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Research paper

Modification of kaolinite clay using benzyltriethylammonium chloride as a surfactant: Preparation and characterization

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Abstract

Natural kaolinite clay from Perak, Malaysia with cation exchange capacity (CEC) of 2.5 meq/100g was modified using cationic surfactant, benzyltriethylammonium chloride (BTEA-Cl), at 0.5, 1.0, 1.5 and 2.0 times the CEC. A number of techniques, namely energy dispersive X-ray (EDX) spectroscopy, X-ray diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and Brunauer-Emmett-Teller (BET) nitrogen adsorption-desorption were then used for characterization of the kaolinite and/or organo-modified kaolinite clays. The presence of alkyl groups as a result of successful intercalation of cationic surfactant within the organo-kaolinite layers of the clay was exhibited by the FTIR spectra. The SEM microphotographs exhibited good dispersion of the natural clay particles and slight agglomeration in the organo-modified clay particles. XRD patterns showed that the d_{001} spacing of the natural kaolinite clay increased from 7.12 Å to between 7.20 - 7.34 Å for the organo-modified clays. Following the BET nitrogen adsorption-desorption technique, all clay samples were of Type IV with narrow hysteresis loops. Surface areas of the clays showed drastic decrease from (25.34 m^2/g) for natural kaolinite clay to between 5.90 - 13.11 m^2/g for organo-modified clays. The results suggested that modification of natural kaolinite clay using cation surfactant had successfully occurred. The modification can therefore be further applied for alteration and improvement of the properties of natural clays for various industrial applications.

Keywords: *Kaolinite; Cation Exchange Capacity; Benzyltriethylammonium Chloride; Organo-Modification; Characterization.*

1. Introduction

Natural clays have been widely used in different scientific applications, because they can be found abundantly in nature and possess unrivaled characteristics. Properties such as high cation exchange capacity and swelling ability make clays popular in various industrial applications as a sorbent, catalyst, ion exchange, additives, etc. [1].

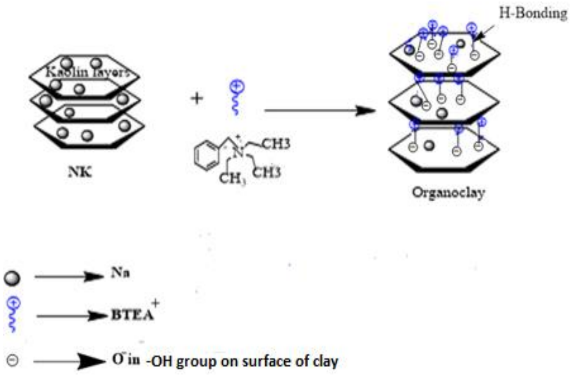
Kaolinite is a clay with empirical structural formula of $Al_2Si_2O_5(OH)_4$ where its structure forms single silica tetrahedral sheet coordinated by oxygen atoms (Si-O-Si) with another single alumina octahedral sheet coordinated to hydroxyl groups, $Al(OH)_3$. Both sheets are combined to form 1:1 ratio of layer [2-3]. Although extensive researches have been carried out on the use of clay as adsorbents, there is a dearth of information in the literature on the utilization of kaolinite clay. In comparison to montmorillonite, kaolinite clay often shows lower surface area, and lower isomorphous substitution which result in lower adsorption capacity and lower cationic exchange ability [4].

In their natural state, the adsorption capacity of kaolinite clays can be modified by various methods to achieve desired chemical, surface, and structural characteristics for use in different industrial applications. The ease of chemical modification of kaolinite by the cation exchange process makes improvement of its hydrophobicity possible to further enhance interactions between organic molecules like enzymes with the clay [5-10].

The kaolinite clay undergoes isomorphous substitutions, which causes it to have a negative net charge. The charge is balanced by alkali metal and alkaline-earth-metal cations such as K^+, Na^+ and Ca^{2+}. The substitution of these inorganic cations by quaternary ammonium cations such as benzyltriethylammonium and hexadecyltrimethylammonium at the exchangeable sites results in formation of organoclay derivatives (Scheme 1) [2, 11].

Characterization of the clays upon modification is necessary, as their applications are very much dependent on the compositional, structural, and physical properties due to the alterations of the layered minerals within the clay. On the other hand, successful utilization of organoclay depends particularly on the chemical stability of cationic surfactants-clay complexes. The nature of the cationic surfactant, the clay, and the chemical composition of the aqueous solution may all affect the stability of the organoclay by influencing the degree of the retention of surfactant via hydrophobic bonding. Long chain quaternary ammonium compounds can either accommodate the outer and/or interlayer surfaces of kaolinite clay by both cationic exchange and hydrophobic bonding. Therefore, the use of varying concentration of the cationic surfactants based on the CEC of the clay is necessary to obtain chemically stable organoclay and ensure complete exchange of inorganic cations [2].

Hence, this study is intended to produce organo-kaolinite by incorporating benzyltriethylammonium chloride (BTEA-Cl), a quaternary amine monovalent cation as surfactant via cation exchange method within the natural kaolinite clay. Effectiveness of the cationic surfactant in modifying the surface of the clay for enhanced adsorption capacity of kaolinite clay was characterized by using XRD, FTIR, SEM and BET.



Scheme 1: A Schematic Diagram of Organo-Modification of Natural Kaolinite Clay (NK).

2. Materials and methods

2.1. Materials

The natural kaolinite was collected from Perak, Malaysia. The surfactant used in this study was benzyltriethylammonium chloride (BTEA-Cl), purchased from Merck, Germany. All other chemicals such as methylene blue, sodium chloride and silver nitrate were of analytical grade. Deionized water (Millipore) was utilized for the preparation of all aqueous solutions.

2.2. Methods

2.2.1. Preparation of the kaolinite clay

The natural kaolinite clay sample was grounded and sieved using analytical sieve shaker (AS200, Retsch, Germany) to obtain 100 mesh of particles. The powder material was heated at 120 ℃ for 5 hours prior to use. The natural kaolinite clay was then analyzed using energy dispersive X-ray (EDX) spectroscopy.

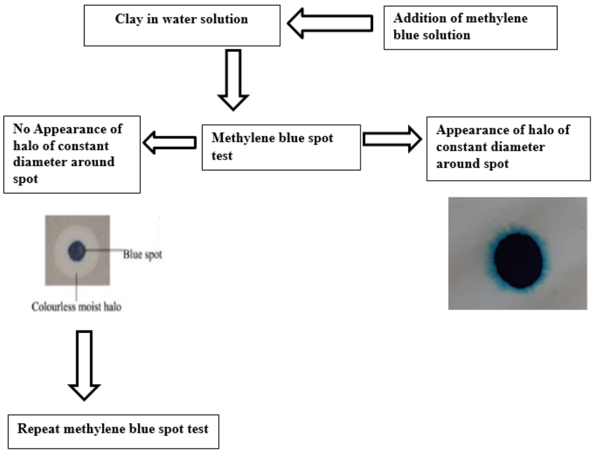
2.2.2. Determination of kaolinite clay cation exchange capacity

Natural kaolinite clay (6 g) was homoionized with 300 ml, 1.0 M sodium chloride, filtered and washed several times with deionized water. Silver nitrate solution was used to detect the presence of chloride residues in the sample after washing. The resultant clay, designated as NK, was dried, before the cation exchange capacity (CEC) of the clay was determined by methylene blue method [12].

The CEC of the clay was calculated by Equation (1) based on volume of methylene blue added to the clay dispersion until saturation point was reached (indicated by the appearance of a halo of constant diameter around a spot of droplet taken from the methylene blue solution). The flow diagram of methylene blue CEC determination procedure is as shown in Scheme 2.

$$\text{Cation exchange capacity (CEC)} = \frac{\text{E} \times \text{V}}{\text{W}} \times 100 \quad (1)$$

Whereby, E is milliequivalents of methylene blue per millilitre, V is volume of methylene blue solution required for the titration, and W is weight of clay sample.



Scheme 2: Methylene Blue CEC Determination Procedure.

2.2.3. Preparation of organo-kaolinite clays

BTEA-Cl of concentrations varying from 0.5 to 2.0 CEC was dis-solved in deionized water. The Na-kaolinite was then added to surfactant solutions, followed by constant stirring of the dispersions at 250 rpm, overnight, and heating of the mixture at 45 ℃ for 10 h. The mixture was then centrifuged at 3000 rpm for 30 min, before it was washed several times with deionized water and dried at 35 °C for 12 h. The organo-clays were designated as 0.5 NK, 1.0 NK, 1.5 NK, and 2.0 NK, referring to the respective CEC values.

2.2.4. Characterization of kaolinite and organo-kaolinite clays

Natural and organo-modified kaolinite clays were characterized using various instruments. In the characterization using X-ray diffractometer (D8 Advance, Bruker AXS), Cu-Kα, run at 40 kV and 40 mA, the samples were placed on the sample holder followed by insertion into the sample chamber and analysis at room temperature with a scan rate of 2θ per minute. X-ray diffractions were recorded using DIFFRAC plus software for data acquisition and analysis.

In the analysis using Fourier transform infrared (FTIR) spectroscopy (Perkin Elmer, Spectrum 400), samples were prepared employing the KBr pellet technique. The (FTIR) spectra were recorded in the range of 500-4000 cm^{-1}.

The analysis using scanning electron microscopy (SEM), Hitachi (S-3400N) of the samples was carried out by sputter coating the samples with a thin film of gold prior to imaging process.

The Brunauer-Emmet-Teller (BET) technique of surface area and porosity analysis was performed using surface area analyser (Micromeritic, ASAP 2020) at 77 K. Prior to nitrogen adsorption, the samples were outgassed at 30 °C for 1 h followed by another 8 h at 40 °C in vacuum.

3. Results and discussion

3.1. Determination of kaolinite clay cation exchange capacity (CEC)

The calculated CEC value of natural clay in this study was 2.5 meq/100 g clay. In general, the CEC value of kaolinite clay is considerably low compared to that of montmorillonite, which is about 100 meq/100 g clay. However, the rate of cationic exchange in kaolinite clay is rapid, and almost instantaneous [13-18].

The value of CEC obtained in this study is in agreement with the findings by Al-Ani & Sarapaa [19], which suggested that the CEC values of kaolinite clays should be in the range of 1-10 meq/100 g clay. They also suggested that lower CEC values are indications of pure kaolinite while higher CEC values indicate existence of additives as a result of successful modifications of the natural clay [20].

In natural kaolinite clay, the edges of crystal where imperfection occurs as a result of bond breakage are electrophilic and capable of trapping hydroxyl groups present in water [21]. This occurrence contributed to the production of silanol (Si–OH) and aluminol (Al–OH) groups at the edges of clay platelets which enable fixation of cations in the mixture [22].

3.2. Characterization of natural kaolinite using energy-dispersive X-ray spectrometer

Results of the elemental analysis of the natural kaolinite clay deter-mined using energy dispersive X-ray (EDX) spectrometer is as shown in Table 1. The results revealed that silica and alumina are major constituents, which existed as Al_2O_3 (36.12%) and SiO_2 (36.04%) along with traces of potassium in K_2O, and iron in Fe_2O_3.

Table 1: Chemical Compositions of Kaolinite Sample

Element	Compound	Compositions %
C	C	24.75
Al	Al_2O_3	36.12
Si	SiO_2	36.04
K	K_2O	1.68
Fe	Fe_2O_3	1.41
	Total	100

3.3. Characterization of kaolinite and organo-kaolinite clays

3.3.1. Analysis using X-ray diffractometer (XRD)

The XRD patterns of natural (NK) and organo-kaolinite are shown in Figure 1. From the XRD pattern of NK, it can be seen that NK possesses crystalline nature constituted predominantly by quartz (Q) phase, together with small amounts of kaolinite (K), muscovite (M), and anatase (A).

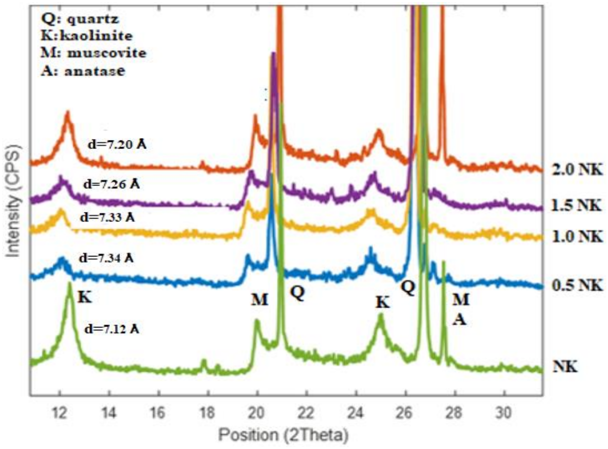


Fig. 1: XRD Patterns of Kaolinite and the Organo-Kaolinite.

The peak at 2θ = 12.4° is the distinctive XRD pattern for kaolinite. In general, X-ray patterns of natural and organo-modified kaolinite showed almost similar structural characteristics where strong peaks at 2θ = 26.7° assigned to quartz (SiO_2) showed no significant change upon modification with $BTEA^+$.

Modification of the kaolinite clay however causes the d_{001} basal spacing to increase from 7.12 Å for NK to 7.34 Å for 0.5 NK, 7.33 Å for 1.0 NK, 7.26 Å for 1.5 NK, and 7.20 Å for 2.0 NK. The expansion of the interlayer space in the clay was due to presence of adsorbed organic modifier ($BTEA^+$) in the interlayers of the clay. The increase could also be due to the presence of smaller particles of clay which may have been formed as a result of treatment with $BTEA^+$ [3, 23], or due to the leaching of Al from the octahedral layer of the clay. Jahan et al. [24] reported that the expansion of the interlayer space in the clay structure is due to the ammonium salt intercalation.

Basal spacing of 0.5 NK was the highest. This could be due to the larger amount of exchangeable alkali metal Na^+ even when lowest concentration of cationic surfactant was used. This could also be due to the high hydration energy of the clay making it able to adsorb water, which causes the basal spacing to expand [25].

In general, the results reported here are better than those reported by Aroke and El-Nafaty [2], where natural kaolinite d_{001} basal spacing increased by 0.0187% indicating the presence of hexadecyltrime-thylammonium ion ($HDTMA^+$) in the clay.

3.3.2. Analysis using Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of natural and organo-modified kaolinite in the range of 500 – 4000 cm^{-1} is shown in Figure 2. The major bands in the FTIR spectra can be observed at 3697 and 3654 cm^{-1} which corresponded to the existence of hydroxyl groups located at the octahedral sheet that are intact with oxygen atoms from the adjacent layers, while major bands at 3621 cm^{-1} corresponded to the existence of hydroxyl groups located in the inner plane of the octahedral sheet, not exposed at the surface of the kaolinite layers [3].

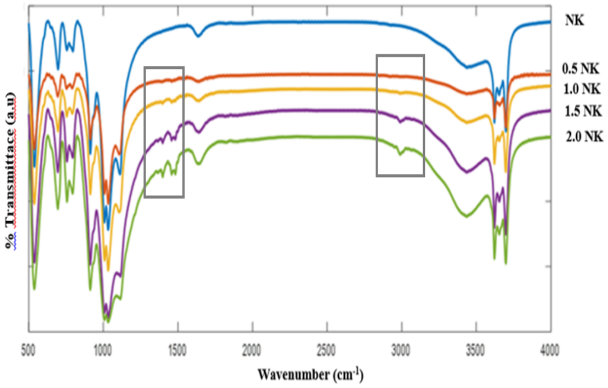


Fig. 2: FTIR Spectra for the NK and Organo-Modified Kaolinite Clays.

On the other hand, bands at 3440 cm^{-1} along with bands at 1636 cm^{-1} existed as a result of vibrations of water molecules. The peaks at 937 cm^{-1} and 913 cm^{-1} indicated the presence of bending of the inner hydroxyl groups linked to Al, peaks at 795, 754, 696 and 537 cm^{-1} corresponded to the vibrations of Si-O-Al groups, and peaks which appeared at 1111, 1032 and 1007 cm^{-1} corresponded to the existence of Si-O-Si molecules in the clay samples. These major bands and peaks of kaolinite were similar to those obtained in previous studies [26-32].

Even after modification of natural kaolinite with $BTEA^+$, the main characteristics of the kaolinite was still maintained. However, width and the positions of the major peaks showed slight shift which corresponded to hydroxyl deformation of the natural clay as a result of modification with $BTEA^+$.

From the FTIR spectra, peaks which corresponded to Si-O stretching was found to be shifted from 1111 cm^{-1} in NK to between 1113-1130 cm^{-1} for modified kaolinite clays, with decreasing intensities. The bands corresponding to the existence of ammonium salt in the clay samples are shown between 2991-2982 cm^{-1}. The intensities of the peaks also showed depletion when compared to that of the natural kaolinite. A similar finding was reported by Ramos et al. [33].

In addition, the peaks at 1474 and 1398 cm^{-1} corresponded to the torsion of the C-H bonds, which is absent in the spectrum of the natural clay sample. A peak at 1457 cm^{-1} corresponding to the existence of CH_3 asymmetric bend can also be observed from the spectra of the modified kaolinite. According to Mota et al. [34], the presence of CH_2 and CH_3 in the FTIR spectrum of the modified clays are clear indications that intercalation of the ammonium quaternary cation within the interlamellar spaces of the kaolinite samples have taken place and that modification using BTEA-Cl had successfully occurred.

3.3.3. Analysis using Scanning electron microscopy (SEM)

The surface morphologies of the clay samples were characterized using SEM as shown in Figure 3. The micrograph of NK showed existence of distorted platelets consisting laminar particle aggregates of varying sizes, which form blocks with variable thicknesses. This indicates that the particles of natural kaolinite consisted of individual layers closely packed together and not fully dispersed. Such formation was due to the domination of hydrogen bonds in the clay structure.

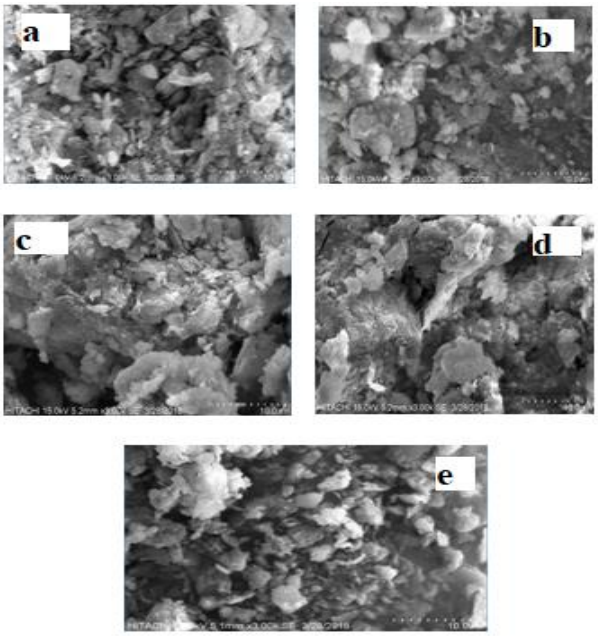
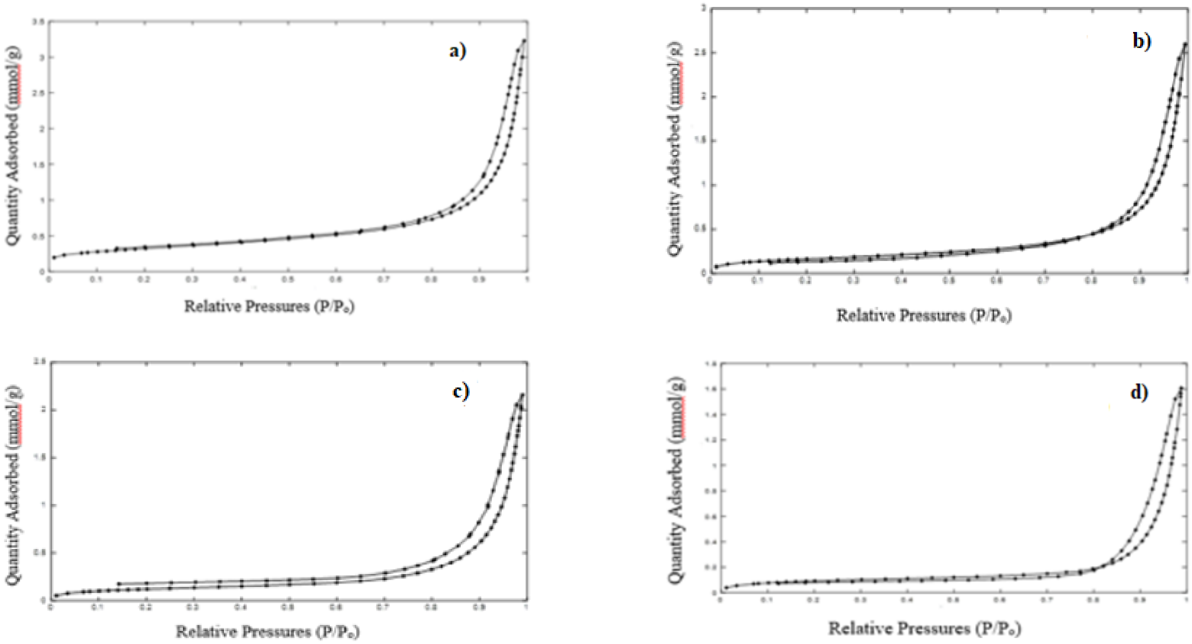


Fig. 3: SEM Images of a) NK, b) 0.5 NK, c) 1.0 NK, d) 1.5 NK, e) 2.0 NK Viewed at 3000x Magnifications.

The NK however showed changes in its morphology upon modification with BTEA$^+$, where the organo-modified kaolinite samples had formed considerably larger aggregates of particles. These were accompanied by smaller particles on the surface of the clay, which indicated the homogeneous distribution of BTEA$^+$ on the kaolinite clay.

3.3.4. Analysis using Brunauer-Emmet-Teller (BET) nitrogen adsorption-desorption technique

Nitrogen adsorption-desorption isotherms as a result of the analysis using BET technique on natural and modified kaolinite clays are as shown in Figure 4. The adsorption isotherms for all the samples showed hysteresis loops indicated as type IV isotherm. These occur on porous adsorbents with pores in the range of 1.5-100 nm. At higher pressure, the slopes show increased uptake of adsorbate as pores become filled with inflection points occurring near completion of the first monolayers. The existence of narrow hysteresis loops is typical of porous solids consisting particle aggregates. These revealed that the porosities of the clay samples were still maintained even after organo-modifications. The low amounts of nitrogen adsorbed at relative pressures, P/Po < 0.2 however, indicated the absence of microporosity in the kaolinite clays. Rapid increase in the volumes of nitrogen adsorbed starting from P/Po ~ 0.8, was due to the filling of the mesopores of the larger particles in the kaolinite clays as well as those particles located at the surface of the clays.



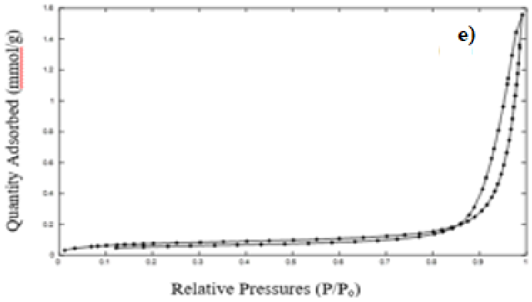


Fig. 4: Nitrogen Adsorption-Desoprtion Isotherms of of a) NK, b) 0.5 NK, c)1.0 NK, d) 1.5 NK, e) 2.0 NK.

Results of the textural analysis of surface area, pore volume, and pore size for natural and organo-modified kaolinite clay samples are summarized in Table 2. The surface area of NK was 25.34 m^2/g and is almost similar to the surface area of kaolinite clay examined by Yanguatin et al. [35]. The surface area of NK however decreased after organo-modification in the order of: NK > 0.5 NK (13.11 m^2/g) > 1.0 NK (9.59 m^2/g) > 1.5 NK (7.30 m^2/g) > 2.0 NK (5.90 m^2/g).

Table 2: Surface Area and Porosity of Natural and Organo-Modified Kaolinite Clays

Clay sample	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (Å)
NK	25.34	0.113	179
0.5 NK	13.11	0.090	244
1.0 NK	9.59	0.075	286
1.5 NK	7.30	0.055	316
2.0 NK	5.90	0.054	385

Higher concentrations of organic modifier (surfactant) used, resulted in lower BET surface areas and pore volumes, which was in agreement with previous work [33]. These results supported the idea that the organic moieties of the surfactant are covalently linked to the edges of -OH groups of individual clay platelets, which then eclipse parts of the kaolinite surfaces, making them inaccessible for nitrogen adsorption [36]. In addition to the pore blocking effect, decrease in the BET surface area of the modified clays was also due to the existence of exchanged cations, which may have clogged pores of the clay.

In general, the lower pore volumes of organo-modified clay samples compared to the natural kaolinite clay was due to pore fillings by the macromolecules of $BTEA^+$ [36-37]. However, modification of kaolinite clay by the cation exchange resulted in increased pore sizes which was an indication that the $BTEA^+$ molecules have been inserted in the mesopore spaces of the clay.

4. Conclusion

The desired properties of kaolinite clay can be achieved by organo-modification by cation exchange process. This was proven by characterization using EDX, XRD, FTIR, SEM and BET nitrogen adsorption-desorption techniques. The outcomes of this study showed that the overall structure of kaolinite clay was not affected after the cation exchange process. Physical properties of the clays, which include surface area, total pore volume and pore size however depend on the amount of organo-modifier employed. In short, the cation exchange process can be further exploited to produce inexpensive and compatible modified adsorbent clays for various industrial applications which may replace the current use of hazardous and expensive adsorbents.

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