



# Influence of the purity of montmorillonite on its surface modification with an alkyl-ammonium salt



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## ABSTRACT

Effect of the purity of montmorillonite (Mt) on its modification with hexadecyltrimethylammonium bromide (HDTMA) was evaluated. Montmorillonite with different grades of purity were prepared using two strategies: size fractionation (physical purification) and combination of chemical dissolution of some impurities and size fractionation (chemical–physical purification). It was found that the physical purification separated some impurities while chemical–physical purification separated almost all impurities from the montmorillonite. The cation exchange capacity (CEC) of the montmorillonite was increased after purification; this increase was much higher for samples that underwent chemical–physical purification, in comparison to those purified only with size fractionation. After modification of the montmorillonite with different grades of purity at the same ratio of HDTMA/CEC, different XRD patterns were obtained. For the modified raw and physically purified montmorillonite the 001 reflection of the XRD spectra were broad ranging between 15 and 18 Å, and for the purer montmorillonite, after the modification with HDTMA the XRD spectra showed very much sharper diffraction peaks at d values of 14.7 and 17.4 Å. The DTG results showed that the HDTMA was adsorbed in the interlayer spaces as HDTMA-Br molecules or HDTMA<sup>+</sup> cations. It was concluded that the form of adsorption of HDTMA either as HDTMA-Br molecules or HDTMA<sup>+</sup> cations is related to the arrangement of charges on the montmorillonite layers which can be altered during its chemical purification process.

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## 1. Introduction

During recent decades montmorillonite has found advanced applications in clay polymer nanocomposites (CPN) (Liu and Wu, 2001; Wang et al., 2004; Thuc et al., 2010; Sehaqui et al., 2013; Wu et al., 2014; Diéguez et al., 2015; Savas and Hancer, 2015), drug delivery systems (Patel et al., 2006; Aguzzi et al., 2007; Joshi et al., 2009; Chen and Evans, 2011; Salahuddin et al., 2011; Jain and Datta, 2014; Saha et al., 2014), adsorption of biomolecules (Assifaoui et al., 2014; Lepoitevin et al., 2014) and enzyme immobilization (Giannelis, 1996; Vaia et al., 1996; Ghiaci et al., 2009a, 2009b; LeBaron et al., 1999; Songurtekin et al., 2013; Hristova and Zhivkov, 2015). It is due to surface characteristics and its unique layered structure (Brigatti et al., 2013), as well as the possibility to finely tune the surface characteristics of the montmorillonite (Schoonheydt and Johnston, 2013).

The surface of montmorillonite has been modified using different species in order to achieve the desired characteristics. Prior to the surface modification process, the montmorillonite is initially separated from other minerals and then modified using different organic or inorganic species (Ojijo et al., 2012; Vasilakos and Tarantili, 2012; Mauroy et al., 2013; Nguyen et al., 2013; Bilgiç et al., 2014; Yu et al., 2014;

Zawrah et al., 2014; Cubuk et al., 2015; Wang et al., 2015). In this process, the most important parameters affecting the final characteristics of the surface modified montmorillonite are defined as the nature of the montmorillonite (Kornmann et al., 2001b), the nature of the modifying agent (Kornmann et al., 2001a), and methods of modification (de Paiva et al., 2008). While the interaction of the modifying agent with montmorillonite surfaces provides interesting information, the purification of the montmorillonite from the bentonite (Kim et al., 2005; Feng et al., 2012) might affect its modification as well.

Different methods have been proposed to purify montmorillonite (Earley et al., 1953; Higashi and Ikeda, 1974; Hassan and Abdel-Khalek, 1998; Ottner et al., 2000; Benna et al., 2002; Neaman et al., 2003; Patel et al., 2007a, 2007b; Thuc et al., 2010). These methods can be categorized into size fractionation, in which the centrifuge force is used to remove content below a specific particle size (Georgakilas et al., 2004; Ghiaci et al., 2009a, 2009b; Sedaghat et al., 2009; Thuc et al., 2010), and chemical decomposition and dissolution of impurities (Hillier and Lumsdon, 2008; Bergaya and Lagaly, 2013). Each method provides montmorillonite with different grades of purity, but the effect of the purification process on its organic modification has been neglected to some extent.

In the present research, montmorillonite was purified using physical and chemical pathway in order to prepare montmorillonite with different grades of purity. The characteristics of the purified montmorillonite

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were analyzed using X-ray diffraction (XRD), thermogravimetric (TG) and differential thermogravimetry (DTG) analysis, scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDS), and cation exchange capacity (CEC). Montmorillonite with different grades of purity were then modified with quaternary ammonium salt (HDTMA-Br) and the results were compared to analyze the effect of purity of the montmorillonite on its surface modification.

## 2. Materials and methods

### 2.1. Chemicals

NaOH (analytical reagent; Merck), HCl (37% w/w, analytical reagent; Merck), and hexadecyltrimethylammonium bromide (HDTMA-Br, >98%; Merck) were used as received. Deionized water was used (the water was purified to a resistivity of  $\geq 18.2 \text{ M}\Omega \cdot \text{cm}$ ) in all experiments. Three bentonite samples were provided by the Zanjan (sample 1, Table 1), Salafchegan (sample 2, Table 1), and Khorasan (sample 3, Table 1) bentonite mines (Iran).

### 2.2. Montmorillonite purification

For the physical purification the size fractions  $<2.5$  or  $<1 \mu\text{m}$  of montmorillonite particles was separated using the centrifuge force (Thuc et al., 2010). Typically the raw bentonite was initially dried at  $110^\circ\text{C}$  for 2 h and 12 g of it was dispersed in 400 ml of deionized water and mixed for 12 h (in all experiment the mechanical overhead mixer at the speed of 400 rpm was used for the mixing process). Then the mixture was centrifuged at 1000 rpm or 2500 rpm for 250 s to separate particles smaller than 2.5 or 1  $\mu\text{m}$ , respectively. The supernatant was collected and dried to obtain the physically purified montmorillonite. Samples named based on their origin (as described above) and the particle sizes. Samples with particle sizes smaller than 2.5  $\mu\text{m}$  were named 1-1, 2-1, and 3-1 and samples with particles smaller than 1  $\mu\text{m}$  were named 1-2, 2-2, and 3-2.

**Table 1**  
Detailed chemical treatment parameters and cation exchange capacity (CEC) of samples.

Sample no.	NaOH concentration (M)	Largest particle size in each sample <sup>a</sup> (micron)	Time of reaction with NaOH (min)	CEC (meq/100 g)	Yield (%) <sup>b</sup>
1	–	Raw sample	–	47	–
1-1	–	2.5	–	61	10
1-2	–	1	–	62	5
1-3	0.23	2.5	10	75	7
2	–	Raw sample	–	73	–
2-1	–	2.5	–	77	9
2-2	–	1	–	87	5
2-3	0.12	2.5	10	87	8
2-4	0.23	2.5	10	95	7
2-5	0.46	2.5	10	101	7
2-6	1.0	2.5	10	98	6
2-7	0.23	2.5	20	99	7
2-8	0.23	2.5	30	100	7
2-9	0.23	2.5	60	98	6
2-10	0.23	2.5	120	96	6
3	–	Raw sample	–	47	–
3-1	–	2.5	–	67	10
3-2	–	1	–	77	5
3-3	0.23	2.5	10	86	7

<sup>a</sup> This is the size which all particles of the samples are smaller than that. The method of how this number is calculated is summarized in the Materials and methods section.

<sup>b</sup> The yield is calculated in percent of sample collected after the purification process compared to amount of sample before the start of the experiment.

The centrifugation time was calculated based on the Stokes' law as described previously (Thuc et al., 2010):

$$t = \left[ \eta \cdot \log_{10} \left( \frac{R}{S} \right) \right] / \left[ 3.81 \cdot N^2 \cdot r^2 \cdot \Delta S \right] \quad (1)$$

with:

t: centrifuge time (s)

R: distance from the deposit surface to the axis of the centrifuge rotor (13.1 cm)

S: distance from the liquid surface to the axis of the centrifuge rotor (4.5 cm)

N: rotation speed (in order to achieve montmorillonite particles smaller than a specific size this number was changed)

r: maximum radius of the desired particles in cm

$\Delta S$ : specific gravity difference between the particles and the liquid dispersion ( $0.00528 \text{ g cm}^{-3}$ )

$\eta$ : viscosity of the fluid ( $0.00748 \text{ P}$  for deionized water).

In the second method, raw bentonite was treated with NaOH and then with HCl prior to the size fractionation step. Typically the bentonite was initially dried at  $110^\circ\text{C}$  for 2 h and a 3% (w/v) solution (200 ml) of bentonite in deionized water was prepared and mixed for 12 h. The mixture was then heated to the boiling point and 100 ml of 0.7 M NaOH was added to it. The solution was mixed vigorously for 10 min and then cooled down quickly by immersion of the beaker in an ice bath. Then the mixture was centrifuged at 5000 rpm for 5 min and settled materials were washed with deionized water several times and the final sedimented material was dried at  $110^\circ\text{C}$  overnight. Afterwards, a dispersion of 3% (w/v) of NaOH treated sample in 1 M HCl was prepared and mixed for 10 min at  $40^\circ\text{C}$ . The mixture was centrifuged at 5000 rpm for 5 min, washed with deionized water several times and again dried at  $110^\circ\text{C}$  overnight. Finally, the  $<2.5 \mu\text{m}$  size fractions of pure montmorillonite was collected using the centrifuge force as follows: the chemically-treated samples were dispersed in 400 ml of deionized water, agitated for 12 h and then centrifuged at 1000 rpm for 250 s to obtain the chemically-physical treated montmorillonite. Samples were named 2-3, 2-4, 2-5, and 2-6 when the treatment with NaOH was done at the concentration of 0.12, 0.23, 0.46, and 1.0 M, respectively. And samples were named 2-7, 2-8, 2-9, and 2-10 when the concentration of NaOH were kept the same for all samples at 0.23 M and the duration of reaction with NaOH was changed for 20, 30, 60, and 120 min (Table 1), respectively.

### 2.3. Modification with HDTMA

Different samples, which were purified with physical or chemical-physical method, were modified and the results were compared. For the first set of experiment the mass ratio of HDTMA/samples and, in the second run, the ratio of HDTMA/CEC of samples were kept the same for all samples in order to achieve the best comparison of the changes after modification (the ratio of HDTMA/CEC of each samples is summarized in Table 2). In a typical modification test, 0.8 g of montmorillonite was dispersed in 80 ml of deionized water for 12 h and then 20 ml of deionized water containing 0.177 g of HDTMA was added and mixed at room temperature for 3 h. The modified montmorillonite was obtained using the centrifuge force at 5000 rpm for 5 min and washed with deionized water several times. The treated materials were then dried at  $65^\circ\text{C}$  overnight.

### 2.4. Characterizations

XRD analysis was carried out using a Philips PW1800. For low angle XRD analysis, the samples were tested with X'Pert Pro MPD (PANalytical) in the range of  $2\theta$  from  $1^\circ$  to  $10^\circ$ . SEM analysis was used

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