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Synthesis and Characterization of Organo-bentonites for possible Use in the Removal of PAHs from Petrochemical Industries Wastewater Effluents

By

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Abstract

Organo-bentonites have been synthesized through ion-exchange reaction using benzyl dimethyl dodecyl ammonium (BDMDA), dioctadecyl dimethyl ammonium (DODMA) chloride; tetraphenyl phosphonium (TPP) and hexadecyl pyridinium (HDP) bromides. The unmodified and modified samples were studied with Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD) technique, and Scanning electron microscopy (SEM). The basal spacing of the unmodified bentonite was 17.123Å and after modification it increased to 22.071Å and 20.066Å at 1.0CEC for BDMDA and DODMA respectively. With 1.5CEC of TPP and 2.0CEC of HDP the basal spacing increased to 20.250Å and 18.205Å respectively. The FT-IR studies also revealed structural differences between the modified and unmodified bentonite samples. The IR spectra of the modified bentonite showed C-H asymmetric stretching at 2928cm^{-1} for BDMD 2920cm^{-1} for DODMA and 2918cm^{-1} for HDP, symmetric stretching at 2853cm^{-1} for BDMD, 2851cm^{-1} for DODMA and 2851cm^{-1} HDP and bending vibrations at 1460cm^{-1} for BDMDA, 1469cm^{-1} for DODMA and 1469cm^{-1}for HDP with respect to long alkyl chains in BDMDA, DODMA and HDP. The vibration associated with pyridinium was observed at 1490cm^{-1} in HDP modified bentonite. The C=C stretching vibrations in the phenyl ring were at 1587cm^{-1} and 1441cm^{-1} while attachment of the phenyl rings to phosphonium ion were observed at 1587cm^{-1}, 1441cm^{-1}, and 1438cm^{-1} with respect to TPP modified sample. Results of the SEM revealed a tendency towards flakes/grain like formation and agglomeration.

Key words: Organoclay; Bentonite; Surfactant; Cation exchange capacity (CEC)

1. INTRODUCTION

Organoclays are hybrids derived from an ion exchange of the inorganic cations (alkali or alkaline earth) located in the interlayer of natural clays with long-chained quaternary ammonium surfactants under hydrothermal conditions. Among the clay minerals, smectites and especially bentonite that consists primarily of the clay mineral montmorillonite (MMT) were extensively used to prepare organoclays because of their excellent properties, such as high cation exchange capacity, swelling behavior, adsorption properties and large surface area[1]. Organic modification of clay minerals has shown significant increase in the attenuation of aromatic hydrocarbons and other organic compounds from refinery effluents[2].

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[1] Banik, N., Jahan, S. A., Mostofa, S., Kabir, H., Sharmin, N., Rahman M and Ahmed, S (2015); Synthesis and characterization of organoclay modified with cetylpyridinium Chloride. *Bangladesh J. Sci. Ind. Res.* **50(1)**, 65-70.

[2] Owabor,C.N., Uzezi M. and Aigbokhan I. (2012). Enhanced Sorption of Naphthalene onto a Modified Clay Adsorbent: Effect of Acid, Base and Salt Modifications of Clay on Sorption Kinetics. *Advances in Chemical Engineering and Science*, 2; 330-335.

Clays are hydrophilic in nature because of the presence of inorganic cations, and therefore ineffective adsorbent for aromatic compounds, but this hydrophilic character can be changed into hydrophobic by organic modification, thereby acting as good sorbents for organic compounds and in other applications[3]. Bentonite consists of 2:1 layers, i.e two tetrahedral silica sheets sandwiching a central octahedral alumina sheet. Due to isomorphic substitution within the layers, the clay has negative crystal charge balanced by exchangeable cations such as Na^+, K^+, Ca^{2+} in the interlayer. Cation-exchange reactions have been traditionally exploited as an effective method to replace these inorganic ions with organic cationic surfactant molecules which intercalate into the clay gallery. It has been recognized that the ion exchange reaction has two consequences; first, the gap between the single sheets is widened, enabling organic cations chain to move in between them and secondly, the surface properties of each single sheet are changed from being hydrophilic to hydrophobic[4]. Depending on the layer charge of the clay mineral and the alkyl chain length of the organic ion, different arrangements of organic molecules between the layers can be formed ranging from monolayers, bilayers, pseudo-trimolecular layer to paraffin type arrangement. Short alkyl chains present in the surfactant are arranged in monolayers, longer alkyl chains in bilayers with the alkyl chain axes parallel to the silicate layers. Three-layer structures of kinked alkyl chains are observed with highly charged MMT and/or long surfactants cations, the pseudo-trimolecular layer. Computer simulations indicated that the interlayer distances generated by mono, bi, pseudo-trilayers and paraffin type arrangements of alkyl chains are 13-15 Å, 17-18 Å and 19-21 Å and >22 Å, respectively[5]. To ensure adequate modification of bentonites, it is necessary to know their cation exchange capacity (CEC) which is the measure of the amount of organic surfactant that can enter between the layers. Thus, an important task for modification is the determination of the amount of surfactants to be bound through ion exchange which is dependent on the CEC of the clay[6]. Ammonium surfactants usually incorporate short aliphatic chains, at least one long

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[3] C.S. Ezquerro, I.R. Gemma, C.M. Cristina and S.B. Javier (2015), Characterization of montmorillonites modified with organic divalent phosphonium cations, *Applied Clay Science* 111, 1-9; W. Abdallah and U. Yilmazer (2011), Novel thermally stable organo-montmorillonites from phosphonium and imidazolium surfactants *Thermochimica Acta 525 (2011) 129– 140;* A. Tabak, B. Afsin, S.F. Aygun and E. Koksal (2007), Structural charachteristics of organomodified bentonites of different origins, *J. Therm. Anal. Cal*. 87; 375–381.

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aliphatic chain (C_{12}–C_{18}), benzyl rings and sometimes hydroxyl groups. Other ammonium surfactants of more complex molecules are employed, although choice of modifiers depends on its application. Modified clays have been employed for the removal of several compounds, such as phenol and BTEX compounds and PAHs as found in effluents from oil refineries, and other industrial processes[7].

Many studies have evaluated the use of organoclays in contaminant remediation such as their ability to adsorb hydrophobic contaminants such as chlorinated phenols, perchloroethylene, pesticides, *m*-cresol, atrazine, *p*-xylene, naphthalene, phenanthrene, acenaphthene, fluorene, pyrene, aniline, phenol, oils, amines grease, BTEX and PAHs[8,9,10].

The present study describes the synthesis and characterization of organoclays from bentonite samples obtained from the deposit in Potiskum in Yobe State, Nigeria using benzyl dimethyl dodecyl ammonium chloride, dioctadecyl dimethyl ammonium chloride, tetraphenyl

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phosphonium and hexadecyl pyridinium bromides as surfactants. The resulting organoclays are intended for use in the removal of PAHs from wastewater effluent of petrochemical related industries.

1.1 **Materials and methods**

1.2 *Materials*

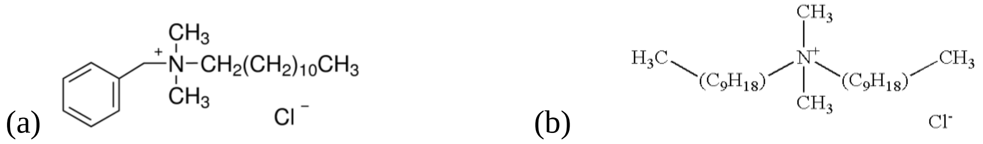
The bentonite used in this study was from the deposit in Potiskum, Yobe State, Nigeria. The chemicals used were of analytical reagent grades (97-99% purity) which include benzyl dimethyl dodecyl ammonium chloride, dioctadecyl dimethyl ammonium chloride, hexadecyl pyridinium bromide and tetraphenyl phosphonium bromide. These were used as purchased from SIGMA ALDRICH. Deionized water was used for the preparation of all solutions.

2.2 ***Methods***

The clay fraction used was obtained by sedimentation process whereby 100g of the bentonite was dispersed in 1L of 10% H_2O_2 solution, then re-suspended in 1 L 0.5 M NaOH solution for 2 hrs with moderate agitation[11]. The resulting suspension was washed with de-ionized water thereafter the supernatant dispersion (particles < 2 μm) was collected and dried at 90ºC in an oven. The cation exchange capacities (CEC) of purified bentonite were determined by the standard ammonium acetate method[12]

2.2.1 ***Preparation of the organoclays.***

The organoclays were prepared using these surfactants with varied structures.



Benzyl dimethyl dodecyl ammonium chloride

(BDMDAC)

Dioctadecyl dimethyl ammonium chloride

(DODMAC)

Hexadecyl Pyridinium bromide

(HDPB)

Tetraphenyl phosphonium bromide

(TPPB)

Fig 1: Structures of the surfactants

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[11] James O. O., Adediran, M.M., Adekola, F. A., Odebunmi, E. O. and Adekeye, J. I. D. (2008); Beneficiation and Characterisation of a Bentonite from North-Eastern Nigeria. *Journal of the North Carolina Academy of Science,* 124(4):154–158.

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Into four separately labeled 250ml conical flasks were individually added 5g of the beneficiated bentonite. Each flask was heated to about 80°C with continuous stirring to enable the complete dispersion of the bentonite samples. To one of the dispersions was slowly added with continuous stirring, 1.05g BDMDAC (surfactant) and maintained at 80°C for 4hours. The resultant product was recovered by vacuum filtration and washed several times with deionized water until no halide anions were detected using the silver nitrate test[13]. The product was then dried at 80 °C overnight and finally ground manually in an agate mortar and sieved into a plastic container. The above procedure was repeated using 1.82g of (DODMAC) 2.38g, of (HDPB) and 1.95g, of (TPPB).

The compounds thus obtained were characterized using FTIR, XRD and SEM equipment following the individual manufacturer's instructions.

The chemical composition of the purified bentonite sample was carried out using an Oxford (X-supreme 8000) instrument. The FTIR analysis was carried out using Cary 630 Agilent Technology USA and the spectra were recorded in the range of 4000–650 cm^{-1} at a resolution of 4 cm^{-1}. Scanning electron microscope (SEM) (Phenom Proxy, PW 100-002, magnification-255x, Accelerating Voltage- 10KV) was used to evaluate the surface morphology of the bentonite samples.

2. Results and Discussion

3.1 Characterization of the beneficiated and organo- bentonite samples

FTIR technique was used to investigate the intercalation between the clays and surfactants used. The morphology and basal spacing of the ordinary and organo-bentonites were investigated by SEM and XRD analyses, respectively.

3.2 ***X-ray fluorescence analysis (XRF)***

The result revealed that the most abundant oxides in the sample are SiO_2 (40.71%), Al_2O_3 (16.74%) and CaO (14.85%); these results were found to be similar to those of previous workers[14].

3.3 ***Fourier transform infrared spectroscopy analysis (FTIR)***

As shown in **Fig. 2**. The bands at 3691 cm^{-1} and 3622 cm^{-1} of the purified bentonite are assigned to OH stretching vibrations in the Si-OH and Al-OH groups of the tetrahedral and octahedral

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[13] Praus, P., Martina, T. Soˇna, Š. and Michal, R. (2006); Study of cetyltrimethylammonium and cetylpyridinium adsorption on montmorillonite. *Journal of Colloid and Interface Science 304; 29–36;* Patel, H. A. Rajesh S.S., Hari C. B., Raksh V. J (2007); Preparation and characterization of phosphonium montmorillonite with enhanced thermal stability. *Applied Clay Science 35; 194-200*; Calderon J.U., Bruce L., Musa R. K. (2008), Thermally stable phosphonium-montmorillonite Organoclays. *Applied Clay Science* 40, 90–98;Bertagnolli C. and Silva, M.G. C. (2012), Characterization of Brazilian Bentonite Organoclays as Sorbents of Petroleum-derived Fuels. *Materials Research*. 15(2): 253-259; Jahan, S. A. Parveen, S. Ahmed S. and Kabir H. (2012), Development and characterization of organophilic clay from bentonite, *Material Science,* **8:** 67-72.

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sheets of the clay respectively. Slight shifts at these bands were observed after the modification; 3691cm^{-1} to 3693cm^{-1}, 3695cm^{-1}, 3695cm^{-1}, 3693cm^{-1} and 3622cm^{-1} to 3624 cm^{-1} in TPP-PK only. The band of low intensity located at lower frequency 1637cm^{-1} in the spectra of the purified bentonite is produced by the bending vibration of adsorbed water, which also changed slightly after the modification, except for HDPB which has been totally replaced by vibration produced by the pyridinium ring.

The most intense bands of the spectrum were found in the low-frequency regions; 1113 cm^{-1}, 1000cm^{-1} and 914cm^{-1} for the beneficiated bentonite which were produced by the stretching mode of Si–O (out-of-plane), Si–O stretching (in-plane) and the bending vibration of AlAlOH respectively. Similar values for the Si-OH, Al-OH, -OH, Si-O Al-Al-OH stretching and bending vibrations were reported[15]. Appearance of other bands that were not present in the spectra of the purified bentonite were observed after the modification. This confirms the attachment of the surfactants into the interlayer gallery of the purified bentonite clay.

The IR spectra of the modified bentonite also showed C-H asymmetric stretching at 2928cm^{-1} for BDMDA, 2920cm^{-1} for DODMA and 2918cm^{-1} for HDP, symmetric stretching at 2853cm^{-1} for BDMDA, 2851cm^{-1} for DODMA and 2851cm^{-1} HDP and bending vibrations at 1460cm^{-1} for BDMDA, 1469cm^{-1} for DODMA and 1469cm^{-1}for HDP with respect to long alkyl chains in BDMDA, DODMA and HDP. The vibration associated with pyridinium was observed at 1490cm^{-1} in HDP modified bentonite. The C=C stretching vibrations in the phenyl ring were at 1587cm^{-1} and 1441cm^{-1} while attachment of the phenyl rings to phosphonium ion were observed at 1587cm^{-1}, 1441cm^{-1}, and 1438cm^{-1} with respect to TPP modified sample.

3.3 ***X-ray diffraction analysis (XRD)***

From the diffraction patterns, the basal spacing of the beneficiated bentonite increased from 17.123Å to 22.071Å, 20.066Å, 20.250Å 18.205Å after the modification with BDMDAC, DODMAC, HDPB and TPPB respectively. This increase resulted in the shift of the diffraction peak toward lower angle from 5.157° to 4.000, 4.400, 4.360° and 4.850° respectively. This implies that the interlayer distances were increased due to the intercalation of the surfactants between the silicate layers as observed from the increase in intensities of the peaks.

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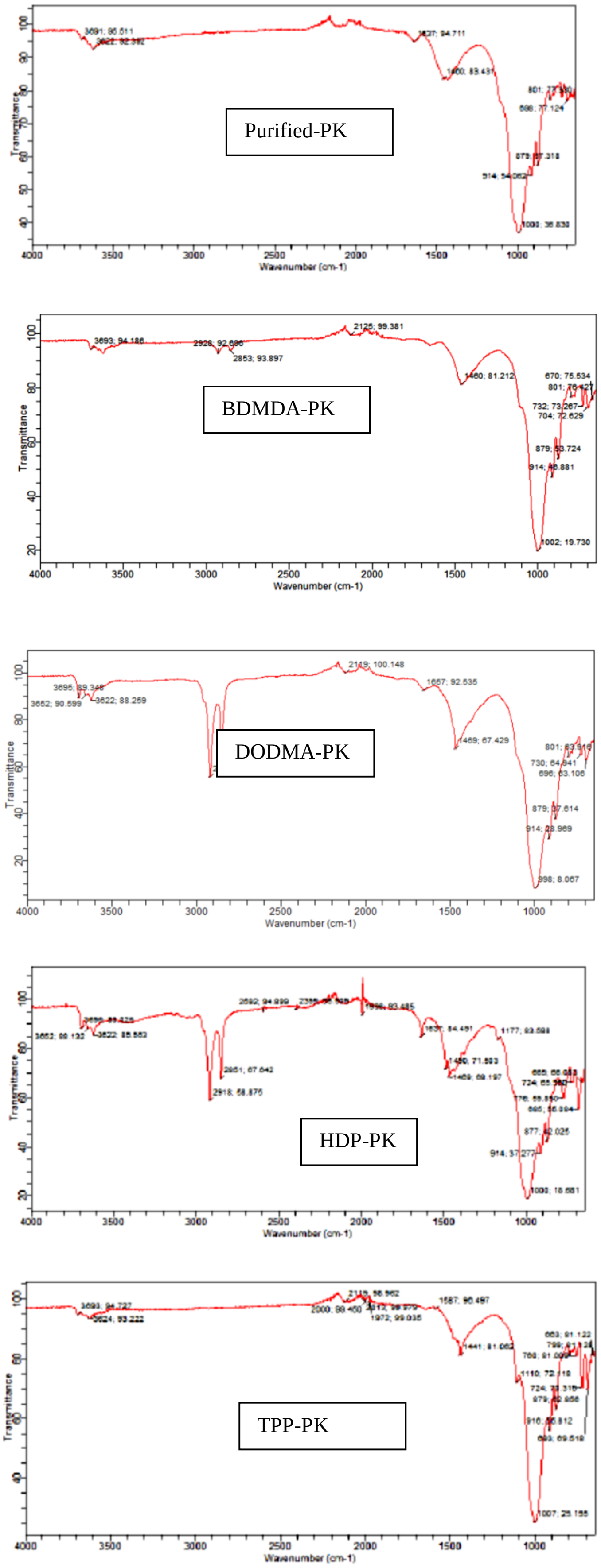
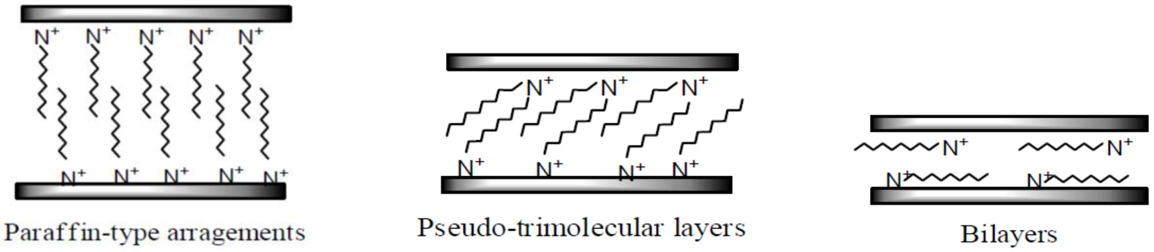


Fig 2: FTIR spectra of purified bentonite (PK) and organo-bentonites (BDD-PK, DOD-PK, TPP-PK and HDP-PK).

All the values obtained from this study (the FTIR and basal spacing) were in close agreement with those reported[16].

The organoclay prepared with surfactant 1.0 CEC DODMA which has two octadecyl chains with a basal spacing of 22.071Å is proposed to have the structure corresponding to paraffin type arrangement (Fig. 3a), while pseudo trimolecular layer arrangements were observed in 1.0CEC BDMDA and 2.0 CEC HDP with a basal spacing of 20.1 Å and 20.3 Å respectively (Fig. 3b). The surfactant cations at 1.5 CEC TPP resulted in the increase of the basal spacing to 18.2 Å is being proposed to have a bilayer arrangement (Fig. 3c).



(a) (b) [c]

Fig 3: Arrangement of intercalated surfactant cations in the interlayer space of MMT (bentonite).

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[16] Praus, P., Martina, T. Soˇna, Š. and Michal, R. (2006); Study of cetyltrimethylammonium and cetylpyridinium adsorption on montmorillonite. *Journal of Colloid and Interface Science 304; 29–36;* Patel, H. A. Rajesh S.S., Hari C. B., Raksh V. J (2007); Preparation and characterization of phosphonium montmorillonite with enhanced thermal stability. *Applied Clay Science 35; 194-200*; Vazquez, A., López, M., Kortaberria, G., Martín, L.and Mondragon, I. (2008), Modification of montmorillonite with cationic surfactants. Thermal and chemical analysis including CEC determination. *Applied Clay Science* 41: 24–36
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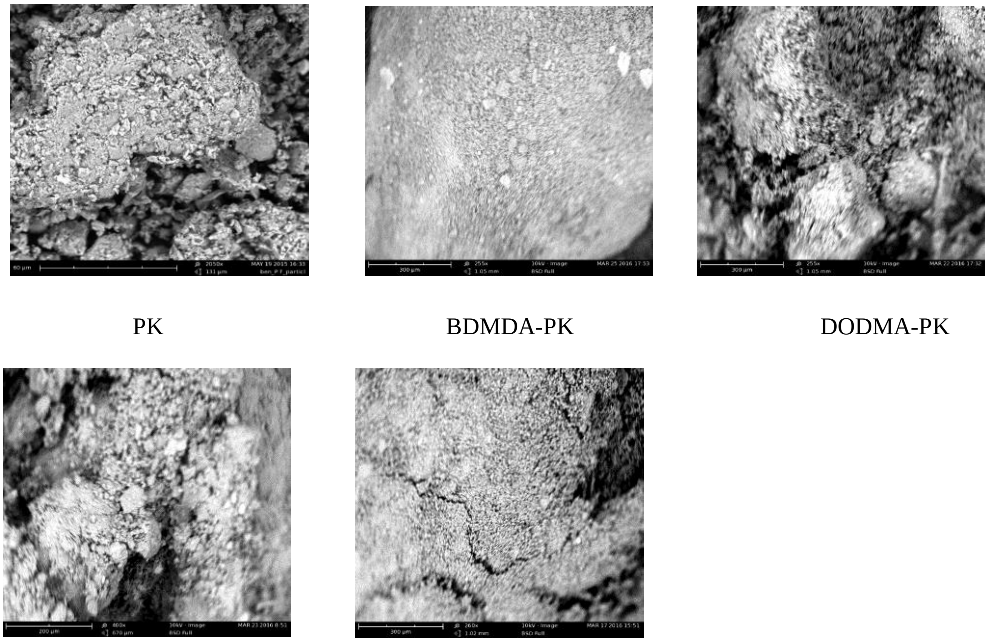
3.4 *Scanning electron microscopy (SEM)*

The SEM images of the purified and organo-bentonite samples are as shown in **Figure 4.** The purified sample, PK showed a smooth surface where large lamellas tend to form big agglomerates with a layer disposition. The aggregates of the purified bentonite appeared significantly larger than those for the organically modified. After the modification significant changes were observed, whereby the surfaces turned rougher with more fractionated lamellas and uniformly dispersed small particles in the form of flakes or grain-like structures. Thus, modification reduced the clay particle size and aggregation as shown in the images of BDMDA-PK, DODMA-PK, TPP-PK and HDP-PK. The differences in the morphological changes in the surfaces are also related to the fact that the surfactants have their individual structures. These changes further provide evidence in the intercalation of the surfactant on the surface of the clay.



PK BDMDA-PK DODMA-PK

HDP-PK TPP-PK

Fig 4: SEM images of purified (PK) and organo bentonites (BDMDA-PK, DODMA-PK. HDP-PK and TPP-PK)

Conclusion

Potiskum bentonite was successfully modified through ion exchange reaction to organo bentonite using BDMDAC, DODMAC, HDPB and TPPB as surfactants. The FTIR, SEM and XRD results of the synthesized organo-bentonites confirmed the intercalation of the surfactant on the surface of the clay. Appearance of bands; CH_2, CH_3, pyridinium, C=C, phenyl ring, and attachment of the phenyl rings to phosphonium ion in the infrared spectra of the organo-bentonites confirm the ion exchange reactions. Changes in the surface morphology of the products showed that modification of surfactant reduced the clay particle aggregation, while the variation in the d-spacing has confirmed the intercalation of the surfactants in the clay structure.

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