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Achieving Stable Intercalation States upon Optimizing Intercalation Reactions Involving Kaolinite Inter-Layer Spaces

Sempeho I. Siafu[1]

[1]sempeho@iae.ac.tz

[1]https://orcid.org/0000-0003-1872-8537

[1]Dar es Salaam University, Tanzania

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ABSTRACT

This study explored the intercalation processes of kaolinite which is a layered phyllosilicate mineral with 1:1 structural configuration capable of incorporation of guest molecules within its interlayer spaces. The experiments utilize X-ray diffraction (XRD) techniques to examine the intercalation ratios of the intercalants (cationic intercalants namely ferrihydrite and hydroxyaluminum as well as anionic intercalant namely DMSO and Methanol) for the analysis of their respective hyperstabilization effects of kaolinite structural expansion. The investigations target a stable intercalation state or S.I.S, which is defined by the constant distance between the interlayers. Findings revealed that, the order of intercalation kinetics progresses through first (76.8% A.I.R, lattice expansion: 3.61–3.62 Å), second (87.4% A.I.R) and third order (89.2% A.I.R) reactions which results into a point called "Stable Intercalation State" which is characterized with constant apparent intercalation ratios (A.I.R). It was also found that kaolinite intercalation is influenced by aging time, temperature, and molecular size thereby impacting the apparent intercalation ratio before the S.I.S point is attained. The present work provides a detailed guideline on improving intercalation through the experimental parameters to pave the way towards understanding stable intercalation states in kaolinite-host structures. The obtained results allow deepening insight into the mechanistic intercalation chemistry of kaolinite with possible end use in controlled release systems.

Keywords: Intercalation, Kaolinite, Intercalant, Nano-composites, Nano-clay, Phyllosilicate

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I. INTRODUCTION

Despite the stable structure of kaolinite 1:1 layered configuration attributable to its electrostatic forces and hydrogen bonding (Tunega & Zaoui, 2020; Zhang et al., 2021), it is possible to insert guest species into the functional layers by either breaking the hydrogen bonds that hold the kaolinite layers together (when polar intercalants are used) leading to expansion of the interlayer spacing or by exchanging the cations in the kaolinite structure leading to changes in the charge distribution and allow for the intercalation of other molecules (Chen et al., 2021; Saha et al., 2022; Theng 2024). That is to say, in the case of polar anionic intercalants such Dimethyl sulfoxide (DMSO) and methanol used in this study, insertion of guest species into the host is initiated by disrupting the hydrogen bonding acting within the kaolinite layers (Lee et al., 2019; Sempeho et al., 2015). On the other hand, intercalation reaction involving cationic intercalants such ferrihydrite and hydroxyaluminum used in this study proceed through the cation exchange by way of replacement of the ions already present in the kaolinite interlayer spaces (Bergaya et al., 2006); (Thomas, 1984) which results into the alteration of the electrostatic forces within the kaolinite layers, facilitating the intercalation of additional molecules (Bergaya & Lagaly, 2011; Mongey, 1996; Saha et al., 2022; Theng, 2024).

This study utilized X-ray diffraction (XRD) technique to determine the intercalation ratios of different kaolinite intercalated materials (Matusik & Klapyta, 2013). The observed variations in the basal spacing was used to provide the experimental narrative behind intercalation states recorded (Hughes et al., 2009). The choice of intercalants is critical based on the inherent characteristics which among others include polarity, molecular size, cationic exchange capacity (CEC), charge distribution and functional groups (Bujdák, 2015; Kinoti et al., 2022).

The structural configuration of kaolinite as one of the layered phyllosilicates involves alternating tetrahedral silica functional layers with the octahedral sheets as described in (Sempeho et al., 2014). Indeed, this property qualifies the kaolinite interlayer spaces as host platform which can accept the insertion of intercalants (guest molecules/ions). Over time, literature has demonstrated that intercalation reactions could be successful upon optimization of some experimental variables including pH, temperature and time while considering the prior variables such as nature of the intercalant, size of the intercalant and the approaches used to carry out the named intercalation reaction namely, the thermal treatment, chemical treatment and ultrasonic treatment (Leal et al., 2021; Maged et al., 2020; Marzban et al., 2021). This paper reports a condition or a state attained when these experimental variables are optimized when kaolinite host interlayer spaces are intercalated with guest organic or inorganic species resulting into a proposed concept which has been named as “Stable Intercalation State” (S.I.S Point).

II. METHODOLOGY

Kaolinite was collected from the Pugu Hills in the Kisarawe district of the Coast region, Tanzania, using the quartering sampling technique as described by Sempeho et al. (2012). Urea (ACS reagent, 99.0-100.5%) was supplied by Sigma Aldrich. Acacia powder (extra pure reagent) was obtained from Junsei Chemical Co., Ltd, Japan. Dimethyl sulfoxide (DMSO, Extra pure, ≥ 99.5%) was provided by Daejung Chemicals & Metals Co. Ltd, Gyonggi-do, Korea. Sodium chloride (Extra pure, ≥ 99.0%) was supplied by Samchun Pure Chemicals Co. Ltd, Gyonggi-do, Korea, and silver chloride (ACS reagent, 99.0%) by Sigma Aldrich. Methanol (extra pure, ≥ 99.5%) and isopropanol were both supplied by Daejung Chemicals & Metals Co. Ltd, Gyonggi-do, Korea. Acacia powder (extra pure reagent) was sourced from Junsei Chemical Co., Ltd, Japan. Deionized distilled water (D.I.) was provided by Prof. Kim’s lab.

An $AlCl_3$ solution (0.1 M) was taken and mixed with NaOH (0.1 M sodium hydroxide solution) in the ratio of 1: 2. After the sample's agitation at 85 ºC for 6 hours, this mixture was allowed to age for 12 hours. After that, a solution of 5% suspension of upgraded kaolinite was prepared and ultrasonically dispersed in the hydroxyaluminum oligomeric solution in excess at 70 °C for 3 hours. The obtained product labeled 'B2' was centrifuged to remove all the unreacted materials including the chloride ions (as confirmed by testing with $AgNO_3$ solution).

The method of intercalation of dimethyl sulfoxide (DMSO) into the interlayer space of kaolinite is described below. A portion of Pugu Kaolinite was mixed with a specific amount of distilled water (D.I.) and DMSO solution with a ratio of D.I : DMSO : kaolinite = 6 : 1 : 1 respectively. This mixture was then agitated using a magnetic stirrer for a period of 21 days to 80 °C with gentle but enthusing addition of water droplets at intervals to avoid drying of the mixture. This stirring was carried out for a total period of 21 days after which the suspension is left to condition at room temperature for one week. The resulting suspension was decanted and excess isopropanol was used to wash the residue before the ethanolic–TMAO dissociated solution was dried on a vacuum oven at 60°C. The resulting powder product was given a code name KPDMSO. KPDMSO powder considered as a precursor was weighed 2 grams and dissolved in 60 ml of methanol solution, then followed by stirring for 5 days at room temperature. After 5 days of continuous stirring, the suspension was allowed to mature for 2 days. Subsequently, it was washed with isopropanol and dried at 60 °C in a vacuum oven, yielding a powdered product labeled KPDM.

IV. FINDINGS & DISCUSSION

There is an existence of “stable intercalation state [S.I.S]” when there is successful intercalation of intercalants into the kaolinite interlayer spaces following first order (unstable intercalation process), second (pseudo intercalation process), and third order interaction reactions. The rationalization of this “S.I.S phenomenon” is accounted for in this section as follows:

4.1 First Order Intercalation Reaction

The *in-situ* oligomerization of ferrihydrite intercalant and subsequent intercalation into the kaolinite interlayer spaces was associated with lattice expansion from 3.61 Å to 3.62 Å and intercalation ratio of 76.8% due to the ability of Fe^{3+} to replace the exchangeable water thereby intercalating functional kaolinite layers. Literature indicated that oligomerization process is associated with an interplay between electrostatic and chemical forces of silicic acid and iron oxide surfaces which in turn act in penetrating the layers using the monomeric [Fe-O-Si]-linkages which potentially can transform into Si-O-Si upon increase in Si concentration if oligomerization in not controlled (Dol Hamid et al., 2011; Hayes et al., 1988). This is because it has been established through research that oligomerization involving ferrihydrite is optimum at pH of 4, 7 and 10 when the surfaces are respectively positive, neutral and negatively charged.

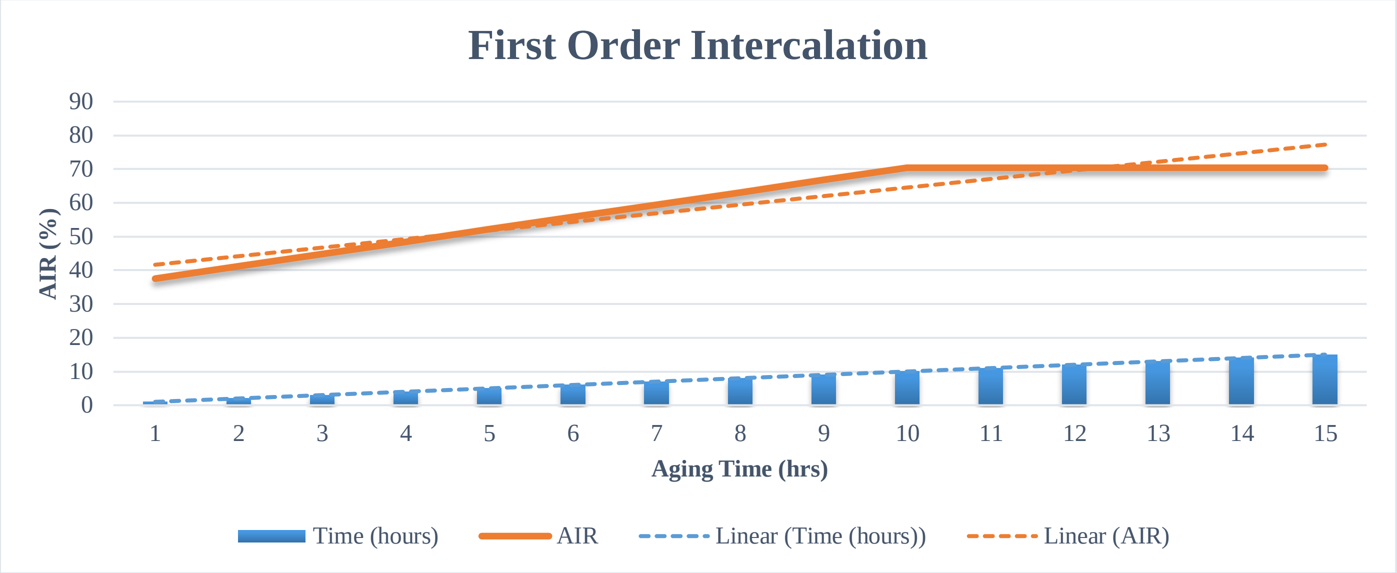

Figure 1

Relationship between the Apparent Intercalation Ratio (A.I.R) and Aging Time for Ferrihydrite Intercalant

4.2 Second Order Intercalation Reaction

In this phase, the oligomerization of hydroxyaluminum aqueous cations was carried out with emphasis on the aging and maturation of the oligomers. Since un-aged hydroxyaluminum solution resulted into negligible intercalation efficiency, there is a need to further investigate the impact of "holding time" on the maturation and aging of the hydroxyaluminum oligomer. On a separate note, intercalation reactions involving cationic oligomerization process are pH sensitive. Nevertheless, preliminary findings revealed that the apparent intercalation ratio of the hydroxyaluminum intercalant directly proportional to the oligomer aging time.

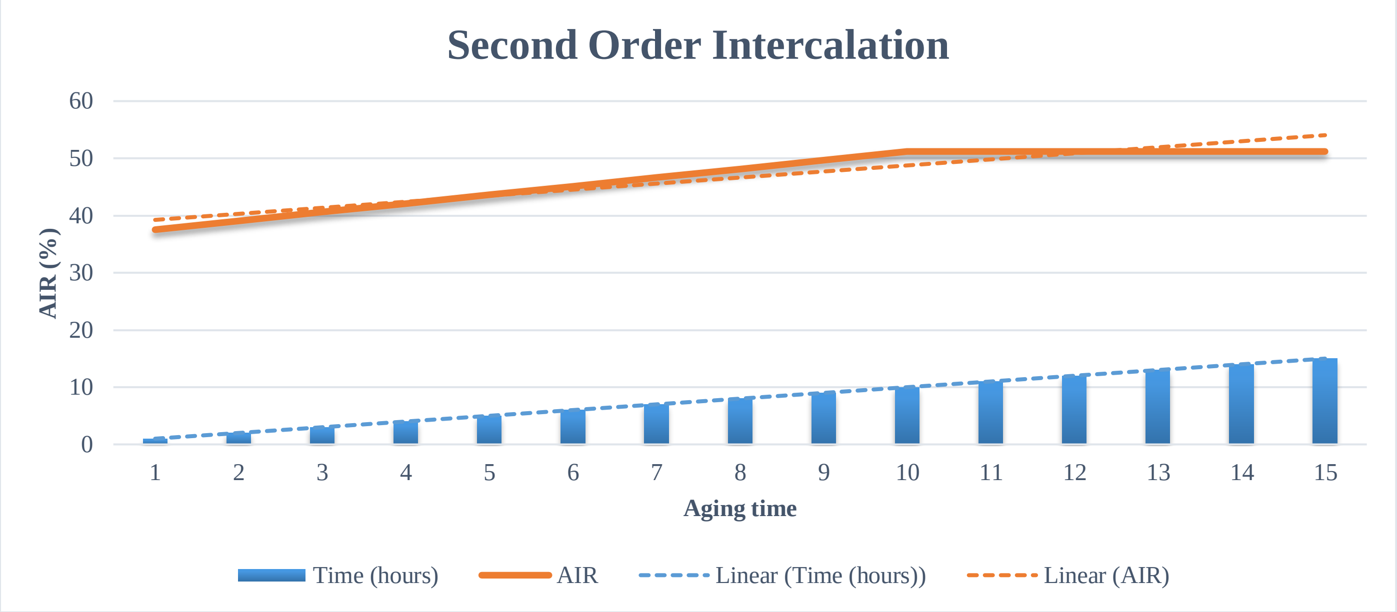

Figure 2

Relationship between the Apparent Intercalation Ratio (A.I.R) and Aging Time for Hydroxyaluminum Intercalant

In additional to that, it was observed that molecular size of the intercalant and temperature do influence intercalation process. However, further analysis of these two parameters are beyond the scope of this paper. Besides, the R-values were also calculated for both reactions and found to be approximately 0.99 indicating a nearly positive linear relationship between AIR and the aging time for the first order and second order reactions. Literature suggest that an R-value which close to 1 signifies a positive linear relationship between the two variables which in our case refer to the AIR and aging time (Asuero et al., 2006).

In view of Figure 1 and 2, it can be seen that the A.I.R is a function of time. The expansion of kaolinite interlayer spaces is directly proportional to the aging time in which the functional kaolinite layers are exposed to the intercalant. The state in which A.I.R remains constant with time is hereby reported as the "Stable Intercalation State" or simply the "S.I.S point.

Nevertheless, the intercept values for both reactions were also calculated and found to be around 35.02 for first order reaction and 33.69 for second order reaction indicating a non-zero intercept. A question could rise as to why the relationship is non-zero while the R-value is close to 1? The underlying assumption behind this observation is the fact the measurements were based on the baseline A.I.R value of 37.53% for the starting materials which was Na-Modified Kaolinite whose activation crystallographic information resulted into this A.I.R value which was the used for both reactions. Another assumption could the time factor was set fixed after each 60 seconds. Therefore, the non-zero intercept for the observed R-values which demonstrate a perfect positive linear relationship is also attributable to the fixed time factor as well as the baseline A.I.R value used.

4.3 Third Order Intercalation Reaction

In view of Figure 3 and 4, the intercalation kaolinite with methanol was associated with an AIR value of 87.4% whereas when intercalant was DMSO the AIR values was found to be 89.2% indicating a superior properties of the later in overcoming the electrostatic forces and some chemical forces acting within the 1:1 functional kaolinite layers. Moreover, the R-values for both intercalant were found to be close to 1 with an intercept value of approximately 31.99 for methanol and 31.79 for DMSO. As previously noted, the initial baseline AIR value was that of Na-activated kaolinite of 37.53 which can be accounted for the non-zero intercept points. The findings also revealed the impact of holding time in the attainment of AIR values until the "S.I.S point" is attained as reflected in the observed positive linear relationship between AIR and aging time.

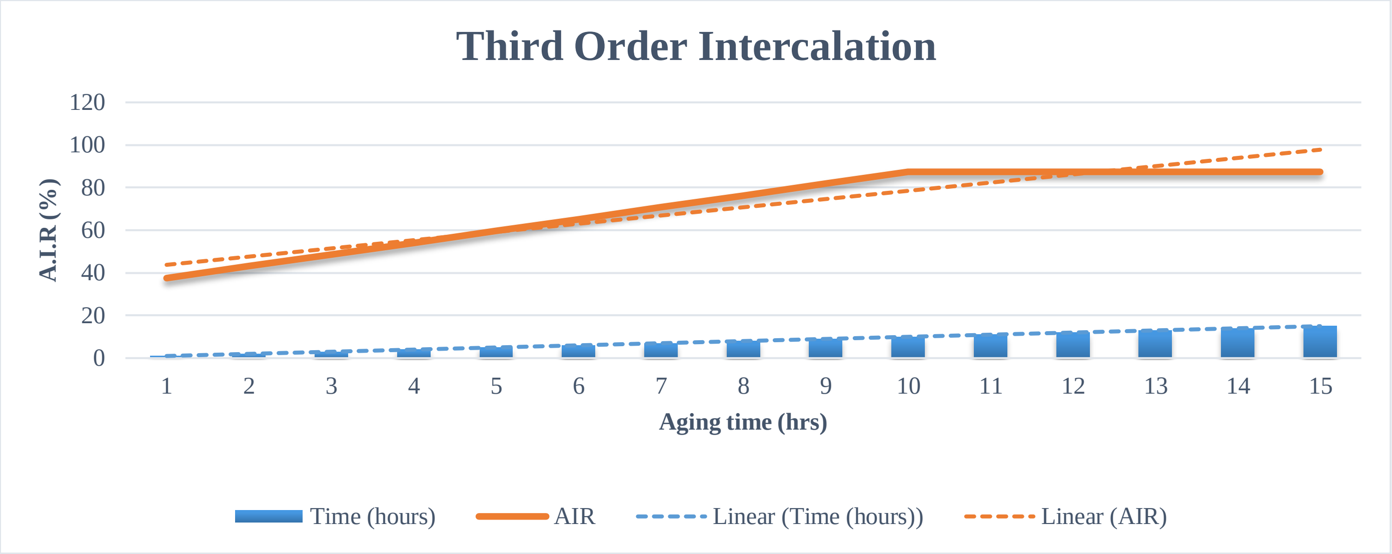

Figure 3

Relationship between the Apparent Intercalation Ratio (A.I.R) and Aging Time for Methanol Intercalant

As a matter of fact, the stabilization of the intercalation state is closely tied to the maturation period, during which the intercalated species undergo a process of aging. This period allows for sufficient time for the intercalating molecules to penetrate the interlayer spaces of the host material, facilitating a reorganization of the internal structure. During this reorganization, the system seeks to minimize its free energy, leading to more stable configurations. This process involves the redistribution of intercalated species within the layers, where they align and arrange themselves to achieve more uniform particle sizes and better-defined surface interactions. This behavior is analogous to the process of Ostwald ripening, where larger, more stable particles grow at the expense of smaller ones, ultimately leading to a more uniform and stable system (Guan & Zhong 2019; Kabalnov, 2001; Voorhees, 1985) as first observed by (Carrado et al., 1997) in the concept of "clay's nucleation and crystallization process" when studying the crystal growth of organohectorite clay as revealed by atomic force microscopy.

As the maturation period progresses, a stable intercalation state is achieved. This is typically characterized by a point where the lattice expansion of the host material becomes constant giving a constant A.I.R values, indicating that the interlayer distance has reached an equilibrium. The intercalated species continue to reorganize within the interlayers, striving for optimal size uniformity, improved surface interaction, and more favorable orientations relative to the host material's layers. This ongoing reorganization reflects the system's attempt to reach a thermodynamically stable state, where all components are optimally positioned within the interlayer spaces.

To accurately confirm that true intercalation has occurred, as opposed to mere surface adsorption of urea particles onto the kaolinite, it is crucial to critically analyze the X-ray diffraction (XRD) patterns of the resulting intercalation compounds. XRD is a powerful tool for identifying the structural changes that accompany intercalation. The appearance of new diffraction peaks, particularly those corresponding to expanded interlayer spacings, is a definitive indicator of successful intercalation. These expanded spacings suggest that the intercalated molecules have penetrated the layers of the host material, causing an increase in the distance between the layers.

Moreover, the stability of these expanded spacings over time, coupled with the attainment of constant changes in A.I.R values (which reflects the proportion of the interlayer volume occupied by the intercalated species), provides further evidence of the attainment of a stable intercalation state. This analysis allows researchers to distinguish between true intercalation, where the interlayer structure is modified, and mere adsorption, where particles simply adhere to the surface without causing significant structural changes. The persistence of these structural modifications in the XRD patterns over the maturation period confirms that the system has reached a stable intercalation state, characterized by uniform particle distribution, well-defined surface interactions, and optimal layer orientation.

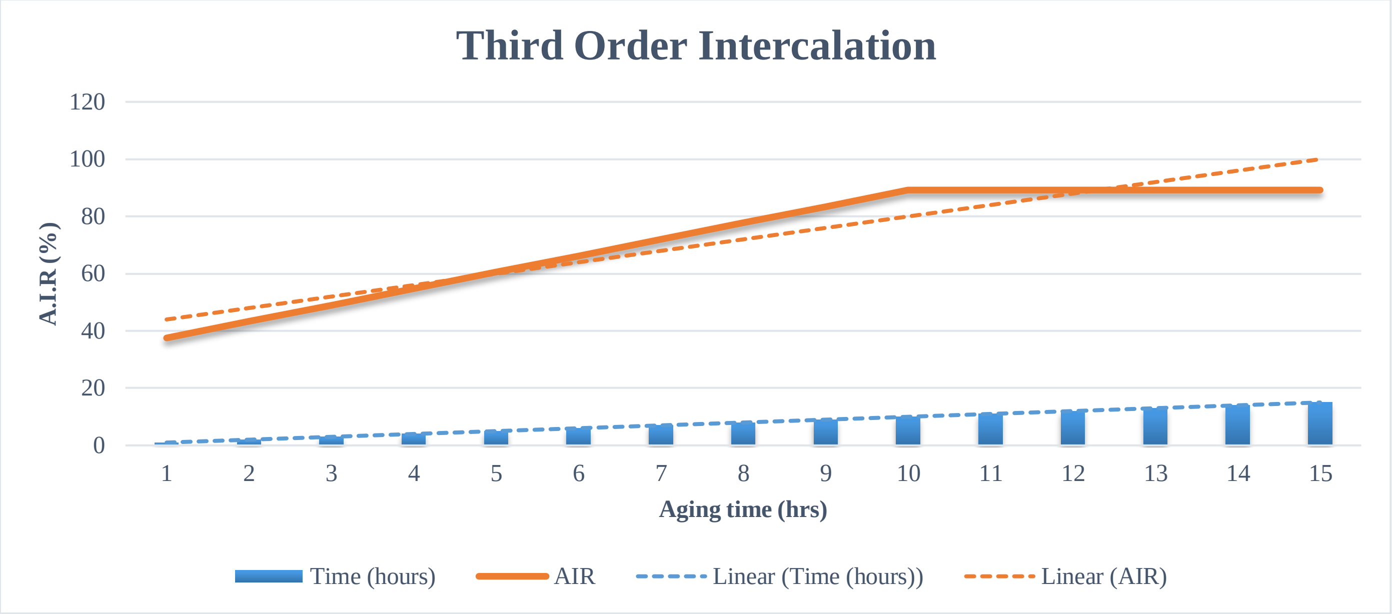

Figure 4

Relationship between the Apparent Intercalation Ratio (A.I.R) and Aging Time for DMSO Intercalant

V. CONCLUSION & RECOMMENDATIONS

5.1 Conclusion

This study’s findings revealed that stable intercalation state (S.I.S) can be obtained by selection of experimental conditions relating to such factors as time of aging, temperature and the nature of intercalant present. The fact that both anionic and cationic intercalants used as guest species were successfully intercalated into the interlayer spaces of kaolinite’s structure shows that kaolinite is capable of controlled intercalation and hence lattice expansion could be predicted. The first, second and third order intercalation reactions bring out the relationship between the structural stability, apparent intercalation ratio and nature of the intercalant as well as varied aging parameters. The findings open up fresh possibilities of the utilization of kaolinite in the designing of controlled delivery systems such as drug delivery systems (DDSs) and controlled release fertilizers (CRFs). Some work could be done particularly in testing the different intercalants and measuring their effects due to the additional improvement of employing different techniques in order to better stabilize the compartmentalized kaolinite systems or their functionality.

5.2 Recommendations

In view of the findings, it is highly recommended to extend experimental studies and literature surveys in order to further investigate the intercalation kinetics related to layered phyllosilicates. The studies could involves release trials and triangulation of the experimentation aspects.

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