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Research paper

Structural, electrokinetic and surface properties of activated palygorskite for environmental application

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ABSTRACT

Unlike smectite, the surface characteristics of palygorskite remain underexplored for its potential application in environmental remediation. In this study, palygorskite from Western Australia was activated through thermal (300 °C for 4 h), acid (4 M HCl for 2 h at 70 °C) and acid-thermal (acid treatment followed by heating at 300 °C for 4 h) treatments, and the structural and physico-chemical characteristics were examined against the raw clay mineral. The influence of activation was systematically investigated using X-ray Diffraction (XRD), Fourier Transform Infra-Red (FTIR) spectroscopy, N₂ adsorption-desorption measurements and solid state ²⁷Al Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) spectroscopy. The XRD patterns indicated preservation of the crystalline structure of palygorskite following all the treatments. These findings were supported by the Al (IV) and Al (VI) coordination peaks (chemical shift ~55 and 2.9 ppm, respectively) which were unaltered in the ²⁷Al MAS NMR spectra of the samples. The acid-thermal activated palygorskite exhibited the highest specific surface area (152.7 m² g⁻¹) and pore volume (0.2137 cm³ g⁻¹) which respectively were 3-fold and 69% greater than the raw palygorskite. The potentiometric titration analyses highlighted the possible role of Al derivatives towards development of the surface charge of the activated palygorskites. Electrokinetic studies described the stability of the activated products (zeta potential values ranging from -5 mV to -32 mV) at different electrolyte (NaNO₃) concentrations. Combined acid-thermal activated palygorskite displayed a stronger specific adsorption of multi-valent cations, and held a direct relevance to environmental remediation. Findings of this study will assist in the development of palygorskite-based adsorbents for heavy metal contaminants remediation.

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1. Introduction

Clay minerals occur as large deposits worldwide, which guarantees their continuing abundance and availability for numerous applications. Clay minerals are phyllosilicate materials consisting of Si-tetrahedral and Al-octahedral sheets joined together in specific proportions. Smectitic clay minerals, such as montmorillonite, have been extensively studied for environmental applications, while fibrous clay minerals like palygorskite have received far less attention due to their controversial and complex geological origin (Churchman et al., 2006; Yuan et al., 2013). Palygorskite has the general structural formula [(OH₂)₄(Mg, Al, Fe)₅(OH)·2Si₈O₂₀]·4H₂O (Frost et al., 2001) with a ribbon-like structure where the two dimensional tetrahedral sheets sandwich the octahedral sheet that discontinues at each inversion of the tetrahedral

sheet. Its abundance, non-swelling properties, reactive silanol groups, stability in salt environment, as well as high surface area are beneficial for its application as an effective adsorbent, barrier, drilling mud and many more purposes (Murray, 2000; Sarkar et al., 2011; Nasedkin et al., 2014).

The worldwide production of palygorskite reached up to 1.3 million tons in 2010 (Murray et al., 2011; Galan and Pozo, 2015). The United States of America is considered as the largest producer (76% of world production), while Anhui Province in China has one of the largest deposits of about 22 million tons. Palygorskite is also found in Greece, Spain, Ukraine, Russia, Turkey, Iran, Guatemala, Senegal and Australia. The origin of palygorskite may influence its chemical composition thus subsequently lead to different physico-chemical properties. For example, palygorskite originating from Australia, Mexico, United States and Israel showed varied fiber length, mineral composition and rheological properties (Neaman and Singer, 2000). The occurrence, structure and properties of palygorskite from China (Zhang et al., 2010; Cheng et al., 2011), United States (Myriam et al., 1998; Suarez

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and Garcia-Romero, 2006) and Tunisia (Frini-Srasra et al., 2007; Frini-Srasra and Srasra, 2010) have been well-discussed in the literature, whereas very few comprehensive studies are found on palygorskite from Australia (Keeling et al., 1995; Churchman, 2010). In Australia, palygorskite deposits are found in Queensland, South Australia, and Western Australia (Keeling et al., 1995; Murray et al., 2011). Potential environmental applications of modified palygorskite from Western Australia through incorporation of a polymer (Rusmin et al., 2015), alkyl ammonium surfactants (Sarkar et al., 2010, 2011, 2012; Xi et al., 2010; Sarkar and Naidu, 2015) and carbon nanoparticles (Sarkar et al., 2015) were recently reported, yet little attention was given to its modification through acid or thermal activation processes. Activation of clay minerals using thermal or acid treatment assists in the removal of impurities and increases the surface functionality, thus provides a simple approach for purifying the material for further applications. Impurities like carbonates in palygorskite often cause pore blocking, thus their elimination creates a highly porous product with an enhanced surface area (Myriam et al., 1998; Gan et al., 2009; Zhang et al., 2010). The enrichment of the silica (SiO_2) groups due to acid activation subsequently generates more reactive silanol ($\text{Si}-\text{OH}$) sites, which enhances surface complexation with heavy metals during adsorption (Myriam et al., 1998; Chen et al., 2007). Meanwhile, palygorskite's thermal activation through calcination at temperatures higher than $300\text{ }^\circ\text{C}$ may result in more exposed active sites ($-\text{OH}$ groups) due to the removal of adsorbed and crystalline waters (Wang et al., 2007; Biswas et al., in press). The calcination also causes significant morphological changes contributed by the dense aggregation of the crystal rods in palygorskite (Chen et al., 2012). Heat treatment ($700\text{ }^\circ\text{C}$) led to the highest adsorption of Methyl Orange by palygorskite due to changes in the electrostatic interaction of dye-cations with the clay mineral surface (Chen et al., 2012).

This research therefore attempts to evaluate the structural and surface properties of palygorskite originating from Western Australia before and after acid-thermal activations. The electrokinetic studies were also conducted to investigate the palygorskite's stability and evaluate the clay-cation interaction in aqueous media. This study especially contributes to the understanding of the characteristics of palygorskite following acid-thermal treatment in relation to their interaction with heavy metal cations in the environment.

2. Materials and methods

2.1. Materials and reagents

A palygorskite from Western Australia was purchased from Hudson Resource Ltd., Australia. Sodium nitrate (NaNO_3) was purchased from Sigma-Aldrich (Australia), potassium nitrate (KNO_3) and calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) were purchased from Biolab, (Australia), lead (II) nitrate ($\text{Pb}(\text{NO}_3)_2$) from Fisher Scientific (United Kingdom), iron nitrate ($\text{Fe}(\text{NO}_3)_3$) from Chem-Supply (Australia), and aluminium nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) was from BDH Chemicals (United Kingdom).

2.2. Activation of palygorskite

A series of activated palygorskites were prepared by employing different acid and thermal treatment approaches (Table 1). Raw palygorskite was used as the starting material, and assigned as "Pal". Meanwhile, palygorskite treated with Milli-Q water ($18.2\text{ M}\Omega \cdot \text{cm}$) (denoted as Pal-MQ) was kept as a control sample to elucidate the influence of acid during activation of the clay mineral in an aqueous medium. The raw palygorskite (Pal) was first ground using a ball-mill and sieved to obtain the particle size $<75\text{ }\mu\text{m}$. Raw palygorskite (10 g) was treated in 100 mL of 4 M HCl under reflux condition at $70\text{ }^\circ\text{C}$ for 2 h. The acid-activated palygorskite (referred as Pal-4M) was then separated from the liquid by centrifugation (4000 rpm, 10 min) followed by

Table 1
List of treatments for palygorskite activation.

Starting material	Treatment details	Sample ID
Raw palygorskite (Pal)	None	Pal
	Palygorskite treated with Milli-Q water at $70\text{ }^\circ\text{C}$	Pal-MQ
	Palygorskite heated at $300\text{ }^\circ\text{C}$	Pal-T
	Palygorskite treated with 4 M HCl at $70\text{ }^\circ\text{C}$	Pal-4M
	Pal-4M treated with 4 M HCl at $70\text{ }^\circ\text{C}$ followed by heating at $300\text{ }^\circ\text{C}$	Pal-4MT

thorough washing with Milli-Q water until no Cl^- ion was detected in the supernatant (as determined by a test with 0.01 M AgNO_3). After drying at $60\text{ }^\circ\text{C}$, Pal-4M was subjected to thermal activation by heating in a muffle furnace at $300\text{ }^\circ\text{C}$ for 4 h. The final product obtained after both the acid and thermal treatments was denoted as Pal-4MT. For comparison purpose, palygorskite undergoing only the thermal activation ($300\text{ }^\circ\text{C}$ for 4 h) was also prepared and referred as Pal-T. The supernatant of Pal-4M and Pal-MQ after activation was analyzed with Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (Perkin Elmer, Optima 5300 V) for determining the concentrations of the leached cations (Mg, Al, Si, Ca, and Fe).

2.3. Material characterization

2.3.1. Structural characterization and surface area analysis

X-ray Diffraction (XRD) patterns of powdered samples were collected on a PANalytical Empyrean X-ray diffractometer using $\text{CuK}\alpha$ radiation operating at 40 mA and 40 kV with a step size of 0.0130 . The patterns were recorded from 4 to $90^\circ 2\theta$ by using a 0.25° fixed divergence slit and 0.50° anti-scatter slit.

For Fourier Transform Infra-Red (FTIR) analysis, samples were mixed with dehydrated KBr at a ratio of 0.5% (w/w), ground into a fine powder and then compressed into discs using a hydraulic press (Pike Technologies). Spectra were collected using an Agilent Cary 600 series spectrometer (Agilent Technologies) in the range of $4000\text{--}400\text{ cm}^{-1}$ by co-addition of 16 scans with a resolution of 8 cm^{-1} .

Solid state ^{27}Al MAS NMR (Magic Angle Spinning Nuclear Magnetic Resonance) measurements of the palygorskite and acid-thermal activated product (Pal-4MT) (approximately 100 mg) were performed using a Bruker 400 MHz spectrometer equipped with a 4 mm zirconia rotor. The spectra were acquired at a spinning frequency of 15,000 Hz, resonance frequency of 104.26 MHz, pulse length of $1\text{ }\mu\text{s}$ and 15 ms acquisition time. The ^{27}Al chemical shift was calibrated relative to pure kaolinite as an external reference. Each spectrum was acquired after 900 scans following a 0.5 s relaxation delay.

Specific surface area (SSA) and pore size distribution were determined by BET (Brunauer–Emmett–Teller) and BJH (Barrett–Joyner–Halenda) methods, respectively, through N_2 gas adsorption-desorption isotherms at liquid nitrogen temperature ($-196\text{ }^\circ\text{C}$) on a Micromeritics Gemini 2380 Surface Area Analyzer. Samples were degassed overnight at $60\text{ }^\circ\text{C}$ under vacuum at 2 Torr.

2.3.2. pH profile

Suspensions of the palygorskite and acid-thermal activated product (Pal-4MT) (0.01% (m/v)) were prepared in acidic, neutral and alkaline aqueous solutions (pH ~ 3.2 , 6.2 and 10.9, respectively, adjusted by using either 0.1 M HNO_3 or 0.1 M NaOH). The clay suspensions were constantly stirred at $25\text{ }^\circ\text{C}$ and the pH changes were recorded simultaneously at given time intervals by a pH meter (Thermo Electron Corporation, model Orion 3Star) until an equilibrium was reached.

2.3.3. Potentiometric titration

Suspensions of clay minerals (30 mg in 300 mL of each of 0.01 and 0.001 M NaNO_3 solutions) were first equilibrated for 24 h in an end-over-end shaker. The suspension was then transferred to a titration

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