



Research paper

Acid activated clays: Materials in continuous demand

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ABSTRACT

Acid activation is a chemical treatment traditionally used on clays, typically bentonites in hydrochloric or sulphuric acid, to obtain partly dissolved materials with enhanced surface properties suitable for new applications or displaying interesting new behaviour. This paper is based mostly on the results of long-running experiments in our laboratories, supplemented by published data from elsewhere. A review of recent literature shows that interest in these materials remains widespread, with several new developments of environmental relevance and in the area of clay-polymer nanocomposites. Acid treatment of vermiculites and of non-swelling clay materials is also included.

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1. Introduction

One application of calcium bentonite with a significant market is the decolourization of vegetable, animal and mineral oils. Most of the calcium bentonite used for filtering and decolourizing oils is acid activated (Odom, 1984). Acid treatment with sulphuric or hydrochloric acid removes the calcium cations from the surfaces and edges of the layers, which increases the overall negative charge. In industry, sulphuric acid is preferred to hydrochloric because it is less expensive and is not as harsh as HCl (Murray, 2007). This makes the acid-activated clays more effective at removing coloured anions from the oil.

The term 'acid-activated clays' has generally been reserved in the industrial literature for partly dissolved bentonites. Bentonite has always had a multitude of markets, and acid-activated bentonite has been a standard product for many decades. Usually a Ca^{2+} -bentonite is treated with inorganic acids to replace divalent calcium cations with monovalent hydrogen ions and to leach out ferric, ferrous, aluminium, and magnesium cations, thus altering the smectite layers and increasing the specific surface area (SSA) and porosity. The overview of the abbreviations used in this contribution is in Table 1. This results in the production of bleaching earths, that is, clays suitable for a range of bleaching or decolourizing applications, in which they compete against naturally-occurring bleaching earths (Siddiqui, 1968; Kendall, 1996; Christidis et al., 1997; Falaras et al., 1999; Hussin et al., 2011). The mechanism of decolourization of crude maize and sunflower oils has been studied by means of adsorption of β -carotene by a low-grade bentonite, containing 50–60% mixed-layered illite (I)-smectite with 80–85%

expandable layers. The decolourization depended on temperature, being a two-step process (Christidis and Kosiari, 2003).

Salem et al. (2015a,b) investigated in detail the treatments of used oils. In the regeneration of waste lubricant oil (Salem et al., 2015a) the nano-porous adsorbents were initially produced by acid treatment of natural clay. The effects of several factors, such as acid type, concentration and residence time, on the porous structure of the adsorbent were evaluated. A reduction of about 0.27 nm was observed in the distance between montmorillonite layers in the presence of sulfuric acid, due to protonation of the layers. Promising results concerning reduction of adsorbent content in the regeneration of waste lubricant oil were obtained. For the regeneration of waste engine oil by active Ca-bentonite powder, the porous adsorbents were prepared by acidification using nitric and sulfuric acid solutions. The optimum properties for methylene blue adsorption by clays activated in the presence of nitric and sulfuric acids were specific surface areas (SSA) of 109 and 89 $\text{m}^2 \text{g}^{-1}$, respectively. The change in SSA values (obtained from the N_2 adsorption isotherms) on treatment with acid was due to the formation of new nano-pores of size 10–12 nm (Salem et al., 2015b).

Taxiarchou and Douni (2014) activated a bentonite from Milos, Greece, with oxalic acid and investigated the effect of acid activation conditions on the bleaching of sunflower oil. The activated materials had excellent bleaching properties and were suitable for industrial use as bleaching earths. Optimum bleaching properties were achieved using a variety of combinations of reaction parameters, sometimes with bleaching ability equivalent to that of the known commercial bleaching earth Tonsil Optimum 210 FF.

Harvey and Murray (1997) declared in their overview of the history and development of industrial clays that acid activation is a very useful procedure for obtaining sophisticated clay materials, even in the 21st

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Table 1
The abbreviations used.

Clay minerals from the Clay Minerals Repository of the Clay Minerals Society http://www.clays.org/SOURCE%20CLAYS/SCSCavailable.html	
Sap-Ca special clay	Saponite, Ballarat, CA, USA
SAz-1 source clay	Ca-montmorillonite, Cheto, Apache County, AZ, USA
SWy-1 and SWy-2 source clay	Na-rich montmorillonite, Crook County, WY, USA
STx-1 source clay	Ca-rich Montmorillonite (White), Gonzales County, TX, USA
Abbreviation	Meaning
AAOC	Acid-activated organoclay
AS	Activated sericite
CEC	Cation exchange capacity
FTIR	Fourier transform infrared
FSM	Folded sheet materials
HTMA ⁺	Hexadecyltrimethyl-ammonium cation
HRTM	High-resolution transmission electron microscopy
LC	Layer charge
L/S	Liquid/solid
MAS-NMR	Magic angle spinning nuclear magnetic resonance
MB	Methylene blue
MS	Mass spectrum
Mt	Montmorillonite
PAAH	Porous acid activated heterostructure
PCH	Porous clay hetero-structure
PILC	Pillared clay mineral
RT	Room temperature
SBR	Styrene butadiene rubber
SSA	Specific surface area
TPD	Temperature programmed desorption

century in the developing countries. Murray reasserted and supported this conclusion several times in his papers and books (Murray, 1999, 2000, 2007; Harvey and Lagaly, 2013). This treatment is one of the most common chemical modifications of clay minerals, used for both industrial and scientific purposes (Komadel and Madejová, 2013 – a reference which forms the basis of the current contribution, supplemented by inclusion of several manuscripts published in 2013–2015).

Acid activation consists of the reaction of clay minerals with a mineral acid solution, usually HCl or H₂SO₄. The goal of this is to obtain a partly dissolved material with increased SSA, porosity and surface acidity (Komadel, 2003; Carrado and Komadel, 2009). The materials thus manufactured are widely available, relatively inexpensive solid sources of protons, and effective in a number of industrially significant reactions and processes. Clay minerals are affordable adsorbents for the removal of industrial contaminants (Zhao et al., 2015b). The authors used HCl as an acid modifier to activate Akadama clay, and adsorption experiments were conducted to evaluate the Cr(VI) adsorption. The optimum application pH was broadened from 2 to 3–9.

Acid attack on clay minerals also occurs naturally, for example in the interaction of acid mine drainage with clay minerals (Galán et al., 1999; Dubíková et al., 2002). Mining waste containing sulphides is the most common and most significant anthropogenic source of acidity. Progressive oxidation leads to the production of protons and sulphates in leaching waters, which generally also mobilize large amounts of metal cations by dissolution of minerals. These waters influence the composition of surface waters but also have an impact on the surrounding soils and terrestrial ecosystems (Komadel and Madejová, 2013).

Very early acid-dissolution studies based on solution analysis of dioctahedral smectites in HCl by Osthaus (1954, 1956) indicated faster dissolution of octahedral than tetrahedral sheets. However, in the 1990s, assays of solid reaction products employing advanced spectroscopic techniques provided clear experimental evidence that acid treatments dissolved central atoms from the tetrahedral and octahedral sheets at similar rates. Luca and MacLachlan (1992) studied the dissolution of two nontronites in 10% HCl by Mössbauer spectroscopy, fitting

the spectra either with two octahedral Fe³⁺ doublets only, or with an additional tetrahedral Fe³⁺ doublet. Acid treatment removed octahedral and tetrahedral Fe³⁺ from the structure at about the same rate. Mössbauer and IR spectroscopies and XRD indicated that the remaining undissolved part had the structure of the untreated nontronite. A ²⁷Al and ²⁹Si MAS-NMR study (Tkáč et al., 1994) on removal of tetrahedral and octahedral Al³⁺ from Mt by 6 M HCl led to very similar conclusions. The rates of dissolution of tetrahedral and octahedral Al³⁺ were also comparable. Three different types of structural units were identified in acid-treated samples, including (SiO)₃SiOH units which, as a result of poor ordering of the framework, have no possibility of cross-linking.

Upon acid treatment, protons penetrate into the mineral layers and attack the structural OH groups. The resulting dehydroxylation is connected with the successive release of the central atoms from the octahedra as well as with the removal of Al from the tetrahedral sheets. Simultaneously, a gradual transformation of the tetrahedral sheets into a three-dimensional framework proceeds. Depending on the extent of acid activation, the resulting solid product contains unaltered layers and amorphous silica, while the ambient acid solution contains cations according to the chemical composition of the clay mineral and the acid used. There are several clay minerals including trioctahedral smectites (Vicente et al., 1995a; Komadel et al., 1996b), dioctahedral smectites (Komadel et al., 1990; Tkáč et al., 1994; He et al., 2002), illite-smectite (Pentrák et al., 2010), sepiolite (Vicente et al., 1995b) and palygorskite (Suárez Barrios et al., 1995), and the final product consists of amorphous, porous, protonated and hydrated silica with a three-dimensional cross-linked structure (Komadel, 1999).

A complex approach to investigation of acid activation of clays is seen in the papers of Kooli and co-authors. Kooli and Jones (1997) acid-activated a natural saponite at room temperature (RT) or 90 °C with different acid/clay ratios and characterized the products by XRD, IR spectroscopy and thermogravimetry. The leaching of Mg from the octahedral sheets was enhanced by increasing the acid/clay ratio and by raising the temperature at which the process was carried out. Textural properties were strongly correlated to the presence of a noncrystalline silica phase formed during the acid activation process. Kooli and Jones (1998) used acid-treated saponite for the preparation of Al- and Zr-pillared acid-activated clays, which incorporated less Al and Zr than the parent saponite, in consequence of the reduced cation exchange capacity (CEC) of the matrix following acid-activation.

Kooli et al. (2005) reported on the intercalation properties of acid-activated montmorillonites treated at different acid/clay ratios with the cationic surfactant cetyltrimethylammonium (C16TMA) hydroxide. The acid activation caused a reduction in the number of cation exchange sites and improved the exfoliation of the silicate sheets at higher pH values. The basal spacing increased from 1.54 to 3.80 nm, depending on the extent of acid activation. The ¹³C CP/MAS-NMR spectra indicated that the intercalated surfactants exhibited a significant degree of gauche conformation in the acid-activated clays.

Further study of the intercalation of C16TMA into the interlayers of a synthetic layered silicate, Na-magadiite, was made by Kooli et al. (2006a) in the presence of different anions, resulting in evidence that the amount of intercalated hexadecyl trimethylammonium (C16TMA) cation depends on the anion type, the maximum content achieved being 1.16 mmol/g. The raw Na-magadiite exhibited a basal spacing of 1.54 nm, increasing to 3.12 nm on intercalation of C16TMA cations.

Kooli et al. (2006b) discussed porous clay heterostructures (PCH) as a new class of solid acids exhibiting pore sizes in the rarely-observed supermicropore to small mesopore region, formed by the surfactant-directed assembly of mesostructured silica within the two-dimensional galleries of smectites. Acid activation was effective in improving the acidity and the mesoporosity of the raw clay mineral. The effect of the clay mineral type on the properties of porous acid-activated clay heterostructures (PACHs) was analysed. In most cases, soft extraction of the surfactants via chemical methods did not improve the stability and the properties of PCH and PACH materials.

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