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Synthesis and characterization of organoclay modified with cetylpyridinium chloride

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Abstract

Bentonite has been subjected to modification through ion-exchange reaction by 1-cetylpyridinum chloride. The modified samples were studied by X-ray diffraction (XRD) technique, Fourier transform infrared (FT-IR) spectroscopy and scanning electron microscopy (SEM). The basal spacing of unmodified bentonite, determined by XRD was 14.99 Å and after modification it increased up to 16.97 Å and 16.22 Å at 1CEC and 2CEC. The FT-IR studies revealed structural differences between the modified and unmodified bentonite samples. The IR spectra of the modified bentonite showed the C-C stretching bands (1465 and 1462 cm^{-1}) and C-H vibrations (near 2926 and 2852; 2854 cm^{-1}). Results of the SEM study revealed a tendency towards lump formation and agglomeration of the organomodified clay particles of bentonite. The possibility of the use of new organoclay to adsorb oils from aqueous solution will be explored.

Key words: Organoclay; Adsorption; Surfactant; Cation exchange capacity

Introduction

Due to their natural availability and the capacity for the chemical and physical modifications clays are used in many scientific applications. The high cation exchange capacity and swelling ability are some features that make clays very desirable in many industrial and scientific applications (Xi *et al.* 2005).

Clays are hydrophilic in nature because of the presence of inorganic cations of bentonite. Thus clay does not adsorb aliphatic and relatively hydrophobic compounds.

Inorganic ions in the clay can be replaced by organic amine salts to form organoclay (Hoidy *et al.* 2009). Bentonite consists of 2:1 (Hwu *et al.* 2001) layers, between which there are exchangeable hydrated ions. Each layer is composed from an octahedral sheet surrounded by two tetrahedral sheets (T.O.T) (Jahan *et al.* 2012). Octahedral sites are occupied mainly by Al^{3+} but partly substituted with Fe^{3+} and Mg^{2+}. The tetrahedral sites of bentonite normally contain Si^{4+} as central atoms with some Al^{3+} substitution.

Organoclay has applications in the area of organic–inorganic hybrids, composites and nano-scale composites (Tiwari *et al.* 2008). Bentonites are used in various fields of technical applications in civil engineering such as food, chemical and pharmaceutical industry (Kaufhold *et al.* 2002). Modified clays are used as adsorbents in vegetable oil refinery and in the removal of organic compounds in waste water (Caualcante *et al.* 2005). Organoclays have been categorized as the good adsorbents for toxic metals as Cr, Pb, Cd, Hg and Zn (Jahan *et al.* 2012). Additionally, organoclay can be used in paints and varnishes where they act as filler, stable against weathering, to provide and improve abrasion and scratch resistance (Hoidy *et al.* 2009).

Organoclays are hybrids derived from an ion exchange of the inorganic cations located in the interlayer of natural or synthetic clays with long-chained quaternary ammonium salts under hydrothermal conditions (Favre and Lagaly, 1991).

In this work, 1-cetylpyrimidinium chloride (CPC) was selected as representative of cationic surfactant. The modification of bentonite through the incorporation of 1-cetylpyridinium cation into the interlayer spaces of the clay has been studied.

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Materials and methods

Materials

The materials used for the synthesis of organoclay are bentonite from local market, 1-cetylpyridinum chloride, hydrochloric acid, acetic acid, sodium bicarbonate, ethanol, sodium chloride, sodium dithionite and hydrogen peroxide (30%) from Merck Germany. The surfactant used in this study is 1-cetylpyridinum chloride (CPC) with a purity of >96%. All the chemicals were used as received without any further purification. Organic solvents for the synthesis and characterization were AR grade and were obtained from Merck Germany.

Method

Bentonite clay sample was dried, grind and stored in a bottle. Purification of clay was done by the method of Tributh and Lagaly (Tributh and Lagaly, 1986). The cation exchange capacity (CEC) of the clay defined as the total amount of exchangeable cations that the soil can adsorb was estimated by Kjeldahl method (Cuadros and Linares, 1995). The CEC of purified bentonite was 110 meq/100g.

Organoclay preparation and characterization

Purification of clay was done respectively by sodium-acetate acetic acid buffer, citrate buffer, sodium dithionite, sodium chloride, hydrochloric acid, sodium chloride and at last distilled water.

For synthesis, 5g of purified bentonite was dispersed in 400 mL of water under continuous stirring for 1 h. The amount of surfactant added was calculated with the CEC value (110 meq/100 g clay) of bentonite. Desired amount of 1-cetylpyridinium was added to 200 mL of water in the separate container slowly. The reaction mixture was stirred for 4 hours at 80ºC. The resulting product was separated by filtration and washed with distilled water for 3 times. Then the product was washed with ethanol. Synthesized organoclay was dried in an oven at 80ºC for 48 hours and grind into powder. The concentrations of CPC were 1 CEC and 2 CEC of bentonite, respectively and labeled as OM1 and OM2.

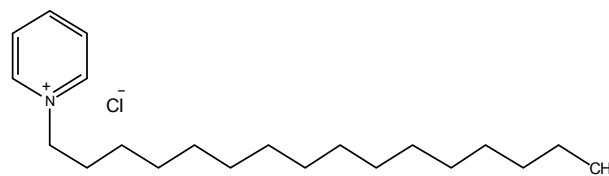In Figure 1, chemical structure of CPC is shown.

Fig. 1. chemical structure of CPC surfactant

The morphology of the prepared materials was evaluated by using scanning electron microscopy (SEM), X-ray diffractometry (XRD) and Fourier transform infrared (FT-IR) spectroscopy. SEM images were taken by Hitachi S-3400N scanning electron microscope. Phase purity of the synthesized samples was examined by using PANalytical (X'Pert PRO XRD PW 3040). The phase developed in the synthesized samples were compared and confirmed using standard JCPDS files. The d-spacing and hK bands were measured by using PANalytical (X'Pert PRO XRD PW 3040). The Fourier transform infrared (FT-IR) spectra were obtained by IR Prestige 21, Shimadzu using KBr disks and the samples were scanned in wave number range of 4000cm^{-1} – 400 cm^{-1} with an average of 30 scans and resolution was 4 cm^{-1}. All FT-IR spectra were recorded and analyzed to know the nature of the functional group attachment.

Results and discussion

FT-IR analysis

In the spectra of pure bentonite doublets at 794 and 779 cm^{-1} correspond to the –CH$_2$ rocking modes (Vaia *et al.* 1994). Then splitting of the –CH$_2$ rocking bands is due to the intermolecular interaction between the two adjacent hydrocarbon chains in a perpendicular orthorhombic sub cell (Zhu *et al.* 2005 and Karaca *et al.* 2013) and further requires an all-trans-conformation for its detection (Synder *et al.*1979). The band in the region of 950-1100 cm^{-1} corresponding to stretching vibration of Si-O group splits into a sharp band at 1033 cm^{-1} with a shoulder around 1088 cm attributed to perpendicular Si-O stretching (Xie *et al.* 2001).

The FT-IR spectra of bentonite, OM1 and OM2 are shown in Fig. 2. (a, b and c) respectively and all the important bands and their assignments are listed in Table I.

As shown in Figure 2a, though OM1 and OM2 show the peaks of the pure bentonite, new characteristic peaks respectively appear at 2926cm^{-1} 2852 cm^{-1} and 2926 cm^{-1}
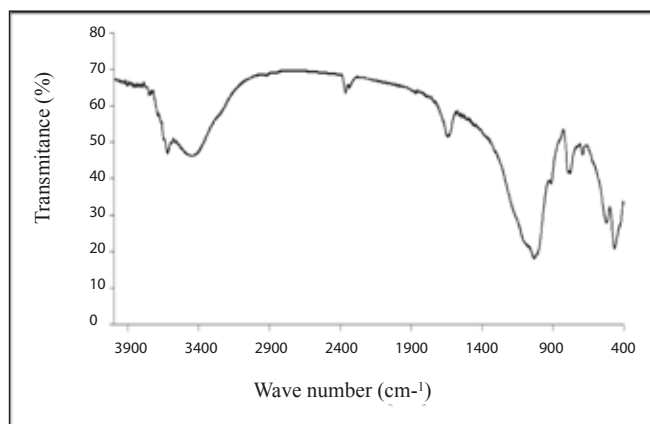
Fig. 2(a). FT-IR spectrum of pure bentonite

2854 cm^{-1} corresponding to the –CH$_2$ asymmetric and –CH$_2$ symmetric stretching vibrations. These bands are absent in the pure bentonite IR spectrum which indicates the incorporation of the surfactant in organoclay. As the bands are very narrow, the variation of their intensity increases with increasing initial surfactant content, indicating the

–CH$_2$ rocking modes, with the increase of surfactant loading , two well-resolved vibration bands at 794 cm^{-1} and 788cm^{-1} were observed, similar to –CH$_2$ scissoring. Splitting of the methylene scissoring and rocking modes not only relate with surfactant loading, but also relate with the chemical structure of the used surfactants.

Spectral hydration features in bentonite have been attributed to the structural OH in the octahedral layer, water adsorbed on the clay external surfaces and water adsorbed in the internal regions. The property of these interlayer water molecules is greatly dependent on the moisture level and the interlayer cation.

The spectra display more obvious absorption band at 3620 cm^{-1} due to the OH stretching vibrations of structural OH groups and the frequency is independent on the surfactant loading which is consistent with the result reported in the literature. In the region of 3100 cm^{-1}-3500cm^{-1}, the spectra show a broad band around 3400cm^{-1} corresponding to the

Table I. Position and assignments of the IR vibration bands observed in the range of 4000-400 cm^{-1}

Assignment	Pure Bentonite	OM1	OM2
Structural OH stretching	3622	3622	3622
Symmetric OH stretching	3450	3427	3427
Asymmetric CH$_2$ stretching	-	2926	2926
Symmetric CH$_2$ Stretching	-	2852	2854
H-O-H bending	1637	1637	1633
CH$_2$ scissoring	-	1490	1487
		1465	1462
Si-O stretching	1033	1035	1035
		916	918
CH$_2$ rocking	-	794	788
		779	

intercalation of higher amount of surfactant in bentonite with increasing initial amount of surfactant. OM1 corresponds to a linear direct cationic exchange of the exchangeable Na$^+$ cation by the cationic surfactant. As shown from Fig. 2a, when the alkyl intercalated into bentonite, a broad band at 1456cm^{-1} splits with the increase of surfactant loading as described in the literature (Zhu et al. 2005) for 1 CEC and 2 CEC. For the

overlapping symmetric (H-O-H) and asymmetric (H-O-H) stretching vibrations and a shoulder around 3150 cm^{-1} due to an overtone of the bending mode. The H-O-H bending vibration shifts significantly from 1637cm^{-1} (OM$_1$) to low frequency of 1633cm^{-1} (OM$_2$). When the surfactants intercalated into the gallery of bentonite, the water bounded directly to the hydrated cations by surfactant cations.
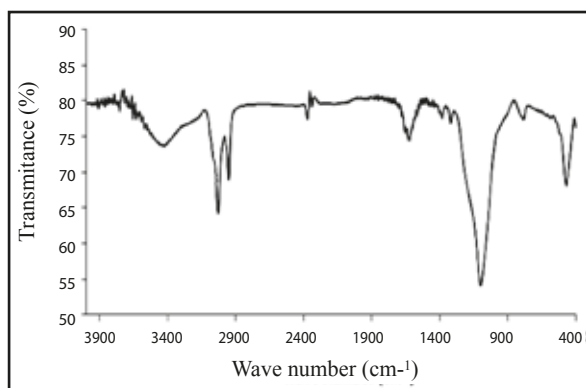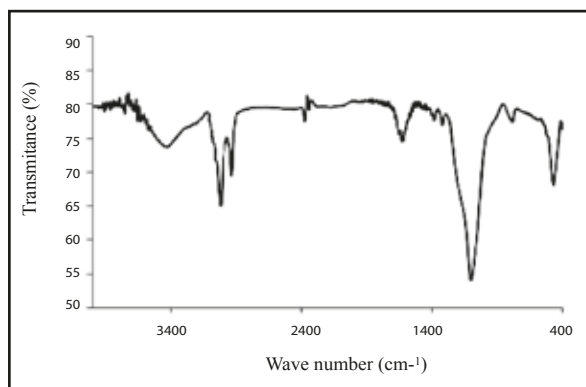
Fig. 2(b). FT-IR spectrum of OM1

Fig. 2(c). FT-IR spectrum of OM2

Fig. 3(a). XRD pattern of purified bentonite

Fig. 3(b). XRD pattern of OM1

Fig. 3(c). XRD pattern of OM2

Therefore, the detected absorption bands are mainly attributed to adsorbed water molecules especially at high surfactant loading. Simultaneously, with the intercalation of surfactants, the surface property of bentonite is modified; that is, the hydrophilic surface of bentonite has been changed to organophilic (Kung and Hayes, 1993 and Mandalia and Bergaya, 2006).

When the surfactant is intercalated into interlayer space of bentonite, the frequency of the Si-O stretching band in the tetrahedral network was changed. However, for the organoclays, the change of the band shape and its frequency strongly depends on the surfactant loading. As seen in figure 2a, frequency of the Si-O stretching band observed at the 1033 cm^{-1} for the pure bentonite. With the increase of surfactant, a shoulder band shifted from 916 cm^{-1} to 918 cm^{-1}. The significant changes in Si-O stretching band suggest that there is an interaction between the surfactant molecules and siloxane (Si-O) surface (Karaca *et al.* 2013 and Xi *et al.* 2005).

XRD analysis

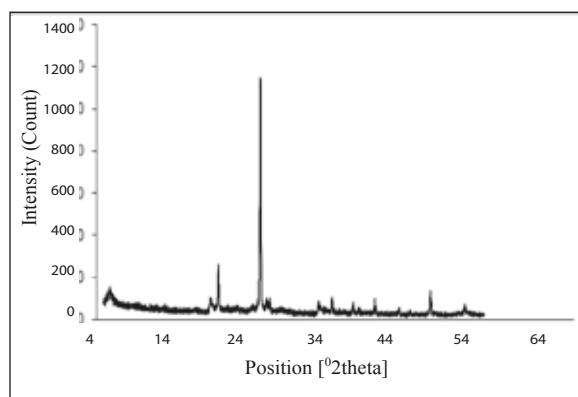One of the most important methods for studying the interlayer spacing is X-ray diffraction (XRD) and the
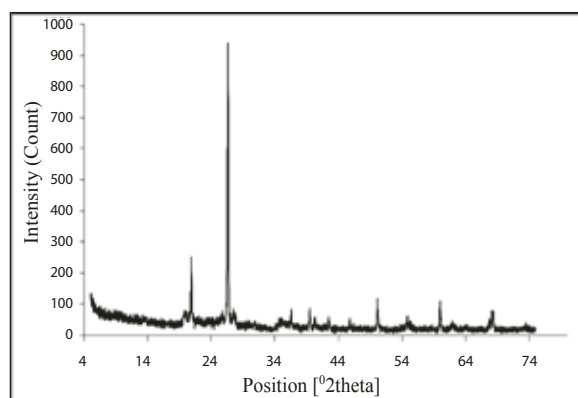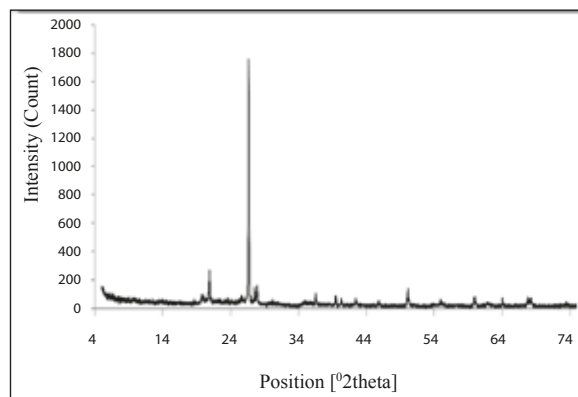
bentonite mineral peak displacement at 2θ is a suitable criterion to evaluate the interlayer spacing specifically a decrease in the 2θ angle and broadening of the peak indicate an increase in interlayer spacing (Jahan *et al.,* 2012). The distance of silicate layer can be calculated by Bragg's law

(nλ = 2dsinθ, d = layer distances). One of the most important properties of layered silicates is the intergallery distance

(d_{001}) between the clay layers. This distance can be calculated with data gathered from X-ray diffraction. It is also reflected in the XRD pattern of purified clay, OM_1 and OM_2 respectively. After purification the diffraction pattern of bentonite was at 5.89^o and the intergallery distance of clay was determined to be 14.99 Å.

The X-ray diffraction pattern of OM_1 is shown in Figure 3b. The peak point was at 5.20^o and the basal spacing of the clay was increased from 14.99 Å to 16.97 Å. When the modifying substance is not able to penetrate into the interlayer space the value of d_{001} does not change (Kozak and Domka, 2004).

The X-ray diffraction pattern of OM_2 is shown in Figure 3(c). The peak point was at 5.44^o and the basal spacing of the clay was increased from 14.99 Å to 16.22 Å.

After the ion exchange reaction, the basal spacing increases from 14.99° to 16.97° for OM_1 and to 16.22° for OM_2 indicating that the CPC was successfully intercalated into bentonite (Hoidy et al. 2009).

SEM analysis

The surface morphology of pure bentonite, OM_1 and OM_2 are shown in figure 4 (a, b and c) respectively. In the SEM images of pure bentonite some phase separations are observed as a heterogeneous surface morphology. It can be seen that the bentonite have massive plates. However, the clay treated with organic surfactant shows significant changes in the morphology. Compared with the morphology of the bentonite, there are many small and aggregated particles and the plates become relatively flat layers. Due to increase of basal spacing in organoclays more voids are seen.
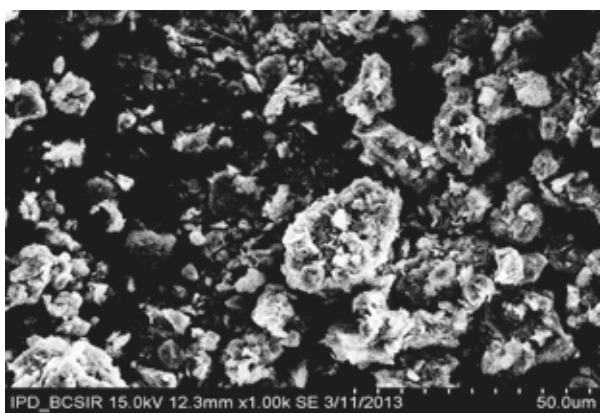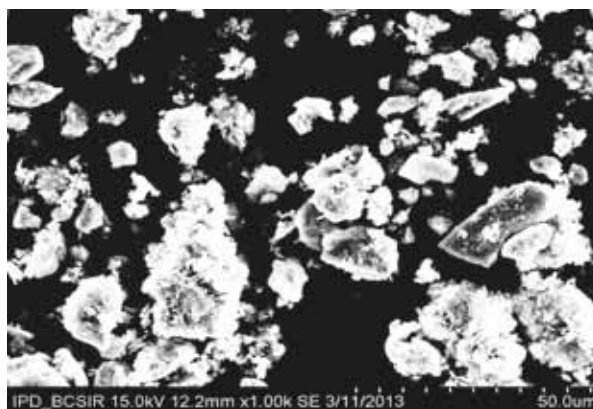

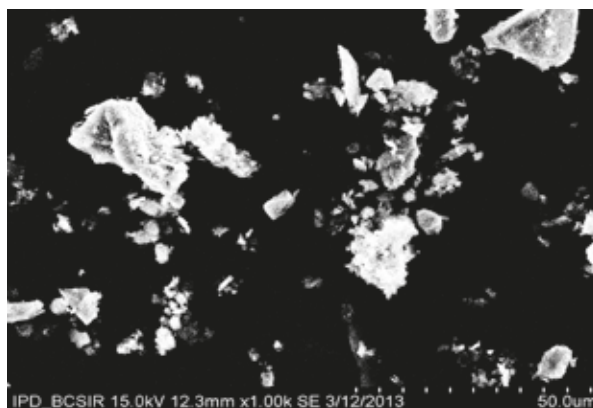**Fig. 4(a). SEM image of bentonite**

Fig. 4(b): SEM image of OM1

Fig. 4(c). SEM image of OM2

At OM_2 the surfactant-bentonite packing density increases and the clay layers are observed clearly.

Conclusion

Systematic investigation of the basal spacing evolution of organoclay during the intercalation of CPC can provide unique perception to the microstructures of organoclays. The intercalated CPC will continue its rearrangement within the interlayer space which can lead to increase of basal spacing value. FT-IR spectrum and basal spacing of pure bentonite and organoclays indicated the incorporation of surfactant and changed to organophilic in different organoclays. This study demonstrates that not only the structure of surfactant but also the morphology of organoclay strongly depends on the surfactant packing density within the bentonite inter layer space. In addition, it can be also proposed that the surface charge magnitude or its distribution on clay mineral might be an important factor for expansion characteristics of organoclay.

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