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# Measurement of Surface Area of Modified Clays by Ethylene Glycol Monoethyl Ether Method

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Determination of clay mineral surface area using Brunauer-Emmet-Teller (BET) method and other methods can be expensive and time consuming in addition to the drawback of measuring only external surface area. The ethylene glycol monoethyl ether (EGME) method is relatively inexpensive and is able to measure not just the area of external surfaces but also internal surfaces. In this study, the surface area of modified and unmodified clay minerals such as kaolinite, palygorskite, saponite and montmorillonite were determined using the EGME method. The modified forms of the clays were acid activated clays, organoclays and homoionic montmorillonites. Acid activated clay minerals were produced by treating the unmodified clay minerals with hydrochloric acid. Organoclays were produced (from only saponite and montmorillonite as they have relatively high cation exchange capacity) by treatment with dodecyldimethylammonium bromide. Homoionic montmorillonites were produced using the relevant metal chloride salt. Clays without interlayer cations such as kaolinites have lower EGME-surface area than those with interlayer cations. The modification of the clay minerals to produce organo clay mineral and acid activated clay mineral led to reduction and increase in the EGME-surface area of the clay minerals respectively in comparison with their unmodified counterparts. Also, the modification of the interlayer cations of montmorillonites to produce homoionic montmorillonites influences the EGME-surface area with potassium-montmorillonites having the lowest EGME-surface area among $Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Zn^{2+}$, $Al^{3+}$ and $Fe^{3+}$-montmorillonite studied.

**Keywords: Clay minerals, Organoclay, Acid activated clay, Homoionic montmorillonite, Surface area.**

## INTRODUCTION

Clay minerals are hydrous alumino silicates and are abundant in soils and sedimentary rocks [1]. They are very important minerals as a result of their surface properties and the fact that they are reactive, hence making them very useful in industrial applications and environmental control [2-4]. For example, the properties of clay minerals such as acidity, high surface area and cation exchange capacity (CEC) make them to play important roles such as catalysts, supports and adsorbents for toxic substances [2,3]. Generally, phyllosilicates contain layer structures in which each layer is made of tetrahedral and octahedral sheets that are joined in either 1:1 ratio such as kaolinite or 2:1 ratio such as smectite [1]. The surface properties of clay minerals is a function of the chemical composition and nature of the surface atoms, extent and type of defect sites, layer charge and the type of exchangeable cations. The behaviour and role of clay minerals in biogeochemistry is principally due to their surface properties which include surface chemistry, cation exchange capacity and surface area [5]. Surface chemistry of clay minerals is a function of the siloxane surface and the hydroxyl surface. The siloxane surface is composed of the basal oxygen atoms of the Si-tetrahedral and is the principal surface for the 2:1 clay minerals such as smectites whereas the surface for the 1:1 clay minerals includes the siloxane surface and the hydroxyl surface from Al-octahedra. The siloxane surface can either be neutral or with permanent charge. The neutral siloxane surface is the least reactive surface in clay minerals and normally exists in 2:1 phyllosilicates where there is no isomorphous substitution. The neutral siloxane surface is also found on Si-tetrahedra side of 1:1 kaolin. The neutral siloxane surface is a Lewis base as it is an electron pair donor but it is really a very weak electron donor [5]. The implication of this is that the clay minerals where the dominant surface is the neutral siloxane surface will tend to be hydrophobic. Talc and pyrophylite are examples of clay minerals with dominant neutral siloxane surface and are hydrophobic. The neutral siloxane surface will hardly interact with polar molecules such as water given that it is non-polar [6,7]. Unlike the neutral siloxane surface that has a very low affinity for polar molecules, non polar organic molecules can interact with the neutral siloxane surface. It

has been reported that some non-polar regions can exist between hydrated cation sites on the basal surface of smectites and vermiculites [8]. These sites can therefore be accessed by non-polar compounds. However, the ability of non-polar compounds to access the non-polar regions of the clay surface is a function of the clay surface charge density, nature of the exchangeable cation and its corresponding enthalpy of hydration. Smectites with relatively low surface charge density and containing weakly hydrated exchangeable inorganic cations (*e.g.* $K^+$ and $Cs^+$) will interact more strongly with organic molecules [8]. Unlike the neutral siloxane surface, the hydroxyl surface interacts strongly with water. The hydroxyl surface is prominent among the kaolin group such as kaolinite. The terminal hydroxyl groups, OH groups located at the broken edges of the clay minerals is chemically more reactive than the basal charge-neutral hydroxyls. The terminal OH groups are under-coordinated and as a result carry a positive or negative charge depending on the type of metal ion and the pH of the aqueous dispersion. The terminal OH groups have the potential to chemisorb certain ions irrespective of the pH. Example, terminal Al-OH and Fe-OH groups have high affinity for phosphate ions [5]. The siloxane surface with permanent charge arises as a result of isomorphous substitution in the clay mineral structure that leads to the enhancement of the Lewis base character of the siloxane surface. This effect is more obvious if the isomorphous substitution is in the octahedral sheet as this leads to a more delocalized negative charge. The negative charge that results from the isomorphous substitution is balanced by exchangeable cations such as $Na^+$, $K^+$, $Mg^{2+}$ and $Ca^{2+}$. These exchangeable cations have different ionic radius, hydration energy and hydrolysis constant. Consequently, the physico-chemical properties of clay minerals will vary in accordance with the exchangeable interlayer cations of the clay minerals [5]. The cation exchange capacity of clay minerals is a measure of their ability to adsorb cations from solution. It has been defined as the quantity of cations that are available at a given pH for exchange with other cations and is usually expressed in milliequivalents/100 g of dry clay [9]. The adsorbed cation replaces or exchanges the original negative layer charge balancing cation in solution. This ability of colloidal particles such as clay minerals to retain and exchange positively charged ions is vital as it has a controlling influence on the mobility of positively charged chemical species both in soils and geochemical cycling of cations in general [10]. Cation exchange capacity is normally associated with clay minerals with interlayer exchangeable cations such as smectites. The cation exchange capacity process is a reversible process. It is also stoichiometric and diffusion controlled. The surface area of clay mineral is derived from external and internal surfaces [11]. It follows therefore that clay minerals with both internal and external surfaces will have surface areas larger than those with only external surfaces. This explains why smectites such as montmorillonites have higher surface areas than kaolinites. The ability of the clay mineral surface to adsorb reacting species increases the concentration of the reactants on the surfaces hence the high surface area confers a local concentration effect to the clay minerals [12]. Clay minerals especially the phyllosilicates have dimensionality less than three making it possible for reacting molecules to have higher chances of colliding than molecules in three dimensions [12]. The combined effects of low dimensionality and local concentration effects, enhances the collision frequency of the reactants on clay minerals and hence promotes reactivity [12]. Clay minerals commonly exist in unmodified-, organo-, acid activated- and cation exchanged forms. Producing organoclay minerals in practice requires the replacement of the interlayer exchangeable inorganic cations with organic cations through ion-exchange reactions. The resultant organoclay modifies the surface of the original clay mineral from being hydrophilic to being hydrophobic [13,14].

Quaternary ammonium ions $[(CH_3)_3NR]^+$ or $[(CH_3)_2NR_2]^+$ are the most common organic cations (where R is an aromatic or aliphatic hydrocarbon) used in the production of organoclay material [15].

For industrial or scientific research purposes, acid activated clay mineral is prepared by washing or treating the clay mineral with strong mineral acids such as sulphuric or hydrochloric acid. This treatment of clay minerals with strong inorganic acids is called acid activation, acid washing or dissolution. During the process of activation, the acid exchanges its protons for the interlayer exchangeable cations and partially dissolves the clay crystalline structure by leaching some of the cations such as $Mg^{2+}$, $Al^{3+}$ or $Fe^{2+}$. The net effect of this is a product with increased surface acidity, specific surface area and porosity, called acid activated clay mineral [16,17]. Acid activated clay minerals can occur naturally in the environment by the attack of acid on clay minerals as is the case with the acid mine drainage interacting with clay minerals [18,19]. The homoionic clay minerals are usually generated by exchanging the interlayer cations of unmodified clays with excess metallic chloride of the required metallic ion to produce the desired homoionic clay mineral *via* cation exchange reactions [20].

The specific surface area of clay minerals can be measured by the low temperature nitrogen adsorption method involving the Brunauer-Emmet-Teller (BET) method in which the nitrogen adsorption isotherm is used in determining the surface area [21]. However, the low temperature nitrogen adsorption BET method is only able to measure the external surface area of clay minerals. Water sorption and methylene blue adsorption methods have been proposed [22,23]. The method of ethylene glycol appears to be fairly successful and have been reported since 1950 [24,25]. The drawbacks associated with these methods are the fact that they require special apparatus, quite expensive and time consuming. The ethylene glycol monoethyl ether (EGME) method which is relatively quick and inexpensive is able to measure both the internal and external surface area of clay minerals [26,27]. However, the EGME-surface area of modified clays is not yet reported. Hence, the EGME method was used in this study to determine the surface area of modified and unmodified kaolinite, palygorskite, saponite and montmorillonite.

## EXPERIMENTAL

Clay minerals used in this study were kaolinite, palygorskite, saponite and montmorillonite (obtained from bentonite). Kaoline (polywhite E) and bentonite (Berkbent

163) were supplied by Imerys and Steetley bentonite & absorbent Ltd respectively and were the sources of kaolinite and montmorillonite respectively. Saponite is a component of the orrock basalt quarry rock samples collected from Burntisland, Scotland. The palygorskite (PF1-1) was supplied by Clay Mineral Society. All the chemicals were supplied by Sigma Aldrich.

**Experimental procedures for the production of modified clays**

**Acid activated montmorillonite:** Hydrochloric acid concentration of 3 M and solid/liquid ratio of 1:3 (w/w) at a temperature of 70 °C for 45 min were employed for producing the acid activated clays. Approximately 10 g of the prepared acid activated clay sample was dispersed in 500 mL deionized water and centrifuged. The supernatant was decanted and the clay repeatedly washed following the same procedure until there was no detectable chloride from the chloride analysis using ion-chromatography.

**Determination of chloride using ion chromatography:** The supernatant collected after the acid-treated clay mineral had been washed repeatedly was analyzed for chloride using a Dionex ICS-1000 ion chromatograph. This ion chromatography system has an AS40 auto sampler and Ion PAC AS14A Analytical column. The flow rate through the column was 1 mL/min. The eluent was a 8.0 mM $Na_2CO_3$/1.0 Mm $NaHCO_3$ solution and the injection loop was 25 µL. Chloride in the sample was detected *via* a conductivity cell that measured the electrical conductance of the sample chloride ions as they emerged from a suppressor thus producing a signal based on specific chemical/physical properties of chloride ions.

**Homoionic montmorillonite clay minerals:** The homoionic montmorillonites were generated from exchanging the interlayer cations of unmodified montmorillonite with $K^+$, $Na^+$, $Ca^{2+}$, $Zn^{2+}$, $Al^{3+}$ and $Fe^{3+}$ to produce, Na-montmorillonite, K-montmorillonite, Ca-montmorillonite, Zn-montmorillonite, Al-montmorillonite and Fe-montmorillonite. 0.5 M solution of the corresponding metal chloride salt was prepared and then 200 mL of each of the solution used to disperse 5 g of montmorillonite clay mineral to have a clay suspension [20]. The suspensions were shaken for 24 h in a mechanical shaker and then subsequently centrifuged. The supernatant was removed and the clay mineral (homoionic montmorillonite) washed repeatedly until the chloride level is negligible.

**Organoclay:** Appropriate amounts of unmodified saponite and unmodified montmorillonite were dispersed in 1.5 L of deionized water and stirred for about 24 h. Solution of dodecyldimethylammonium (DDDMA) bromide corresponding to 35 % cation exchange capacity of the clay was added to the clay suspension and stirred for 24 h. Thereafter, the clay suspension was centrifuged and the supernatant rejected while the clay was washed several times by deionized water and centrifuging. The organoclay obtained was dried at 48 °C and stored in a dessicator.

**Characterization of clay samples**

**XRD:** The basal spacings of the clay samples were measured by XRD. The samples were prepared for XRD measurement by orienting the clays in a glass slide following standard procedure. The slides were air dried and placed in a desiccator containing silica gel to prevent rehydration. Glycolated and heat treated (300 °C) samples were also prepared following standard procedure. The XRD was observed using Cu-$K_\alpha$ generated at 40 Kv and 40 mA using PANalytical X'Pert Pro MPD fitted with an X'Celerator machine. The data was collected over a range of 2-70° 2θ with a nominal step size of 0.0167° 2θ and nominal time per step of 1.00 second. Data were interpreted by reference to X'Pert accompanying software program High Score Plus in conjunction with the ICDD Powder Diffraction File 2 database and the Crystallography Open Database.

**FTIR:** The samples were prepared using KBr pellets at sample concentration of about 1 % and the Fourier transform infrared spectra of the clay samples were recorded on Thermo Nicolet Nexus 870 fitted with a transmission accessory and equipped with a DTGS detector. The spectrum of the clay sample was collected, by collecting 100 scans over a wavenumber of 4000-400 $cm^{-1}$ at 4 $cm^{-1}$ resolution.

**Cation exchange capacity:** The cation exchange capacity of the clay samples was determined following the standard ammonium acetate method [28].

**pH:** The pH of the clay suspension (250 mg in 10 mL deionized water) was measured with a pH meter.

**Total organic carbon:** Total organic carbon (TOC) was measured to characterize the organoclay produced in this study. Approximately 100 mg of organoclay sample in a porous crucible was treated with sufficient (about 1 mL) hydrochloric acid at a concentration of 4 M in order to remove any carbonates that may be present. After the acid has drained from the crucible for about 4 h, the crucible and sample were dried overnight at 65 °C. Residual (organic) carbon was then determined using a Leco CS244 Carbon analyzer. This instrument uses a flow of oxygen that enables the sample to be ignited in an induction furnace so as to convert all residual carbon in the sample to carbon dioxide. The infrared detector in the instrument measures the carbon dioxide. Prior to running the sample, a blank was run to detect any background residual carbon in all the apparatus that are to be used.

The organic carbon content is calculated as follows:

$$\text{Organic carbon } (\%) = C_s - C_{bl} \quad (1)$$

where $C_s$ and $C_{bl}$ are organic carbon content of sample and blank respectively.

**Surface area determination:** The surface area of the clay samples were measured by the EGME method following the method of Carter *et al*. [29] as modified by Cerato and Lutenegger [27]. The main pieces of equipment employed were a rotary vacuum pump, analytical balance, aluminium weighing dishes (about 6 cm diameter) and glass desiccators. The chemicals used were calcium chloride (desiccant), Ca-montmorillonite (used as a standard) and EGME.

To prepare the desiccant, 100 g of oven dried $CaCl_2$ was mixed with 20 mL EGME in a beaker, thoroughly stirred and put in glass dish and positioned in the base of the desiccator. An aluminium dish was weighed to four figures and recorded as M1. Approximately 1 g of clay (dried overnight at 80 °C and allowed to cool) was added to the dish and the new mass recorded as M2. This procedure was repeated for a further four clay samples including the control sample. Immediately

after weighing, 3 mL EGME was added to the dry clay in each dish. The dishes were transferred to desiccators containing a mixture of dried $CaCl_2$ and EGME desiccant. Dishes were arranged around the circumference of the desiccant tray cover. The desiccator lid was replaced and allowed to stand for 1.0-1.5 h. The system was evacuated overnight under vacuum. Vacuum was released and dishes weighed rapidly every 12-16 h until a stable mass was achieved which was recorded as M3.

The surface area was calculated from the equation:

$$S = [(M3-M2)/(M2-M1)]/K \quad (2)$$

where, S = surface area, M1 = Weight of dish (g), M2 = Weight of dish and dry sample (g), M3 = Weight of dish and dry samples and EGME, K = Weight of EGME required to form a monolayer over 1 $m^2$ surface = $2.86 \times 10^{-4}$ g.

## RESULTS AND DISCUSSION

**XRD and FTIR:** The $d_{001}$ reflections at 17.2, 12.5 and 10.6 Å on ethylene glycolation, air dried and heat treated are indicative of montmorillonite with monovalent cation in the interlayer whereas the $d_{001}$ reflections at 16.2 Å, 14.5 Å and 12.7 Å on ethylene glycolation, air dried and heat treated, respectively are indicative of trioctahedral smectite such as saponite with a divalent metal in the interlayer. The FTIR absorption band at 3623 $cm^{-1}$ is due to OH-stretch of Al-Al-OH typical of montmorillonites. The acid activated-, organo- and unmodified saponite showed absorption band at 3570 $cm^{-1}$ due to $Mg/Fe^{2+}$-OH stretch vibration of Fe-rich saponite [30]. The layer collapse on heat treatment of the organoclay samples is lower than that for the unmodified clay samples and is due to the intercalation of the dodecyldimethylammonium (DDDMA) ion in the organoclay. The absorption bands at 2861 and 2935 $cm^{-1}$ observed with the organoclay samples are due to $CH_2$ symmetrical and asymmetrical vibration stretch respectively from alkyl chain moiety of the dodecyldimethylammonium.

The unmodified kaolinite sample seemed to be contaminated by montmorillonite and illite ($d_{001}$ reflection at 17.2 Å on ethylene glycolation for montmorillonite contamination and $d_{001}$ reflection at 10.0 Å which remained unchanged on heat treatment on ethylene glycolation for illite contamination) (Table-1). This contamination may be due to the intergrowth of these minerals with kaolinite [31,32].

The broad IR absorption band observed at 3623 $cm^{-1}$ in the spectra for acid activated and unmodified montmorillonite corresponds to OH-stretching of Al-Al-OH which is typical of dioctahedral smectites such as montmorillonites. Both acid activated kaolinite and unmodified kaolinite showed doublet absorption band at 3619 and 3700 $cm^{-1}$ typical of kaolinites. The OH-stretching band at 3616 $cm^{-1}$ is characteristic of palygorskite. The bands at 3400 and 3541 $cm^{-1}$ are assigned to bound molecular water and unbound zeolitic water molecules respectively within the palygorskite channels. However, the acid activated montmorillonite and saponite and some of the homoionic montmorillonites did not show any absorption band at 1430 $cm^{-1}$ (which is normally assigned to carbonates such as calcite) as the carbonates must have been digested during the acid activation process and cation exchange reaction.

### EGME-surface area of the modified clays

**Acid activated clay samples:** The EGME-surface area of the acid activated clay samples was higher than that for their organo-, homoionic- and unmodified counterparts. This is suggested to be due to the ability of the activating acid (HCl) to digest non-clay materials such as carbonates (absence of FTIR absorption band at 1430 $cm^{-1}$) and partially leach out the cations located in the crystal structure of the clay during the acid activation process. Consequently, there is the delaminating of the clay that gives rise to increased surface area [16,17,33,34]. The increased surface area resulting from acid activation finds application in the refining of vegetable oils [33,34] and catalysis of esterification reactions [20,35]. The order of the increase in surface area of the acid activated clay samples is the same with unmodified clay samples: KA < SA < PA < BA. Also, the acid activated clay samples have increased acid sites hence producing the lowest pH when dispersed in water (Table-2).

TABLE-1
BASAL SPACING OF 001 REFLECTIONS AND SELECTED FTIR ABSORPTION BANDS OF THE CLAY SAMPLES

| Sample | XRD | | | FTIR | |
|---|---|---|---|---|---|
| | d-spacing (Å) | | | Absorption band ($cm^{-1}$) | |
| | Ethylene glycolated | Air dried | Heat treated (300 °C) | | |
| Acid activated montmorillonite (BA) | 16.8 | 14.8 | 10.1 | 3623 | |
| Organo-montmorillonite (BO) | 16.8 | 14.2 | 13.2 | 3623, 2935, 2861 | 1430 |
| Unmodified montmorillonite (BU) | 17.2 | 12.5 | 10.6 | 3623 | 1430 |
| Acid activated kaolinite (KA) | 7.2(17.2) (10.0) | 7.2 (10.0) | 7.2 (10.0) | 3619, 3700 | |
| Unmodified kaolinite (KU) | 7.2(17.2) (10.0) | 7.2 (10.0) | 7.2 (10.0) | 3619, 3700 | |
| Acid activated palygorskite (PA) | 10.6 | 10.6 | 10.6 | 3616, 3400, 3541 | |
| Unmodified palygorskite (PU) | 10.6 | 10.6 | 10.6 | 3616, 3400, 3541 | |
| Acid activated saponite (SA) | 16.2 | 13.6 | 12.2 | 3570 | |
| Organo-saponite (SO) | 14.8 | 14 | 13.8 | 3570,2935,2861 | 1430 |
| Unmodified saponite (SU) | 16.2 | 14.5 | 12.7 | 3570 | 1430 |
| Na-Montmorillonite (B-Na) | 17.2 | 12.7 | 10.0 | 3623 | 1430 |
| K-Montmorillonite (B-K) | 17.1 | 12.6 | 10.3 | 3623 | 1430 |
| Mg-Montmorillonite (B-Mg) | 17.1 | 14.5 | 10.1 | 3623 | 1430 |
| Ca-Montmorillonite (B-Ca) | 17.2 | 14.4 | 10.3 | 3623 | 1430 |
| Zn-Montmorillonite (B-Zn) | 17.1 | 14.6 | 10.2 | 3623 | |
| Al-Montmorillonite (B-Al) | 17.0 | 14.4 | 10.3 | 3623 | |
| Fe(III)-Montmorillonite (B-Fe) | 17.0 | 14.5 | 10.3 | 3623 | |

TABLE-2
EGME-SURFACE AREA, pH AND CATION EXCHANGE CAPACITY (CEC) OF THE CLAY SAMPLES

| Sample | pH | Surface area ($m^2$/g) | CEC (meq/100 g) | TOC (%) |
|---|---|---|---|---|
| Unmodified montmorillonite | 9.0 | 645 | 83.3 | 0 |
| Organo-montmorillonite | 9.0 | 471 | - | 7.3 |
| Acid activated montmorillonite | 4.1 | 722 | - | 0 |
| Unmodified saponite | 9.2 | 473 | 35.4 | 0 |
| Organo-saponite | 9.1 | 330 | - | 3.4 |
| Acid activated saponite | 4.3 | 532 | - | 0 |
| Unmodified palygorskite | 6.5 | 502 | 16.5 | 0 |
| Acid activated palygorskite | 4.2 | 567 | - | 0 |
| Unmodified kaolinite | 5.0 | 36 | 3.5 | 0 |
| Acid activated kaolinite | 4.4 | 39 | - | 0 |
| Na-Montmorillonite | 7.8 | 570 | 83 | 0 |
| K-Montmorillonite | 7.8 | 455 | 76.4 | 0 |
| Mg-Montmorillonite | 7.8 | 522 | 81 | 0 |
| Ca-Montmorillonite | 7.6 | 598 | 79.1 | 0 |
| Zn-Montmorillonite | 5.9 | 525 | 73.8 | 0 |
| Al-Montmorillonite | 4.7 | 513 | 65.9 | 0 |
| Fe(III)-Montmorillonite | 4.9 | 646 | 88 | 0 |

**Organoclay:** The EGME-surface area of organoclay is lower than the other types and forms of clay (Table-2). This is mainly due to the existence of hydrophobicity (introduced into the clay by the organic cation) that hinders access to the interlayer surface by the EGME which is polar and hydrophilic. The organic phase of the organoclay in this study was confirmed by the FTIR absorption bands at 2861 and 2935 $cm^{-1}$, TOC values of 7.3 and 3.4 % and XRD (heat treated) layer collapse of 13.2 and 13.8 Å for organomontmorillonite and organosaponite respectively (Tables 1 and 2).

The intercalation of the interlayer of the montmorillonite and saponite with a large organic cation such as didecyldimethylammonium ion blocks off the hydrophilic interlayer that ordinarily would have been available for the EGME to access.

**Homoionic interlayer clays:** The implication of having $K^+$ in the interlayer of the clay is that the attraction of water in the interlayer will be reduced due to the lower hydration energy of $K^+$ as its charge/radius ratio is relatively low. This makes the interlayer of K-montmorillonite not as hydrophilic as Na-montmorillonite.

Consequent upon $K^+$ having a relative large size, the K-montmorillonite would have the hydrophobic siloxane surface exposed and this would normally cause this clay sample to possess reduced ability to host hydrophilic compounds [15]. The same reason of exposition of the hydrophobic siloxane surface accounts for why the surface area of K-montmorillonite is lower than that of Na-montmorillonite given that the EGME (which is a polar compound) would not be able to access the exposed hydrophobic siloxane surface in the interlayer of the potassium-montmorillonite clay sample. The ability of K-montmorillonite to attract hydrophobic compounds into the hydrophobic siloxane surface has been reported [8].

## Conclusion

The EGME-surface area of clay minerals depends not only on the type but also the form of the clay mineral. Hence dioctahedral smectite such as montmorillonites have a higher EGME-surface area than trioctahedral smectites like saponites. Clays without interlayer cations such as kaolinites have lower EGME-surface area than those with interlayer cations. The modification of the clay minerals to produce organo- and acid activated clays leads to reduction and increase in the surface area of the clays respectively in comparison with their unmodified counterparts. Also, the modification of the interlayer cations of montmorillonites to produce homoionic montmorillonites influences the EGME-surface area with potassium-montmorillonites having the lowest EGME-surface area among Na-, K-, Mg-, Ca-, Zn-, Al- and Fe-montmorillonite. Modification of clays that leads to delamination of the clay layers without reducing the hydrophilicity of the clays will ultimately lead to increase in EGME-surface area hence acid activated clays have relatively high EGME-surface are. However, modifications that introduce or lead to increase in the hydrophobicity of the clay minerals reduce the EGME-surface area of clay mineral.

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