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The influence of pH on organovermiculite structure stability

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ABSTRACT

There is a large amount of research and application studies in the topic of organically modified vermiculites and their properties. In this work, the stability of two organovermiculites, one modified with hexadecyltrimethylammonium ($HDTMA^+$) and the other modified with hexadecylpyridinium (HDP^+) ions, was investigated at pH values from 1 to 14 at laboratory temperature. The organovermiculites in the pH range of 4–10 were stable. In addition, the $HDTMA^+$-vermiculite was stable in strong alkaline media and under extreme acidic conditions as well. However, HDP^+-vermiculite underwent significant decomposition when exposed to strong acidic or alkaline conditions (pH 1, 2 and 12, 14). The prepared and tested materials were investigated using X-ray diffraction (XRD) method, Fourier transform infrared (FTIR) spectrometry, total organic carbon content (TOC), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The leaching of structural cations was determined as well.

1. Introduction

Many researchers are interested in the study of organoclays and their potential applications (Bergaya et al., 2011; de Paiva et al., 2008; Groisman et al., 2004; He et al., 2006; Lee and Tiwari, 2012; Simha Martynková et al., 2007; Yariv and Cross, 2002). Among clay minerals, the subgroup of phyllosilicates 2:1 is often organically modified due to their layered structures. Modifying the clay mineral surface polarity by interlayer cation exchange of inorganic ions for onium ions (e.g. quaternary ammonium, phosphonium or pyridinium cations) alters the phyllosilicate properties and enables the thermodynamically favourable penetration of other organic species in the interlayer space (Zhu and Zhu, 2008). Because of this characteristic, they are used in many industrial applications. Their application for removal of non-polar organic compounds from waste water in various environmental technologies is one of these possibilities.

Only a few research studies have focused on organoclays' stability influencing factors, namely, the influence of pH (Breen and Watson, 1998; Kooli, 2009a,b; Madejová et al., 2012; Moronta et al., 2002; Palková et al., 2011). The pH influence studies tend to restrict their investigations to its role on adsorption of phenols, aniline and other ionisable compounds. Breen et al. (1997) studied the resistance of various organoclays modified with different organic cations. He found that organic cations with long aliphatic hydrocarbon chains were more resistant than tetramethylammonium to displacement by H^+.

A more studied area is acid-activated clay mineral, where natural clay mineral is treated with an inorganic acid (HCl, H_2SO_4) at elevated temperature (Komadel and Madejová, 2013; Rožić et al., 2010). Some authors investigated intercalation of organic cations to acid-activated clay minerals or they studied acid activation of organoclays (Breen and Watson, 1998; Komadel and Madejová, 2013; Kooli, 2009a,b; Moronta et al., 2002). The effect of alkaline treatments on the mineral stability has been extensively studied on smectites and kaolinites (Honty et al., 2010; Sánchez et al., 2006; Savage et al., 2002).

A few studies have examined the behaviour of vermiculite under strong acidic conditions (Maqueda et al., 2009; Okada et al., 2006; Perez-Rodriguez et al., 2011; Temuujin et al., 2003). Vermiculite is phyllosilicate 2:1 and has a high isomorphous substitution in the octahedral and tetrahedral sheets, which leads to a relatively higher negative charge on the layers and higher cation exchange capacity (Simha Martynková and Valašková, 2010). It can be organically modified, and the organovermiculite product exhibits a high adsorption capacity for hydrophobic molecules. It is an efficient adsorbent material

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Table 1
Characterisation of prepared organovermiculites.

Organovermiculites	f_{OC} (%)	d_{001} (nm)	Cation exchange (%)
$HDTMA^+$-vermiculite	29.5	2.800	90
HDP^+-vermiculite	30.5	2.800	84

for the removal of organic pollutants from waste water and air with high adsorption efficiency (Plachá et al., 2008, 2010).

The aim of this work was to study the influence of pH on the stability of organovermiculites modified by two different organic cations, namely, hexadecyltrimethylammonium and hexadecylpyridinium in an aqueous environment. These cations are similar in their chemical aspect; however, the first is strictly aliphatic, and the second has in part an aromatic structure (pyridinium cycle). The interactions between ammonium and pyridinium cations and the vermiculite surface are different, as it was described in previous works (Plachá et al., 2008, 2010). This influences the appropriate conditions for the application of organoclays for waste water treatment technologies. Moreover, the question is, would it be possible to use organoclays in extreme pH conditions (in case of strong acidic or alkaline wastewater) without significant alteration of their structure?

2. Experimental details

2.1. Materials

Natural Mg^{2+}-vermiculite from Letovice (Czech Republic) with particle sizes less than 40 μm was used for the organovermiculite synthesis. Its crystallochemical formula $(Si_{3.13}Al_{0.86}Ti_{0.02})$ $(Mg_{2.33}Fe_{0.45}Al_{0.01})$ $O_{10}(OH)_2$ $(Mg_{0.19}Ca_{0.02}\ K_{0.01})$ $8.8H_2O$ was calculated on the base of elemental analysis using x-ray fluorescence spectrometry methods. The cation exchange capacity (CEC) of this vermiculite is 144 cmol(+)/kg as determined by the Cd^{2+} exchange method using absorption atomic spectrometry as found in the studies of Plachá et al. (2008, 2010) and Simha Martynková et al. (2007).

Sodium chloride (NaCl), hexadecyltrimethylammonium bromide ($HDTMA^+$) $C_{19}H_{42}N^+Br^-$ and hexadecylpyridinium chloride monohydrate (HDP^+) $C_{21}H_{38}N^+Cl^-\cdot H_2O$ were used for vermiculite intercalation. NaOH and H_2SO_4 solutions (0.1 $mol\cdot dm^{-3}$) were used for pH value adjustment of the tested aqueous solutions. All solutions were prepared with analytical grade chemicals and ultra-pure water (Milli-Q Academic system). All chemicals were supplied by Sigma Aldrich.

2.2. Analytical methods

A number of different analytical techniques have been used for characterisation of the prepared organovermiculites, as well as for identification of organovermiculites' structure alterations after the treatment under different pH conditions.

Table 2
Characterisation of organovermiculites after treatment in different pH.

pH	HDP^+-vermiculite		$HDTMA^+$-vermiculite	
	f_{OC} (%)	d_{001} (nm)	f_{OC} (%)	d_{001} (nm)
1	28.6	3.131	28.4	3.960
2	28.6	2.904	28.7	3.520
4	28.9	2.886	30.1	2.700
6	28.9	2.857	30.7	2.720
7	29.1	2.810	30.9	2.840
8	28.9	2.840	30.3	2.910
10	28.9	2.940	30.1	2.880
12	28.4	2.840	29.4	3.520
14	29.0	2.940	26.2	4.240

The pH values of aqueous solutions were measured using a pH meter Inolab, pH 730. The XRD patterns were acquired using X-ray Powder Diffractometer INEL (Debye-Scherrer configuration, position sensitive detector PSD 120, conditions: reflection mode, Cu Kα radiation, 28 kV and 15 mA). The quantities of organic carbon were determined with a MULTI N/C 3100 (Carl Zeiss Jena) TOC analyser. The ICP-OES spectrometer Yvon Jobin 24 was used for the analysis of Al^{3+}, Fe^{3+}, Mg^{2+} and Ti^{4+} cations concentration in the aqueous solutions after the organoclay treatments at various pH. The Flame AAS spectrometer Unicam 969 was used for the analysis of Na^+ cations in the interlayer space. The FTIR spectra in the middle IR region (4000–400 cm^{-1}) were obtained using KBr pressed disc technique by FTIR spectrometer IR 2000, Perkin-Elmer (Michelson interferometer).

A scanning electron microscope Philips XL 30 Series (SEM) equipped with detectors for secondary and back-scattered electrons was used for microscopic observations of morphology changes of organovermiculite particles. The transmission electron microscopy (TEM) morphology studies were conducted on an FEI Tecnai T20 operating at 200 kV. The TEM samples were prepared on standard copper grids (700 mesh) by gently pressing a small fraction of the sample on to it.

2.3. Preparation of organovermiculites

Two organovermiculites were prepared from the starting Mg^{2+}-vermiculite as described by Plachá et al. (2008, 2010). First, a monoionic Na^+-vermiculite was obtained by saturation of the natural form repeatedly with 2 M NaCl aqueous solution and washed with distilled

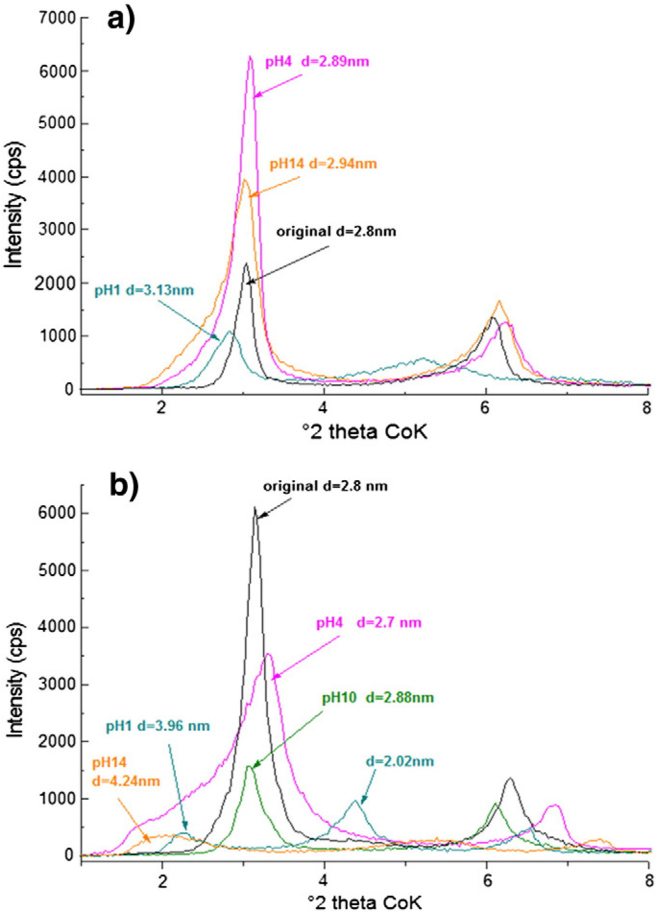

Fig. 1. The XRD patterns of modified vermiculites treated with aqueous solutions of different pH: (a) the $HDTMA^+$-vermiculites and (b) HDP^+-vermiculites.