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Journal Name

ARTICLE

Recyclability of Organically Modified Clays for Oil Absorption and Recovery

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The organically modified layered silicates (OLS) were prepared from the ionic exchanging intercalation of the natural clays such as sodium montmorillonite (MMT) by fatty alkyl amines such as n-octadecylamine (ODA) and used for hydrocarbon recovery. The comparisons of OLS modified by different stoichiometry of ODA and by poly(oxypropylene)-amines were conducted. The OLS were characterized by X-ray diffraction (XRD) to study the correlation between their basal spacings of interlayer distance and the efficiency of oil absorption. With different equivalent of ODA to the cationic exchanging capacity (CEC) of clay, the basal spacings were expanded from the pristine 12 Å to 28 Å (0.5 CEC), 30 Å (1.0 CEC), 30 Å (1.5 CEC) and 34 Å (2.0 CEC). After crude oil absorption, the OLS further gained their organic compositions and expanded *d* spacings to 45–48 Å or even evolved into featureless in XRD. The oil absorption efficiency up to 9 times of oil-on-clay in mass was observed, and the OLS showed the characteristics of OLS/oil aggregation into oil lumps from water. The oil absorption-desorption cycles were repeated for three times, demonstrating the feasibility of clay reuses and oil recovery. Our findings implied the stability of clay/oil structure and process suitability of employing fatty amines as the intercalating organics for the clays. The high oil-absorbing efficiency and recyclability indicate the practical applications including the remedy of oil pollution in water, enhancing oil recovery and hydraulic fracture or shale-oil fracking process.

1. Introduction

Two main issues in the petroleum industry are the efficiency of oil exploration and the possible occurrence of oil-spill incident in the environment. Environmental pollution by crude oil has occurred and seriously contaminated the environment because it causes great harm to the agriculture and many other species. Thus the problem of oil spills must be carefully treated to prevent possible damages to the ecological system.

The current methods of remedying crude oil spill can be categorized into physical, chemical, and biological methods. The physical methods include adsorbents¹⁻³ and skimmers.⁴ The most commonly chemical methods include dispersion⁵ and in-situ burning.^{6,7} For the bioremediation,⁸⁻¹⁰ the materials were used to stimulate microbial growth enhancing the biodegradation. Among these methods, the adsorbents of physical method have several advantages. For example, the adsorbents can recover the crude oil with high capacity and minimum harmful effects on ecosystem with low costs.

The most common adsorbents are activated carbon¹¹ and superhydrophobic materials.^{12,13} For the superhydrophobic materials, there were several studies focused on the surface modification of sponges¹⁴⁻¹⁶ or filter papers.¹⁷ The superhydrophobic materials selectively absorb crude oil and make oil to separate out from water phase due to their different

surface energy. Furthermore, the resin,¹⁸ graphene aerogel,¹⁹ and hydrogel²⁰ have also been studied as oil adsorbents. Among these crude oil absorption materials, searching for a low-cost, high absorption efficiency, recyclable, and environmental-benign material for oil-spill remediation is fast growing in demand.

Clay minerals such as sodium montmorillonite (MMT) are abundant in the natural deposits and used widely in industry due to their properties of high surface area and ionic characteristics for absorption. One of conventional methods to modify their properties is intercalation of hydrophobic organic ammonium cations in the clay layer spacing through ion exchange reaction. The organically modified layered silicates (OLS) became more compatible for organic interaction. Previously,²¹ we had developed the uses of poly(oxypropylene)-diamine salts for the clay modification. The intercalation could render the hydrophobic property to the resulted organoclays and encapsulate guest molecules and organic species, making them suitable for many industrial applications including catalysts,²² adsorbents, and polymer nanocomposites.²³⁻²⁵ One specific application of above method has been demonstrated in our previous work²⁶ in which we used the poly(oxypropylene)-amine-salt (POP) as the hydrophobic organics for clay and encapsulated with iron-oxide nanoparticles (FeNPs), then an intriguing dual functions of hydrophobic mobility under magnetic field were developed.

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**Table 1.** Characteristics of the n-octadecylamine intercalated clays and their oil absorption efficiency

Intercalation Agents	Amine/clay (CEC) ^a	Intercalated organoclays			After oil absorption		Efficiency (absorbed oil/organoclay, w/w) ^c
		Organic fraction (wt%) ^b	<i>d</i> spacing (Å)	Oil added/organoclay (w/w)	Organic fraction (wt%) ^b	<i>d</i> spacing (Å)	
None (MMT)	--	0	12	0/1	0	12	None
C ₁₈ H ₃₇ NH ₃ ⁺	0.5	21	28	4/1	85	17	4/1
	1.0	28	30	6/1	86	45	6/1
	1.5	37	30	8/1	91	48	8/1
	2.0	42	34	9/1	94	Featureless	9/1

^a equivalent ratio of amine-H⁺ to MMT (CEC: cation exchange capacity, 120 mequiv./100 g)

^b determined by TGA

^c efficiency was calculated from equation (1) for the weight ratio of oil/organoclay, and the endpoint was defined by the oil/clay aggregation and clear separation from water.

Moreover, we have demonstrated removing crude oil from water up to 15 folds weight based on the organoclays.²⁷ It was also found that the aggregation of the oil/clay absorption was temperature-dependent, thus the oil-absorbed clay could aggregate into lumps and separate from water through temperature control. This phenomenon was similar to Lower Critical Aggregation Temperature (LCAT) due to the presence of poly(oxypropylene)-amines intercalated in the clay galleries. However, the organoclays are not reusable for the oil absorption and desorption process.

In this work, we adopted the n-octadecylamine-HCl salts (ODA) as the hydrophobic intercalating organic agents for preparing oil-absorbing organoclays. Different compositions of ODA/MMT by varying their ionic exchanging stoichiometry were achieved. A series of organoclays comprising of different equivalents of ODA to the clay ionic exchange capacity (CEC) in the clay's layered structure were thus prepared to study the oil-absorbing efficiency. After absorbing crude oil, the ODA/MMT/Oil aggregates were phased out in large lumps from water medium. By comparing with the POP-intercalated clays, the organoclays with ODA intercalation won out by superior recovery and reusable characteristics for oil absorption, which was demonstrated by the process of toluene extraction after oil absorption. The recovery efficiency up to 90% over multiple repeating tests showed the stability of the ODA/MMT structures and potentials for oil-spill remediation in the environment.

2. Experimental section

2.1 Materials

Sodium form of montmorillonite (MMT) is one of the natural occurring phyllosilicate minerals with the generic structure of 2:1 tetrahedral and octahedral aluminosilicate sheets. The clay mineral, supplied by Nanocor Co. (USA), are the aggregates of primary units of plates in stacks. The average sheet is estimated to be in the dimension of ca. 100 x 100 x 1 nm³ and 8–10 sheets in one primary stack. The silicate clay with layered structure consist of exchangeable metal ions with the estimated cationic exchange capacity (CEC) of 1.20 mequiv./g. The n-octadecylamine (ODA) was purchased from Alfa Aesar (USA). The batch of crude-oil samples used in this work was supplied by Taiwan CPC (a refinery in Taiwan).

2.2 Preparation of Organoclays

The organoclay was prepared by intercalation of the ODA salts, according to the procedures reported previously.²¹ In a typical procedure, MMT (1.20 mequiv./g) was swelled in deionized water (10 wt%) at 80 °C for 3 hours. The ODA was separately treated with hydrochloric acid in an acidification equivalent of the clay CEC value and added to the MMT slurry in water. After the continuously stirred at 80 °C for 0.5 h, the diffraction for characterizing the interlayer *d* spacing.

2.3 Effect of Oil Absorption

In a beaker (100 mL) equipped with a magnetic stirring bar, a portion of petroleum crude oil in the form of black and viscous liquid (0.5 g) in water (20 g) slurry and then added the organoclays (0.5 g) at ambient temperature under agitation for 10 minutes. The absorption efficiency was determined by the saturation of oil absorption by the added organoclay after agitation in generating the clay/oil aggregated lumps that were clearly separated out from water. The weight ratio of oil/organoclays were determined.

2.4 Characterization

X-ray powder diffraction (XRD) was performed by using a Shimadzu SD-D1 diffractometer with Cu target ($k = 1.5408 \text{ \AA}$) at a generator voltage of 45 kV and current of 40 mA to measure the basal spacing (d spacing) of organoclay. The basal spacing was calculated according to Bragg's equation ($n\lambda = 2d\sin\theta$). The thermal analysis was conducted by thermal gravimetric analyzer (TGA, Perkin-Elmer Pyris 1 model). The organic fraction was estimated from the weight loss by programming the temperature from 100 °C to 800 °C at the rate of 10 °C/min.

3. Results and discussion

3.1 Intercalation of MMT with n-Octadecylamine Salts

The organoclays were prepared by the ionic exchange intercalation of the layered silicates with n-octadecylamine-HCl-salts (ODA). The ODA were treated with hydrochloric acid and allowed the incorporation of the organics in the layered silicate structures. After the organic modification, the basal d spacing of the layered silicates were expanded from 12 Å to 28 Å by the

incorporation of 0.5 equivalent ODA salts on the basis of the clay CEC, as indicated in Table 1. In another composition of ODA/MMT at the increased amount of ODA to clay at 1.5 equivalent CEC, the clay spacings remained at 28–30 Å but further expended to 34 Å at 2.0 equivalent of ODA addition.

It was noted that the basal spacing expansion of the intercalated MMT by ODA is different from poly(oxypropylene)-amine (POP-amine) which was reported previously.²⁷ The relatively smaller spacing expansion was observed for ODA/MMT. Instead of expanding up to 34 Å at 2.0 equivalent of ODA addition, the spacing of POP-amine/MMT was expanded from 12 Å to 73 Å when introducing the amount at 1.0 CEC ratio and up to 84 Å at 2.0 CEC ratio, also indicated by organic fraction (ODA fraction).

3.2 Oil Absorption and Spacing Change of the Layered Silicate

The oil absorption efficiency and d spacing characterization of various ODA-intercalated MMT are summarized in Table 1. With the intercalation of ODA, the interlayer of layered silicates was expanded from 12 Å to 28–34 Å depending on the amount of organic incorporation based on the clay CEC or equivalent ionic exchange capacity. For the organoclays with ODA intercalation below 1.0 CEC such as 0.5 CEC, their oil absorption could cause a decrease of d spacing. For example, the d spacing of organoclay at 0.5 CEC, ODA decreased from 28 Å to 17 Å after absorbing oil. In contrast, the interlayer spacing of organoclays at 1.0 CEC and 1.5 CEC increased dramatically after absorbing crude oil, as also indicated by the increase of organic fraction (the fraction of ODA + crude oil).

This indicates that the organoclays are required to be properly designed with ODA for the application of oil-absorption. The

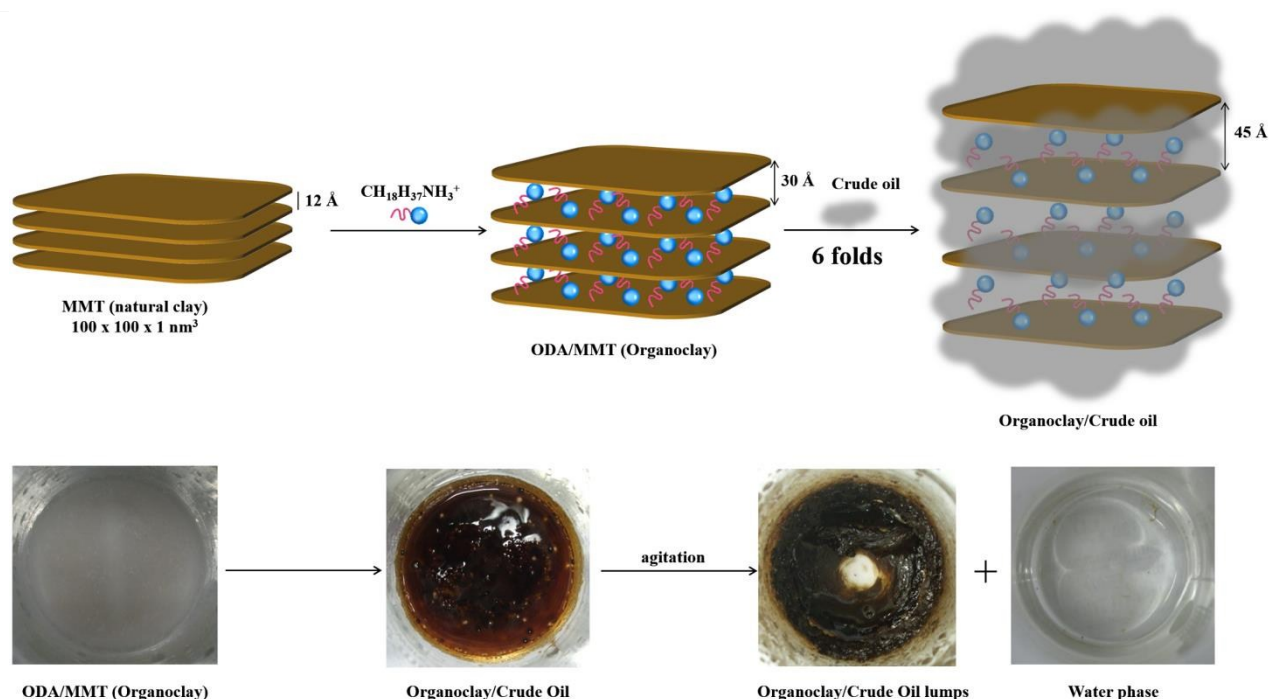


Figure 1. The process of crude oil absorption by $\text{C}_{18}\text{H}_{37}\text{NH}_3^+(\text{ODA})/\text{MMT}$ (1.0 CEC) with d spacing enlargement and oil/water separation

ODA below 1.0 CEC intercalation was too weak in hydrophobic aggregation in the clay interlayer to absorb oil in significant amount. It appears the C18-alkyl groups of ODA in the silicate interlayer spacing provide the hydrophobic force for absorbing oil and subsequently altering the multilayered structures of the silicates. For the organoclays with 1.0 CEC intercalation, the ODA aggregates absorbed oil and increased the d spacing from 30 Å to 45 Å based on XRD analyses. Similar phenomenon was observed for 1.5 CEC clay and even reaching featureless of XRD pattern indicating too much oil to detect the silicate layer structures. By comparing various ratios of ODA/clay in intercalation, it was found the organoclays with a high capacity of oil absorption tended to form oil/clay lumps which clearly separated out from water phase, implying the potential application for oil/water separation. The occurrence of increasing d spacings of organoclays from 30 Å to 45-48 Å indicated the absorbed oil actually being encapsulated in the interlayer. The water phase separation from the oil-lump aggregates was illustrated (Figure 1).

3.3 Oil Absorption Efficiency

The oil absorption efficiency (η) was estimated on the basis of the following equation, where $m_{\text{oil absorbed}}$, $m_{\text{octadecylamine (MODA)}}$ and m_{MMT} are the mass of absorbed oil, ODA, and MMT, respectively.

$$\eta = (m_{\text{oil absorbed}}) / [(m_{\text{MODA}}) + (m_{\text{MMT}})] \quad (1)$$

The oil absorption efficiency from the organoclays with different CEC intercalation of ODA is demonstrated in Figure 2. The oil absorption efficiency was calculated by equation (1). It was noticed that the absorption efficiency of organoclay increased with intercalated amount of ODA. It seems the amount of ODA as the hydrophobic segregation in the silicate layer spacing had built the hydrophobic force for absorbing incoming

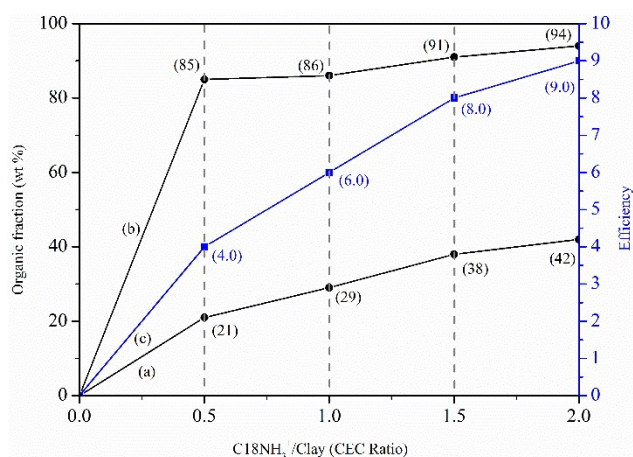


Figure 2. The organic fraction and efficiency of ODA/MMT with different CEC ratios (from 0.5 to 2.0) for oil absorption, curve (a) the organic fraction before oil absorption, curve (b) the organic fraction after oil absorption, and curve (c) the calculated oil-absorption efficiency in correspondence with (b)

oil and forming secondary aggregates among the clay units. At 0.5 CEC intercalation, the ODA in the clay spacing was below the critical concentration for hydrophobic phase aggregation, hence the oil absorption behavior was different from that of above 1.0 CEC organoclays. With the intact hydrophobic aggregation in clays, the 1.0 CEC clay enabled to absorb about 6 folds of oil by weight, and further expanded the d spacing up to 45 Å (XRD) and form large oil/silicate aggregates which clearly separated from water. The overall performance and the correlation of ODA intercalation to oil absorbing efficiency are summarized by three curves in Figure 2.

Table 2. The recyclability and oil recovery efficiency of C₁₈H₃₇NH₃⁺/MMT (ODA/MMT) within three cycles

C ₁₈ H ₃₇ NH ₃ ⁺ /MMT	Organic Fraction (%)	d spacing (Å)	Oil Recovery (%)
Before oil absorption	28	30	--
1 st absorption	84	45	--
1 st extraction	29	22	95
2 nd absorption	90	49	--
2 nd extraction	28	22	90
3 rd absorption	94	48	--
3 rd extraction	32	23	92

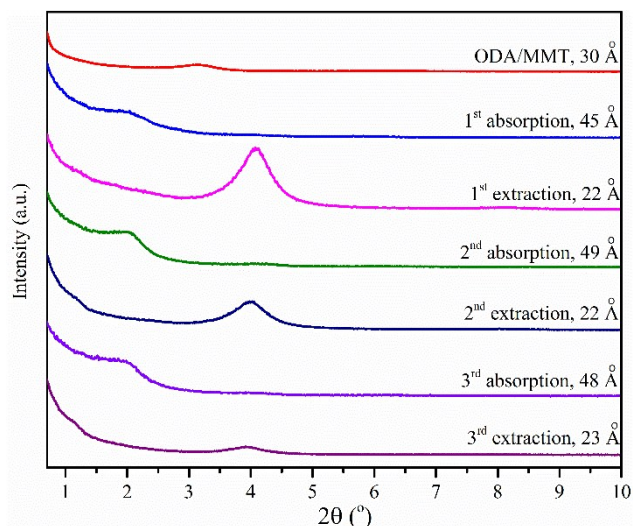


Figure 3. Basal spacing changes of $C_{18}H_{37}NH_3^+$ (ODA)/MMT/Crude oil recovery within three cycles

3.4 Oil Recovery by Absorption-Desorption Cycle

The recyclability for oil absorption and desorption were then investigated. After the oil absorption of the exemplified organoclay (1.0 CEC of ODA intercalation), the oil desorption was performed by toluene and water extraction. Before oil absorption, the organoclay is amphiphilic and dispersible in water. After oil absorption, the crude oil/organoclay aggregated into lumps and separated from water phase. Owing to the solubility difference between crude oil and octadecyl amine in toluene, the crude oil can be extracted into toluene phase and the organoclay be re-dispersed in water phase. In one example, 14 g of crude oil absorbed organoclay was added to an extraction flask and followed by adding 86 g water and 150 g toluene. After a simple shaking and standing for a few minutes, the crude oil was extracted into toluene phase. After removing the toluene phase, the bottom water/organoclay phase was repeatedly adding another portion of 150 g toluene for extraction. The toluene addition can be repeated for several times until completing the oil removal. The organoclay was recovered in water phase and re-used for another oil absorption cycle.

The recovery of crude oil was measured for the efficiency. Several cycles of absorption-desorption were performed, and summarized in Table 2.

By XRD and TGA characterization, the oil recovery efficiency remained over 90% for three cycles of oil absorption, extractive desorption and re-absorption. It was demonstrated that the organic fraction increasing to 84, 90, and 94 weight percent after oil absorption and decreasing to 28, 29, and 32 weight percent after desorption for all three cycles. The XRD analyses

also revealed the repeatable basal spacing in absorption-desorption cycle, i.e. expanding to ~ 45 Å after absorption and shrinking to ~ 22 Å after desorption. This reversibility in basal spacing change indicated the stability of ODA intercalated MMT, which was supported by the stability of ODA hydrophobic phase aggregation in the silicate galleries. It is worth to note that high efficiency of oil absorption and reusability of the organoclay are two essential factors for the practical applications in many oil recovery processes.

4. Conclusions

A series of C_{18} -alkyl-amine (ODA) modified organoclays of layered silicates (OLS) were prepared and used for the oil absorption and hydrocarbon recovery from water. By varying the compositions of intercalated alkyl-amine, the OLS showed adjustable interlayer spacing structure, ranging from the pristine 12 Å to 28-34 Å depending on the added amount of amine-salt in clays. These OLS demonstrated the ability of oil absorption at high efficiency of 9 times by weight measurement of the oil/clay ratio. It was further demonstrated that the oil-absorbed OLS able to self-aggregate into oil lumps, separate out from water and easily be recoverable. Moreover, through a simple process of toluene extraction, oil lumps could be washed away and the OLS recyclable. Three cycles of absorption-extraction process demonstrated the recyclability up to 95% efficiency. This ODA modified organoclays showed the potentials for remediation of oil spill in water and process of hydrocarbon recovery in oil field.

Acknowledgements

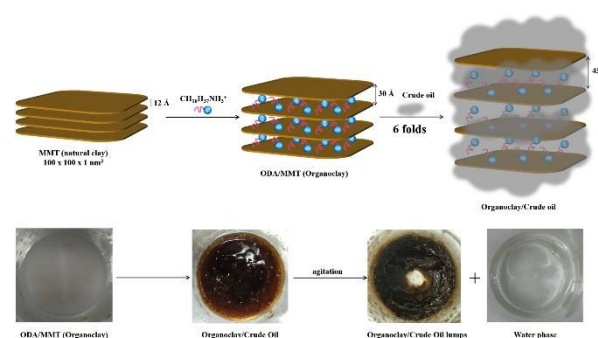
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Graphical Abstract/ Table of Content



The ODA modified organoclay could be used as crude oil absorbents with high recyclability and stable reusability.