS reagent, 99.0%) was supplied by Sigma Aldrich, sodium hydroxide (extra pure grade, min. 93.0%) was supplied by Duksan pure chemical, Korea and $Fe(NO_3)_3$ and NH_4OH (99.99%) was supplied by Junsei chemical Co. Ltd, Japan.

Sample Purification

Wet beneficiation technique was achieved by simple size separation using “Classifier”. The method involved the separation of fine platy kaolinite from coarser quartz, feldspar mica and other impurities using different setting velocities associated with particle size as governed by Stockes’s law. Beneficiated kaolinite sample was labeled as S1. The procedures were adopted with some modifications from [11].

Intercalation of kaolinite interlayer spaces

Ferrous contaminated kaolinite sample was made into a suspension and then agitated for 6 hours followed by a 15 days maturation where after, drying was done in a vacuum oven at 70°C; the dried sample was labeled as S2. On the other hand, two beakers were taken; in the first beaker a known amount of beneficiated Pugu kaolinite was dispersed in a 0.1 M NaCl solution and treated ultrasonically at 50°C for 30 hours and then magnetically stirred for more 30 hours under constant stirring. The product was filtered under vacuum filter and washed several times to remove excess chlorides. Washing was stopped after a negative reaction with $AgNO_3$. In the second beaker, 1:1 molar solutions of $Fe(NO_3)_3$ and NH_4OH were thoroughly stirred for 6 hours at 85°C and aged for 15 days where the OH/Fe ratio was 2. Thereafter, a 25 ml of this aged solution was agitated with 5% kaolinite suspension from the first beaker at 70°C and matured for one week, thereafter washing was done and dried in a vacuum oven and labeled as S3. All the samples prepared were characterized with FTIR-ATR using Bruker Optic GmbH (alpha model, Laser class 1) Spectrometer with attenuated total reflectance (ATR); XRD using Rigaku 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); TG/DTG using TG/STA Linseis STA PT 1000 simultaneous TG/DTG thermal analyzer at a scanning rate of 5°C per min from room temperature to 800°C under nitrogen atmosphere as well as X-ray Fluorescence (XRF) using Semi-Quantitative XRF analysis technique (SIEMENS SRS 3000 X-ray Fluorescence (Rhodium anode, 8 analyzer crystals with beryllium windows 125 μm). Besides, the particle size analysis was carried out using sub-sieve analysis technique which involves the application of Andreasen pipette sedimentation method.

Analysis and Results

Composition and particle size analysis

Raw kaolinite as a starting material was tested for both chemical composition (**TABLE 1**) and particle size distribution (**TABLE 2**). Particle size analysis using Andreassen pipette sedimentation technique revealed that the clay portion of the starting raw kaolin was only 60.42% whereas upon wet beneficiation trials the clay portion of the purified kaolinite was 99.64% thereby indicating the level of purity of the kaolinite sample used in this study. Besides, this outcome shows the effectiveness along with the efficiency of the wet beneficiation procedure employed.

TABLE 1. **The chemical composition of the raw and beneficiated kaolin.**

Element	Weight Percent	
	Raw Pugu kaolin	**Beneficiated Pugu kaolin**
Si	63.64	54.99
Al	31.43	40.20
Na	0.43	0.09
Mg	0.16	0.13
S	0.25	0.08
Cl	0.76	0.04
K	1.39	0.96
Ca	0.06	0.04
Ti	0.80	1.02
Cr	0.03	0.04
Mn	0.01	0.01
Fe	1.01	2.00
LOI	0.03	0.40
Total	100	100

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TABLE 2. **Particle size distribution.**

Grain size (μm)	Kaolin (% weight)	Beneficiated Kaolin (% weight)
(>63 μm)	37.57	0.35
(2-63 μm)	54.95	78.53
(<2 μm)	2.39	21.03
(<63 μm)	57.34	99.56

Analysis of the minor and major phases basing on the X-ray diffractograms of the whole rock powder mount of the beneficiated kaolinite indicated that the dominant phase was kaolinite and the minor phase was illite (**FIG. 1**).

For the purpose of distinguishing layer types and clay mineral groups; oriented clay preparation was carried out on the beneficiated kaolin samples. As I have described elsewhere that; "To identify the clay minerals present, the oriented samples were analyzed by X-ray diffraction method as untreated air-dried, glycolated and heated at 550°C for two hours. When the air-dried samples were diffracted, peaks were developed on the diffractogram which revealed three main clay minerals namely kaolinite, illite, and clinochlore" [12]. The results from oriented air-dried samples above were not enough to confirm the clay mineral groups obtained. Thus, identification and hence confirmation of these clay minerals were achieved from the differences on the diffractograms obtained by glycosylating the samples, drying them, then diffraction process carried out; and by heating the samples at 550°C for two hours prior to the diffraction process. Diffraction results (**FIG. 2**) shows that some of the diffractogram peaks in the beneficiated kaolin samples were not affected by the two prescribed treatments.

This behavior of stability in chemical treatment (glycolate) and heat transformation (at 550°C) confirmed the presence of illite [12]. However, when the samples were glycosylated, dried and diffracted some peaks were shifted in some samples. But on heating the samples at 550 °C followed by diffraction, these shifted peaks collapsed. This characteristic of altering the diffraction patterns is a distinguishing characteristic of the kaolinite group" [12]. That said, the major kaolin mineral observed on both the original and beneficiated kaolin samples was kaolinite subordinated with illite.

Inducing kaolinite intercalation via synthesized ferric oligomers and naturally oligomerized iron (III) cations

The observation made in the course of experiments done revealed that: despite being a chemically induced process, intercalation reactions in the ferric contaminated kaolins (**PLATE 2**) is a simultaneous and naturally occurring phenomenon; nevertheless, the intercalation process is quite slow following low intercalation ratios calculated in the laboratory. Empirically, intercalation ratios determined from X-ray patterns and peak positions for the beneficiated kaolinite (**PLATE 3**) intercalated with laboratory-synthesized and aged Fe^{3+} cationic oligomers (S3) was found to be 70.41% associated with lattice.

Expansion along the c-plane of about 3.62 Å of the kaolinite interlayer spaces and that the crystal sizes were between 80.01 and 23.85 nm. On the other hand, intercalation reactions basing on natural oligomerization of Fe^{3+} cations indicated a crystal lattice (d001) expansion of about 3.61 Å attributable to the intercalation of Fe^{3+} cationic oligomers within the interlayer spaces of 1:1 kaolinite functional sheets and this was associated with intercalation ratio of about 37.53%; the resultant crystal sizes were between 64.58 and 19.25 nm.

PLATE 2. **Ferric (III) contaminated kaolin (S2).**

PLATE 3. **Beneficiated kaolin (S1).**

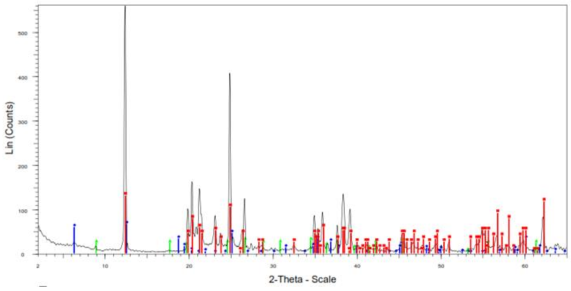

FIG. 1. **Whole rock clay analysis for the beneficiated kaolin.**

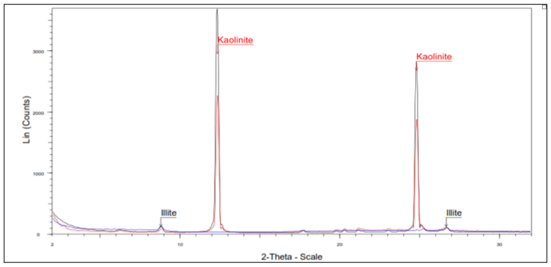

FIG. 2. **Oriented clay analysis for the beneficiated kaolin.**

Profoundly, intercalation reaction following naturally oligomerized Fe^{3+} cations was seen to be associated with a loss of XRD peak intensity as seen in sample S2 (**FIG. 3**). Although the experimental setup differs, this phenomenon concurs with the observation made by Bhatachary and Gupta [9]. Interestingly, a significant rise in the XRD peak intensity was observed after kaolinite intercalation using the lab. Synthesized and aged Fe^{3+} oligomeric cations; this may be ascribed to the intercalation trends so far explained between the two extremes. Besides, analysis on the indexed diffracted patterns revealed that there was the original FCC crystal Bravais lattice structure was maintained in both extremes as seen **TABLE 3**.

TABLE 3. **Indexed X-ray pattern to show hkl values.**

Peak#	**2θ**	**$3*\mathrm{Sin}^2\theta/\mathrm{Sin}2\theta_{\mathrm{min}}$**	**h^2+k+l^2**	***hkl***
1a	12.1635	25.35170023	25	500
1b	24.9128	7.628159189	8	220
2a	12.086	35.83796077	36	600
2b	24.6743	32.69682641	33	522
3a	12.0576	40.10639453	40	620
3b	24.6009	43.73818682	44	622

Molecular vibrational studies with ATR/FTIR revealed that: the structure of kaolinite is maintained when kaolinite is either interacted with naturally oligomerized Fe^{3+} cations or intercalated with lab prepared ferric oligomers. Maintenance of kaolinite structure was vivid when looking at the presence of characteristic absorption bands for kaolinite located between 3696-3618 cm^{-1} in both extremes corresponding to typical OH- stretching vibration for kaolinite mineral (**FIG. 4**). Owing to their weak intensity and their band positions, the Al-Fe^{3+} OH vibrations are known to be difficult to analyze [13,14]. That is to say, the formation of Fe^{3+} oligomeric intercalated kaolinite is associated with the formation of Al-Fe^{3+} OH bands whose peak position and intensity are a bit puzzling to assess.

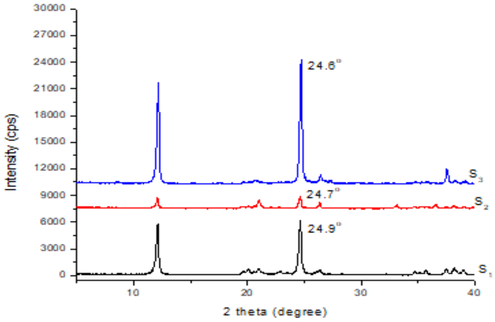

FIG. 3. **X-ray diffractograms for S1, S2 and S3 showing peak positioning and intensity.**

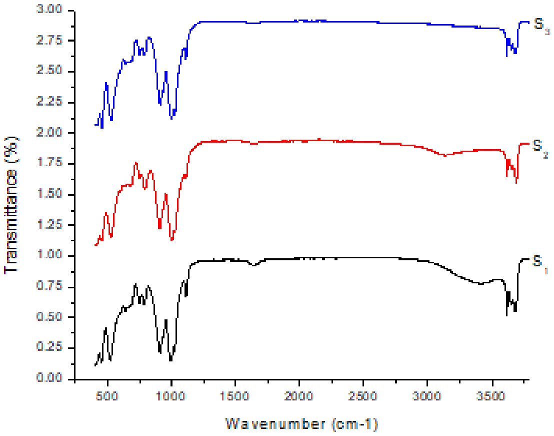

FIG. 4. **FTIR/ATR diffractograms for S1, S2, and S3.**

However, in most cases the vibrational frequencies for the Al-Fe^{3+} OH bands do occur around 1200-800 cm^{-1} [15]; that may also go up to about 1250-1400 cm^{-1} in the complex trigonal and tetragonal forms [16-18]. 6, weak-less intense bands can be observed between 2400-2000 and between 1500-1800 cm^{-1} suggesting that the interaction between the ferrihydrite oligomers and the kaolinite' Si-OH matrix during the intercalation process was weak. This observation closely agrees with the Fe-F interaction found between 1530-500 cm^{-1} elsewhere [13]. A simple generalization from this observation may be that: though it is possible to prepare the kaolinite intercalated with ferrihydrite oligomers as stipulated in this paper, the interaction involved between the intercalant and the kaolinite functional layers is less intense or weak whether the intercalant is synthetic or natural as noted in S2 and S3; however despite the weak interaction, intercalation is possible and there is a possibility to optimize the interaction since the intercalation ratio was seen to increase from S2 to S3.

The appearance of unique broadband at around 3141 cm^{-1} in the S2 was noticed; it was ascribed to the presence of impurities due to the natural iron-rich clay used. A similar observation related to the same reason was made at around 1001 cm^{-1} absorption band and this corresponds to the C-N or Si-O bands [19] thereby giving out a clue that there were:

(i) Some organic forms of impurities present

(ii) and the natural intercalant materials

This was proven to be true due to the absence of these two bands in the S3 since it was prepared from pure intercalant solution of Fe^{3+} Oligomer. The presence of ferrohydrate oligomers in the kaolinite interlayer spaces did not affect the nature of X-ray pattern obtained; as can be seen, the distinctive kaolinite absorption bands at 3689-3618 cm^{-1} were retained after intercalation interaction (**FIG. 4**). A similar observation was recorded for the absorption bands at: 1113 cm^{-1} related to the apical Si-O stretching modes of kaolinite [20]; 1024 to 999 cm^{-1} related to the Si-O planar vibrational modes [21]; 910 to 909 cm^{-1} related to the OH deformation of inner hydroxyl groups due to Al-OH bending of kaolinite [22-24]; 788 to 796 cm^{-1} related to the Al-O-Si asymmetric bending; 526 to 459 fingerprint related to the Si-O-Al (VI) vibrations for the octahedral Al^{3+} as can be seen in the **FIG. 4** [22,24,25].

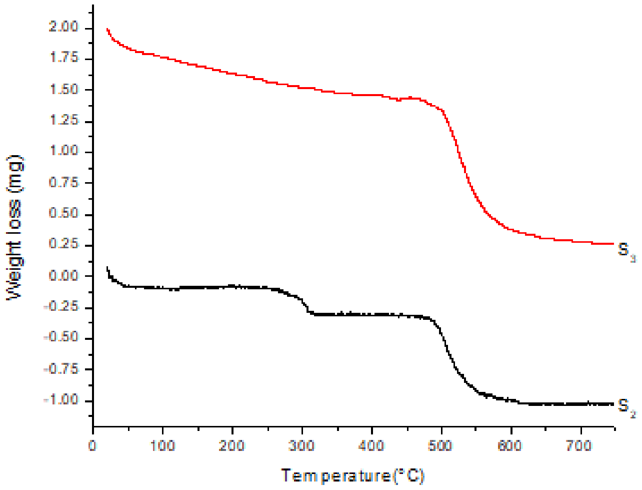

FIG. 5. **Thermograms for S2 and S3 showing purity and decomposition of intercalants.**

In view of **FIG. 5**, decomposition pattern for S2 and S3 and the purity of the intercalants can be contemplated. The thermal behavior established for S2 and S3 under N2 atmosphere in order to determine their thermal stability between 0°C to 800°C revealed that both kaolinite intercalated with laboratory synthesized Fe^{3+} oligomers (S3) and kaolinite intercalated with naturally oligomerized cationic Fe^{3+} oligomers (S2) exhibited three degradation phases in common namely; 25°C-375°C phase, 425°C-450°C phase and the 475°C-800°C phase. However, S2 exhibited some deviations around 250°C-325°C; the trend named as deviation was attributed to the differences in purity between the two samples in that: intercalant for S3 was pure since it was prepared in the lab under controlled conditions whereas intercalant for S2 was impure since it was oligomerized under natural conditions without any scientific manipulation. Nonetheless, if purity is set as a constant parameter, the thermal properties of S2 and S3 are close to each other indicating the likeness of Fe^{3+} cationic oligomers in both extremes.

Conclusion

Suitability of layered silicates as excipients in controlled release systems such as Drug Delivery Systems (DDS), Controlled Release Fertilizers (CRFs) etc., has been a topic of concern to researchers in this century owing to the possibility of the occurrence of ion substitution in the cationic exchangeable region between the nanolayers of aluminosilicates known to undergo intercalation reactions. Intercalation reactions have been studied for several decades and shown to be able to widen the interlayer spaces of the functional sheets of the layered aluminosilicates minerals which include among others, smectites, kaolins etc. Nevertheless, among the layered aluminosilicates kaolinite has been observed to be resistant to direct intercalation force involving organic molecules thereby creating a need to use intermediate intercalation reaction agents such as DMSO, methanol, and chlorhydrol just to mention a few whose results have been quite appealing. This study was hence set to investigate whether naturally oligomerized Fe^{3+} cations can act as an intermediate intercalation compound for use in the kaolinite intercalation reactions along with the laboratory synthesized cationic Fe^{3+} oligomers. Comparative analysis was involved to determine the degree of intercalation ratios to which naturally oligomerized Fe^{3+} cations and laboratory synthesized cationic Fe^{3+} oligomers differ in the way they intercalated the kaolinite interlayer nano-spaces. As a matter of fact, the findings suggested that laboratory synthesized cationic Fe^{3+} oligomers are strong intercalants and so, can be used as intermediate intercalation stage to attain an intercalation ratio of about 70.4%. Furthermore, the findings revealed that the iron-rich kaolinite has a natural tendency for Fe^{3+} oligomerization thereby naturally intercalating the kaolinite interlayer spaces. This observation is by its own, unique and the presented findings have attempted to explore that phenomenon. The study of cationic Fe^{3+} oligomerization and its usefulness in the controlled release systems is important because (i) it will challenge literature on the likelihood to intercalate the 1:1 kaolinite structure with easy, (ii) it will result in novel synthetic pathway for the industrial production of intercalated compounds such as controlled release fertilizers and drug delivery systems.

Conflict of Interest

The author declares that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

The author would like to thank Miss Niconia Amos Bura and the Institute of Adult Education, Tanzania, for their support in the preparation of this paper.

REFERENCES

1. Sempeho SI, Kim HT, Mubofu E, et al. Encapsulated urea-kaolinite nanocomposite for controlled release fertilizer formulations. J Chem. 2015:17.

2. https://onlinelibrary.wiley.com/doi/10.1002/9781119951438.eibc0093

3. Sempeho SI, Kim HT, Mubofu E, et al. Dynamics of kaolinite-urea nanocomposites via coupled DMSO-hydroxy aluminum oligomeric intermediates. Ind J Mat Sci. 2015:1-10.

4. https://ruor.uottawa.ca/bitstream/10393/24379/1/Czarnecka_Anna_2013_thesis.pdf

5. Parolo ME, Fernández LG, Zajonkovsky I, et al. Antibacterial activity of materials synthesized from clay minerals. Microbiology series. 2011;3:144-51.

6. Basak BB, Pal S, Datta SC. Use of modified clays for retention and supply of water and nutrients. Current Science (Bangalore). 2012;102:1272-8.

7. http://www.ukessays.com/essays/biology/controlled-release-fertilizers-and-nanotechnology-traces-biology-essay.php

8. Aguzzi C, Cerezo P, Viseras C, et al. Use of clays as drug delivery systems: possibilities and limitations. Appl Clay Sci. 2007;36:22-36.

9. https://link.springer.com/referenceworkentry/10.1007/978-3-642-11274-4_1104.

10. https://onlinelibrary.wiley.com/doi/book/10.1002/9780470145326

11. Lugwisha EH, Siafu SI. The properties of feldspathic dental porcelain from Tanzanian aluminosilicate materials. IJDR. 2014;4:2260-5.

12. Mureddu M, Ferino I, Musinu A, et al. MeO x/SBA-15 (Me= Zn, Fe): highly efficient nanosorbents for mid-temperature H_2S removal. J Mater Chem A Mater. 2014;2:19396-406.

13. Yvon J, Cases JM. FTIR reflectance vs. EPR studies of structural iron in kaolinites. Clays Clay Miner. 1994;42:308-20.

14. https://scisoc.confex.com/crops/wc2006/techprogram/P16046.HTM

15. https://onlinelibrary.wiley.com/doi/abs/10.1002/0470027320.s4104

16. Peak D, Luther GW, Sparks DL. Boric acid and borate adsorption mechanisms on amorphous iron oxides: An *in situ* ATR-FTIR spectroscopic studies. Geochim Cosmochim Acta. 2003;67:2551-60.

17. Peak D, Ford RG, Sparks DL. An *in situ* ATR-FTIR investigation of sulfate bonding mechanisms on goethite. J Colloid Interface Sci. 1999;218:289-99.

18. https://ruor.uottawa.ca/handle/10393/24379

19. Balan E, Saitta AM, Mauri F, et al. First-principles modeling of the infrared spectrum of kaolinite. Am Mineral. 2001;86:1321-30.

20. Aroke U, El-Nafaty U. XRF, XRD and FTIR properties and characterization of HDTMA-Br surface modified organo-kaolinite clay. IJETAE. 2014;4:817-25.

21. Dawley MM, Scott AM, Hill FC, et al. Adsorption of formamide on kaolinite surfaces: A combined infrared experimental and theoretical study. J Phys Chem C. 2012;116:23981-91.

22. Liew YM, Kamarudin H, Al Bakri AM, et al. Processing and characterization of calcined kaolin cement powder. Constr Build Mater. 2012;30:794-802.

23. Mgbemena CO, Ibekwe NO, Sukumar R, et al. Characterization of kaolin intercalates of oleochemicals derived from rubber seed (*Hevea brasiliensis*) and tea seed (*Camellia sinensis*) oils. J King Saud Univ Sci. 2013;25:149-55.

24. Heah CY, Kamarudin H, Al Bakri AM, et al. Study on solids-to-liquid and alkaline activator ratios on kaolin-based geopolymers. Constr Build Mater. 2012;35:912-22.

25. Tironi A, Trezza MA, Irassar EF, et al. Thermal treatment of kaolin: effect on the pozzolanic activity. Procedia Materials Science. 2012;1:343-50.