

## Synthesis and characterisation of organo-beidellite

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### Introduction

Today, there are growing concerns about the presence of environmental pollutants in many parts of the world. In particular, a lot of attention has been drawn to the levels of water and soil contaminants (de Paiva et al., 2008). The majority of these contaminants consist of NOCs (non-ionic organic compounds) and can enter our waterways through industrial activities, mining operations, crop and animal production, waste disposal and accidental leakage (de Paiva et al., 2008; Park et al., 2011). Therefore, there is an increased interest in the synthesis of new materials that can be used to remove potentially carcinogenic and toxic water contaminants.

Smectite type organoclays are widely used in numerous applications, such as sorbent agents for environmental remediation, due to their unique properties (Jiunn-Fwu et al., 1990; Sheng et al., 1996; Zhou et al., 2007; Bektas et al., 2011; Park et al., 2011). This investigation focuses on beidellite (SBId-1), which belongs to the smectite clay family. Their properties include high cation exchange capacity (CEC), swelling properties, porous, high surface area and consequential strong adsorption/absorption capacity (Xi et al., 2007). However, swelling clays in general are not an effective sorbent agent in nature due to their hydrophilic properties. The hydrophilic properties of the clay can be changed to organophilic by intercalating a cationic surfactant. Many applications of organoclays are strongly dependent on their structural properties and hence, a better understanding of the configuration and structural change of organoclay is crucial.

Organoclays were synthesised through ion exchange of <sup>21</sup>CODTMA (MW: 392.5 g mol<sup>-1</sup>) and characterised using XRD and FTIR spectroscopy. This study investigates the structural and conformational changes of beidellite intercalated with octadecyltrimethylammonium bromide.

### Results and Discussion

The increasing of basal spacing of the clay can be determined by XRD. The *d*-spacing (*d*<sub>001</sub>) of untreated beidellite (1.5 nm) increases after the intercalation of <sup>21</sup>CODTMA. The data displayed in Figure 1 confirms the increasing *d*-spacing as the concentrations of the surfactant increased. However, after reaching a surfactant loading of 1.00 CEC, the *d*-spacing plateaued. This suggests that the bi-layer of beidellite has reached its uptake limit and excess surfactant molecules are adhered to the surface of the clay by van de Waals forces. This is confirmed by the surfactant peaks observed at 1.5

CEC, 2.0 CEC and 1.00 CEC (surfactant peaks are not shown in the XRD pattern). It also indicates that upon 50 % surfactant loading and above, the conformation of surfactant molecules appeared to be in a pseudotrimolecular layer arrangement and lateral monolayer arrangement at a 25 % surfactant loading.

Infrared spectroscopy is used to probe the intermolecular environment of the beidellite and organo-beidellite samples. The regions of interest are 1) the hydroxyl bending at  $1600\text{ cm}^{-1}$ , 2) the C-H stretching at  $2900 - 2800\text{ cm}^{-1}$  and 3) the hydroxyl stretching region between  $3700$  and  $3400\text{ cm}^{-1}$ . The shift of wavenumbers in symmetric  $\nu_s(\text{CH}_2)$  and asymmetric  $\nu_{as}(\text{CH}_2)$  stretching region provide an insight of molecular environment of the intercalated surfactant molecules.

Bands at  $2927$  and  $2849\text{ cm}^{-1}$  (Figure 2a) decreased in wavenumbers whilst increasing in intensity upon an increased concentration of loaded surfactant. These bands observed are also becoming more pronounced as the CEC increased. Changes in the wavenumber position of  $\nu_{as}(\text{CH}_2)$  stretching (from  $2927$  to  $2916\text{ cm}^{-1}$ ) bands suggested that it is sensitive to the conformational changes of amines within the clay interlayer. Xi et al. (2005) reported that  $\nu_{as}(\text{CH}_2)$  stretching modes are more sensitive to conformational ordering than symmetric  $\nu_s(\text{CH}_2)$  stretching modes (Xi et al., 2005). The hydroxyl-stretching region as shown in Figure 2b decreased in intensity as the concentrations of the surfactant increased. The spectra profile in this region ( $3000 - 3550\text{ cm}^{-1}$ ) changes significantly with the concentration of the surfactant molecules. The bands in these region are attributed to the physically adsorbed water.

The broad band at  $1634\text{ cm}^{-1}$  is observed in the HOH bending region of beidellite and is displayed in Figure 2c. The intensity of the band decreased as the surfactant loading increased. This phenomenon also suggested that the physical properties of organo-beidellite have been altered from hydrophilic to hydrophobic (organophilic). The decrease in band intensity in this region can be attributed to the amount of hydrogen bonded water molecules. In short, it is fair to conclude that as the concentration of surfactant increased, more hydrogen bonded water molecules will be replaced by the cationic surfactant molecules (Xi, Ding et al., 2005).

## **Conclusion**

XRD and FTIR technique have been used to study the changes in the basal spacing and wavenumbers of beidellite intercalated with <sup>21</sup>CODTMA. An increase in basal spacing suggesting the inorganic cation has been exchange with an organocation. Infrared spectroscopy also showed that upon intercalation, changes in wavenumbers and intensity of the bands occur as the CEC increased.

Further studies on the adsorption of phenolic compounds, such as nitroaromatics, polychlorophenol and other common environmental contaminants, will have to be performed for organo-beidellite to study its adsorption mechanisms. This type of organoclay can potentially be used as a good adsorbent agent for a number of environmental pollutants.

## **References**

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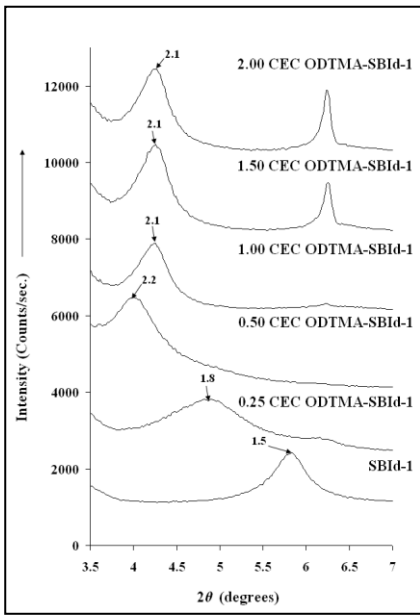
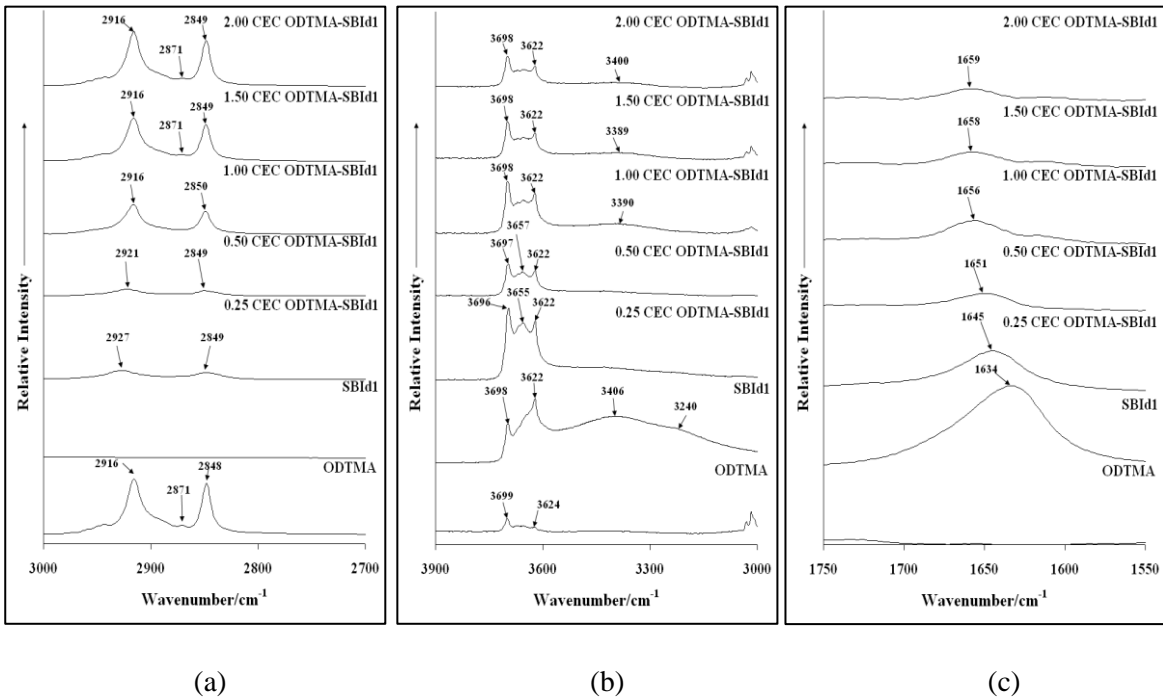


Fig.1. XRD pattern of beidellite and organo-beidellite.



(a)

(b)

(c)

Fig. 2. (a) IR spectrum showing C-H stretching region of beidellite and organo-beidellite, (b) HOH stretching region, (c) Hydroxy bending region