

Synthesis of organo-nanoclay from bentonite Iraqi

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ARTICLE INFO

Received: 19 / 5 /2022
Accepted: 28 / 5 /2022
Available online: 3/5/2017
DOI: 10.37652/juaps.2015.124460

Keywords:
Organo-nanoclay,
bentonite,
cation exchange,
TEM,
XRD.

ABSTRACT

In this study, bentonite clay was modified to organo-nanoclay by interaction of cetyltrimethyl ammonium bromide (CTAB). Organoclay has been characterized by fourier transform infrared spectroscopy (FT-IR) and solid state UV-Vis spectroscopy, while properties for clay characterized by microscopy (EFTEM), X-ray diffraction (XRD). The analysis confirmed the interaction and the nano properties of the synthesized material.

1. INTROUCTION:

Organoclays are defined as forms of important type of modified clay material [1]. They are montmorillonites that have been modified with organic surfactants [2]. Organoclays are prepared from exchanging the original interlayer cations in clay mineral by organocations [3].

The properties of organoclay changes the surface properties for clay mineral from hydrophilic to hydrophobic [4]. Intercalation of organic surfactant between layers of clays can not only change the surface properties from hydrophilic to hydrophobic, but also greatly increase the basal spacing of the layers [5]. In addition, the alkylammonium or alkylphosphonium cations (Figure 1.1) could progress functional groups that can react with the polymer matrix or in some cases initiate the polymerization of monomers to improve the strength of the interface between the inorganic and the polymer matrix [6].

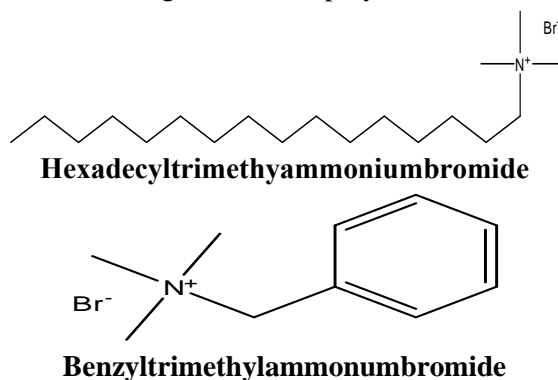


Figure 1.1: Chemical structure of alkylammonium or alkylphosphonium cations.

The organoclay which exhibits definite gallery spacing between the platelets, is called organo-nanoclay, where organo-nanoclay has properties over organoclay such as size of particles and high capacity [7]. The nano-size dimension, extensive surface area, and peculiar charge characteristics of nanoclay materials lie behind their large propensity for taking up ions and organic compounds therefore, nanoclay suitable for preconcentration in solid phase extraction [8]. Ultra sonication is a good method to achieve preparation of organo-nanoclay [9]. The synthesis of organoclays depends on the mechanisms of the interactions that the clay minerals can have with the organic compounds [10]. Organic compounds can form complexes with the interlayer cations, the interlayer cations can be exchange by various types of organics cations [11]. Organo-montmorillonites are synthesized by grafting cationic surfactants such as quaternary ammonium compounds into the interlayer space. It has been demonstrated that replacement of the exchange ions by organic cations can create a hydrophobic or organophilic surface [12]. Organically modified layered-silicates or organo-nanoclay have become an attractive class of organic-inorganic hybrid materials because of their potential use in wide range of applications such as in polymer nanocomposites for example polypropylene and polystyrene [13]. These modified organo-clays are used in a wide range of particular applications, such as adsorbents for organic pollutants [14,15], and metal ions [16,17]. Currently, an important application of the organoclays in the polymer nanocomposites [18,19].

2. EXPEREMENTAL

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2.1. MATERIALS AND CHEMICALS

Bentonite powder was obtained from general company for the manufacture of glass and ceramics (Ramdi, Iraq). Cetyl trimethyl ammonium bromine (CTAB was purchased from Sigma – Aldrich (Texas, USA). Hydrochloric (37%) acids were purchased from Qrec (New Zealand).

2.2. Instrumentation

2.2.1. Solid state UV-VIS spectrometer

UV-VIS measurement was conducted using Perkin Elmer-Lambda 35 (Massachusetts, USA) which placed in Universiti Sains Malaysia (USM) (Penang, Malaysia). The organo-nanoclay was scanned from 190 to 420 nm.

2.2.2. Fourier transform infrared spectroscopy (FT-IR)

Fourier transform infrared (FT-IR) spectra were obtained using Perkin Elmer System 2000 (Massachusetts, USA) at USM, Penang, Malaysia. Spectra of solid were performed using KBr disc and scanned from 400 to 4000 cm^{-1} .

2.2.3. X-ray diffraction (XRD)

X-ray diffraction (XRD) patterns of bentonite and organo-nanoclay were carried out using a Philips PAN alytical XPERT- PRO Diffractometer operating at 40 kV and 20 mA between 2 and 60 (2θ) at a step size of 0.03 with $\text{CuK}\alpha$ radiation ($n = 1.5418\text{\AA}$). This test has been done at University of Basrah (Basrah, Iraq).

2.2.4. Energy filtered transmission electron microscopy

Energy filtered transmission electron microscopy (Libra 120, Carl Zeiss, Germany) operating at 120 kV using magnification ranging from 3 – 100 kx. Organo-nanoclay was prepared by dispersing in ethanol using an ultrasonic bath for 5 min. Drop of the sample was placed on a carbon coated copper grid and let it to dry for several minutes in air at room temperature. This test has been done in USM (Penang, Malaysia).

2.3. Preparation of organo-nanoclay

Bentonite clay modified to organonoclay based on a previous report [20]. Bentonite powder was sieved by 200-mesh (75 μm) and washed with water for (3 times). CTAB (3.0 g) was dissolved in 80 ml HCl (4×10^{-3} M) then the solution salt was stirred vigorously at 80 °C until dissolution 3.0 g of bentonite powder were added to

the solution with continuous stirring and heating at 80 °C for 3 hrs. The product was left to dry for 12 hours. The residue was sonicated with water (30 min) to remove the unreacted CTAB and to achieve the nanoclay. In Figure 2.1 shown schematic synthesis of organo-nanoclay.

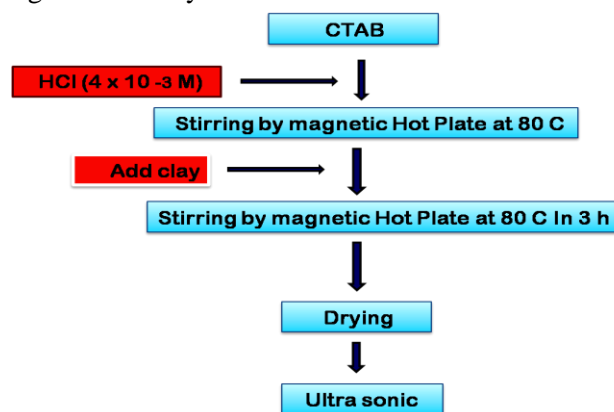
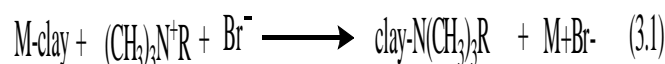


Figure 2.1 schematic synthesis of organo-nanoclay.

3-RESULTS & DISCUSSION

3. 1. Preparation of organo-nanoclay

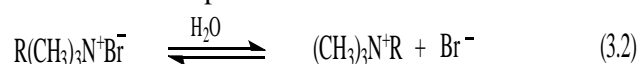
The target organo-nanoclay has been synthesised by method based on the exchange of the interlayer cations by CTAB [158]. Clay minerals of adsorbing certain cations and retaining them in exchangeable state, for a given clay. The maximum amount of any one cation that can be taken up is constant and is defined as cation exchange capacity (CEC) [21]. Cation exchange capacity (CEC) is the quantity of positively charged ions held by the negatively charged surface of clay mineral, therefore the interaction of the CTAB with clay depends on the exchange of the interlayer cations by CTAB according to the equation [22]:



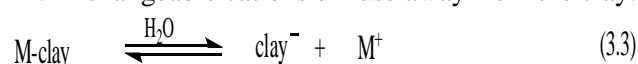
where M^+ refers to the interlayer cations, R is the cetyl group.

The mechanism of the interaction is as the following: in first step dissociates a positive ammonium cation in aqueous solution while second step exchangeable cations are diffused away from the clay, in least ammonium cation attract negative charges on the surface of clay layers.

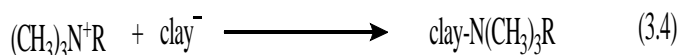
I. Dissociates a positive ammonium cation.



II. Exchangeable cations diffuse away from the clay.



III . Ammonium cation attractnegative charges on the surface of clay.



3. 2. Characterization of organo-nanoclay

The organo-nanoclay has been synthesised and characterized by fourier transform infrared spectroscopy (FT-IR), solid state UV-VIS analysis, X-ray diffraction (XRD) andenergy filtered transmission electron microscopy (EFTEM) to prove it.

3.2.1.Fourier transform infrared spectroscopy (FT-IR)

FTIR analysis was used to identify the changes of the functional groups present on the clay. FT-IR showed the interaction of surfactant (CTAB) with clay. The difference between the FT-IR spectra of clay and organo-nanoclay shown in Figure 3.1 and 3.2, respectively.

The FT-IR spectra of clay show the absorption bands assignable to the stretching of OH hydroxyl group at 3400cm⁻¹. These bands are observed at 3620 cm⁻¹ and 3690 cm⁻¹ due to the stretching of Al-OH and Si-OH, respectively.

The organo-nanoclay shows absorption bands at the frequency 2929 and 2859 cm⁻¹ respectively, corresponding to the asymmetric and symmetric vibrations of CH₂- groups from the alkyl chains. The intense absorption band at around 1493 cm⁻¹ refers to the groups from CTAB (Table 3.1). The rest of the bands are similar to the spectrum of clay [23].

Table 3.1: Bands characterized in organo-nanoclay.

Region (cm ⁻¹)	Bands
1493	C–H symmetric bending of (N+)–CH ₃
2929 and 2859	CH ₂ - groups
3400	OH-group

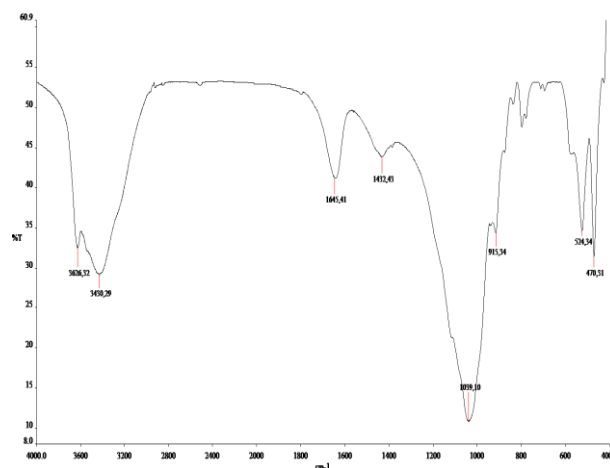


Figure 3.1: FTIR spectrum of bentonite clay.

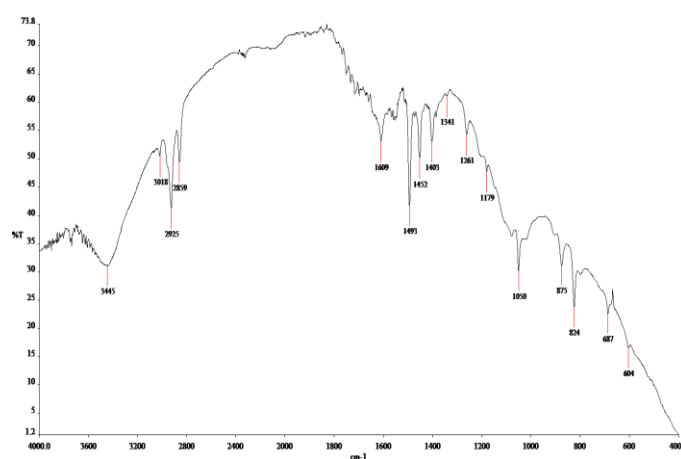


Figure 3.2: FTIR spectrum of organo-nanoclay.

3.2. 2. Solid state UV-VIS analysis

The UV-VIS analysis was used to characterization the target compound from UV-VIS. It clearly shows the difference in the intensity of the absorption due to the hydroxyl group at 190 nm in spectrum of organo-nanoclay from the clay spectrum. Figures 3.3 and 3.4 show the solid state UV-VIS spectra for the clay and organo-nanoclay samples.

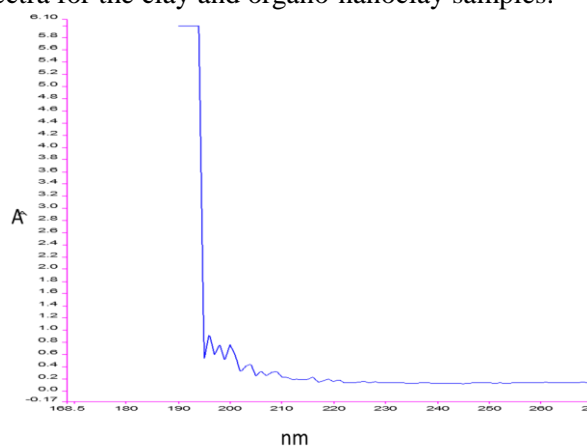


Figure 3.3: Solid state UV-VIS spectrum of bentonite clay.

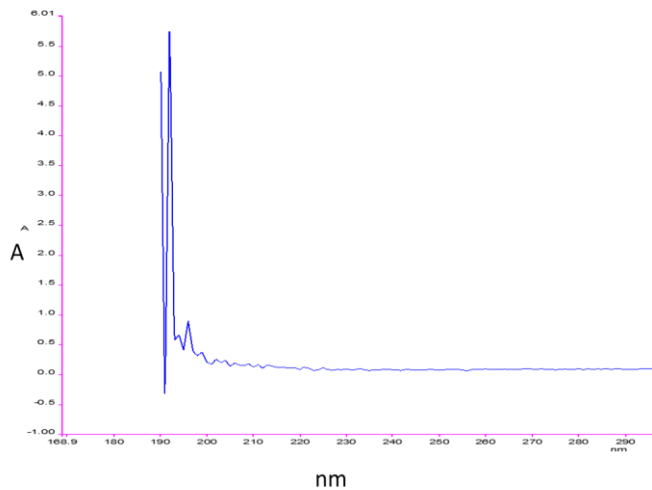


Figure 3.4: Solid state UV-VIS spectrum of organo-nanoclay.

3.2. 3. Energy filtered transmission electron microscopy (EFTEM)

Energy filtered transmission electron microscopy (EFTEM) based on an electron beam to interact with a sample to form an image on a photographic plate or specialized camera [24]. Energy filtered transmission electron microscopy (EFTEM) used for measuring particle size and characterization of samples. The examination of microscopic images by EFTEM has clearly shown the material properties of nanoparticles, where clear images nanoscale shapes are seen. The results indicate that surface morphology of organo-nanoclay have nanotubes diameters ranging between 18-53 nm (Figure3.5.d). Microscopic images of EFTEM shown in Figure 3.5.

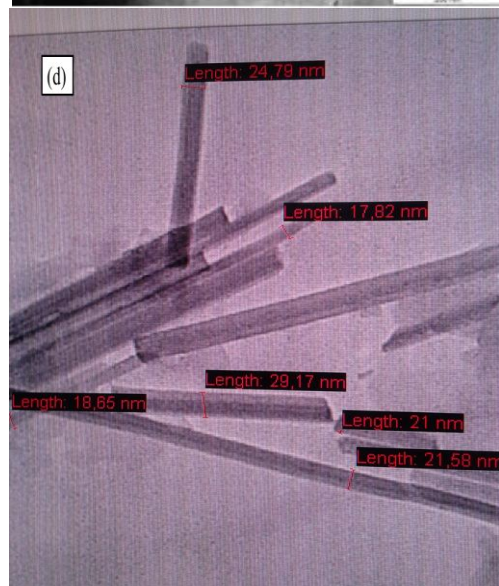
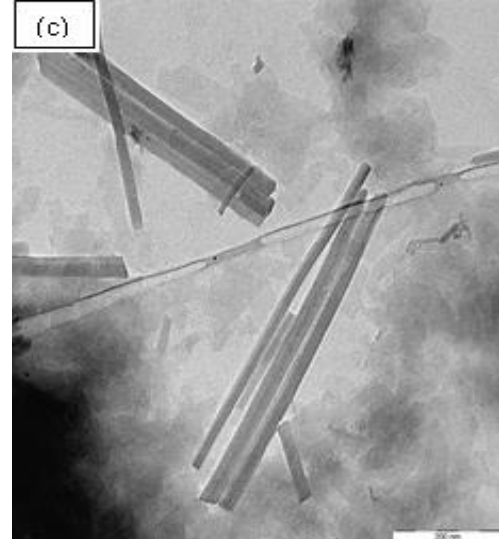
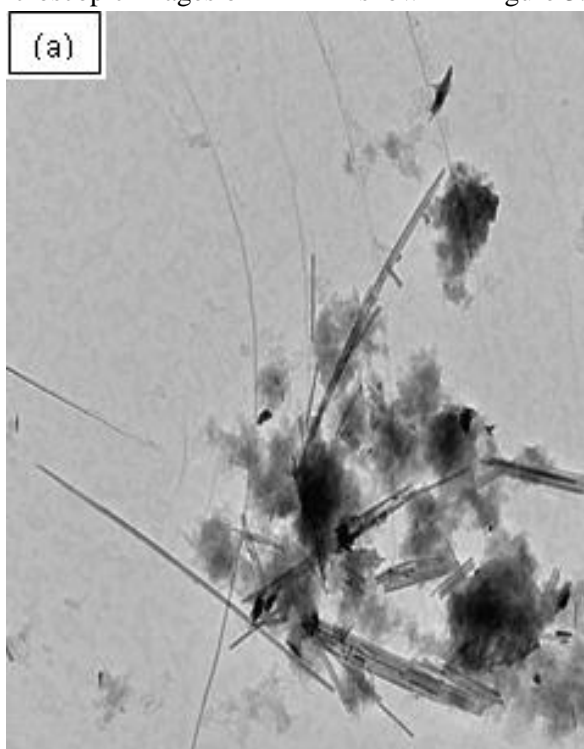


Figure 3.5: EFTEM image of organo-nanoclay (a) at 2 μ m scale (b) at 500 nm scale. (c) at 200nm scale (d) EFTEM shows of organo-nanoclay nanotubes diameters for organo-nanoclay.

3.2. 4. X-ray diffraction (XRD)

The recorded values X-ray diffraction (XRD) for bentonite and organo-nanoclay are listed in tables 3.2 and 3.3 respectively. It is clearly obvious from tables that the organo-nanoclay exhibits an increase in d-spacing compared to the original unmodified clay, indicating the formation of intercalated structures [25]. Figure 3.6 shows the X-ray diffraction pattern of bentonite, while Figure 3.7 shows the X-ray diffraction pattern of organo-nanoclay. The increase in the value of basal spacing depends on two factors, one is the presence of large hydrophobic groups from surfactant, and the second is the decrease in surface energy of clay [26]. Hydrophobic groups lead to an increase in d-spacing, and this is evident in table 3.2 and 3.3, respectively.

Table 3.2: Basal spacing, and $^{\circ}2\theta$ of bentonite clay.

Pos. [$^{\circ}2\theta$.]	Height	d-spacing [nm]
5.8270	19.04	15.16736
8.4512	7.45	10.46277
14.4554	1.88	6.12764
19.9066	6.25	4.46026
26.7178	39.79	3.33667
28.4228	4.44	3.14026
29.5106	13.87	3.02695
30.8652	2.16	2.89712
41.5731	2.08	2.17054

Table 3.3: Basal spacing, and $^{\circ}2\theta$ of organo-nanoclay.

Pos. [$^{\circ}2\theta$.]	Height	d-spacing [nm]
2.1215	40.39	41.64335
7.4890	9.59	11.80479
14.9057	1.66	5.94354
20.8740	11.31	4.25570
21.4980	58.95	4.13357
24.5537	13.73	3.62563
26.7018	34.39	3.33863
29.4420	7.45	3.03384
31.3908	2.95	2.84980
58.6690	3.88	1.57234

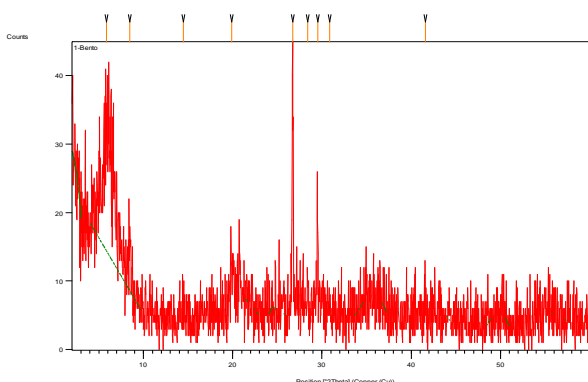


Figure 3.6: X-ray diffraction pattern of bentonite clay.

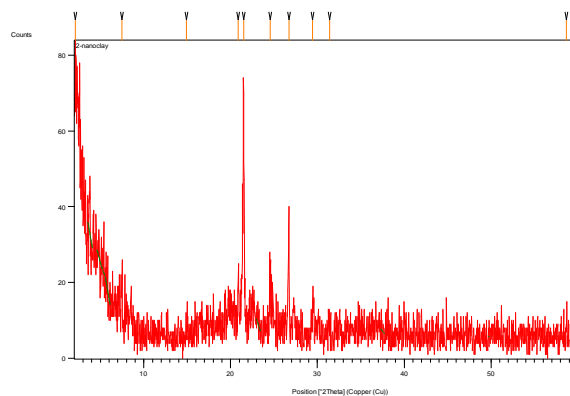


Figure 3.7: X-ray diffraction pattern of organo-nanoclay.

4. CONCLUSIONS

Organo-nanoclay has been successfully synthesized. Organo-nanoclay in current study, has main advantages from simply prepared, cheap starting materials and simple pre-conditioning procedure. Furthermore, it exhibits nano-particles properties which can provide a larger surface area.

ACKNOWLEDGMENT

The work was supported by university of Anbar and universiti sains Malaysia (USM).

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