



Research paper

Acid-leached mixed vermiculites obtained by treatment with nitric acid

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ABSTRACT

Two samples of pristine vermiculites (V and V*) were reacted with nitric acid under controlled conditions. Structural and textural studies were performed using chemical composition, X-ray diffraction (XRD), ²⁹Si and ²⁷Al NMR, adsorption/desorption gaseous nitrogen measurements, SEM and TEM. Acid-activation increased the specific surface area and porosity of the samples and led to partial leaching of iron, aluminum and magnesium from the octahedral sheets. Acid leaching of the two vermiculite samples with 3 and 4 mol L⁻¹ HNO₃ at 80 °C for 4 h nearly removed all the MgO, Al₂O₃ and Fe₂O₃, and left behind SiO₂-containing residue. The elements were easily extracted from both samples and the dissolution rate decreased in the order Mg²⁺ > Al³⁺ > Fe³⁺. XRD showed the formation of products with low crystallinity for both vermiculites treated with high acid concentrations.

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1. Introduction

Acid activation is the most commonly used technique to enhance the chemical and physical properties of clay minerals (Komadel and Madejová, 2006). Acid treatments have been used to increase the surface area of clay minerals and to obtain solids with high porosity and a large number of acidic sites. Changes to the structural, physico-chemical, textural and surface properties during acid activation of vermiculite were reported by several authors (Suquet et al., 1991, 1994; Ravichandran and Sivasankar, 1995, 1997; Temuujin et al., 2003; Okada et al., 2006; Maqueda et al., 2007; Steudel et al., 2009). Concomitant use of grinding and acid treatment has been applied (Maqueda et al., 2007; Maqueda et al., 2009; Perez-Rodriguez et al., 2011). These studies showed that grinding vermiculite significantly influenced its leaching behavior, favoring the formation of new phases upon heating, such as akaganeite. Despite the large number of studies on vermiculite leaching, the typical procedures utilize HCl or H₂SO₄, but few researchers have used 0.8 and 1.0 mol L⁻¹ nitric acid as a leaching agent (Del Rey-Perez-Caballero and Poncelet, 2000; Jin and Dai, 2012).

Acid treatment is cited as a simple and low-cost method to obtain mesoporous vermiculites because it partially destroyed the vermiculite and gives rise to large cavities within Si-enriched phases (Jin and Dai, 2012). Consequently, the adsorptive properties are enhanced, and the surface acidity, surface area, porosity, as well

as pore volume are increased (Jin and Dai, 2012). These properties are important to catalyst separation and recovery. Additionally, the formation of Si–OH groups on the surface of clay minerals by acid treatment is improved, and this can influence the mineral's interaction with other species in solution (Alves et al., 2013), which can modify their applications. Therefore, the resulting acid activated clay minerals have a potential to industrial applications as catalysts (Del Rey-Perez-Caballero and Poncelet, 2000; Ishii et al., 2005), adsorbents to dyes (Zhao et al., 2008; El Mouzdahir et al., 2010) and diethyl phthalate (Yu et al., 2012), selective catalysts for NO reduction (Chmielarz et al., 2010), catalytic support to TiO₂ for the photodegradation and mineralization of methylene blue (Jin and Dai, 2012), support to luminescent complexes (Silva et al., 2014) and precursor for clay polymer-nanocomposites. The properties of lixiviated solids depended on the adopted treatment. For example, by comparing the adsorption and degradation capacities of the photocatalysts on mineralization of methylene blue (Jin and Dai, 2012), the solids which lixiviated at the same conditions with nitric acid were superior than those obtained using sulfuric acid.

Therefore, in this work, the use of nitric acid for the acid treatment of vermiculite is proposed. The main objectives of this study were (1) to investigate the influence of different concentrations of nitric acid in the preparation of porous vermiculites, and (2) to compare the properties of the final solids resulting from different commercial vermiculites. Nitric acid was chosen in this work because lixiviation occurred at reduced time compared with treatments using other mineral acids (HCl and H₂SO₄) producing porous solids with special structural and textural properties. The final products are being used in pyrolysis of low density

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polyethylene. Plastic waste can be decomposed by thermal and catalytic processes to obtain fuels or chemicals (Aguado et al., 2008). The preliminary study demonstrated that the catalytic activity was very dependent on the lixiviated solid, in other words, the preparation and characterization of these solids are important to understand the contribution of the surface on these catalytic processes.

2. Experimental

2.1. Material and methods

2.1.1. Starting material

Two samples of vermiculite (V* and V) from Santa Luzia (Paraíba, Brazil) were used as precursor materials. The two samples were chosen due to composition, structural and textural differences which can influence the properties of the final solids. The chemical exchange capacities (CEC) were 135 and 60 mmol/100 g for V* and V, respectively. The CEC were compared with other CEC determinations to based-vermiculites obtained by using the same method, 85 mmol/100 g for vermiculite/chlorite/biotite (Ishii et al., 2005) and 48–149 mmol/100 g for Palabora vermiculite (Del Rey-Perez-Caballero and Poncelet, 2000) and 293 mmol/100 g for Palabora vermiculite (El Mouzdahir et al., 2009).

2.2. Preparation of acid-activated vermiculites

A series of activated vermiculite was prepared as follows. First, 10.0 g of pristine vermiculite was immersed in 100.0 mL of HNO₃ at various concentrations (0.3, 0.5, 0.8, 1.0, 2.0, 3.0, and 4.0 mol L⁻¹). The solution was refluxed at 80 °C for 4 h under mechanical stirring, and then washed with distilled water multiple times until a pH of 6.0 was achieved. The solid/liquid ratio was 1/10 (w/w). The resulting samples were dried at 120 °C. The samples were named V_x, where x is the concentration of acid in aqueous solution.

The treatment with HNO₃ at 1.0, 2.0, 3.0, and 4.0 mol L⁻¹ concentrations was repeated for sample V*.

2.3. Characterizations

Chemical analyses of the clay mineral samples were performed via atomic absorption spectrometry (AAS) using a Perkin-Elmer 5100 model instrument with an air-acetylene flame, after previous digestion of samples with an acidic mixture of HF/HNO₃ and HCl. The dissolved metals were analyzed by AAS. The silicon and aluminum contents were analyzed gravimetrically after fusion with sodium carbonate as previously described (Jeffery and Hutchison, 1981).

The cation exchange capacity (CEC) was measured by using ammonium chlorite buffered at pH 7.0 according to Bache (1976). After the saturation with 0.01 ammonium salt, the nitrogen content of dried samples was measured in a PerkinElmer model 2400 analyzer.

The original and lixiviated vermiculites were characterized by X-ray diffraction (XRD) using nickel-filtered CuKα (λ = 0.154 nm) radiation (40 kV, 30 mA) on a Shimadzu model XRD-600 diffractometric apparatus in the range of 2θ = 1.5–70° and at a scan rate of 0.67° s⁻¹ at room temperature. The samples as flakes were randomly orientated.

The infrared spectra of the samples in KBr pellets were obtained by Fourier transform infrared (FTIR) measurements in the 4000–400 cm⁻¹ range with 32 scans and a resolution of 4 cm⁻¹ using a Bomem MB series spectrophotometer.

Nuclear magnetic resonance spectra of the samples were obtained on a Bruker AC 300/P spectrometer at room temperature at frequencies of 59.6 and 78.2 MHz for ²⁹Si and ²⁷Al, respectively. For each run, approximately 1 g of the solid sample was compacted into a 7 mm zirconium oxide rotor. The ²⁹Si spectra were acquired using a 90° pulse of 60 μs and a recycle time of 100 s, and were referenced to tetramethylsilane (TMS). The ²⁷Al spectra were acquired using a 15° pulse of 1 μs and recycle time of 1 s in an aqueous acid solution of Al(NO₃)₃, used as reference. PeakFit V4.12 software was employed for deconvolution using fitted Gaussian–Lorentzian line shapes.

The surface area was determined using the BET method and a Flowsorb II 300 Micromeritics analyzer. To remove adsorbed water on the surface, the samples were desiccated at 383 K.

A JEOL 6360-LV scanning electron microscope and a transmission electron microscope (TEM, JEOL IEM-200CX) at an accelerating voltage of 200 kV were used to study the morphology of the materials. SEM images were collected from samples to be suspended in acetone and sputter-coated with a thin conducting layer of gold for 400 s.

3. Results and discussion

The studied samples were originated from a Brazilian commercial deposit. This vermiculite is resulted from the change of phlogopite and biotite and occurs mainly within zones of complex mafic, ultramafic and carbonatite (Ritz et al., 2014). The chemical analysis of the as-received and lixiviated samples is presented in Table 1. Based on data, the average unit cell compositions for V* and V samples were [(Si_{5.9}Al_{2.1})(Mg_{5.1}Al_{0.23}Fe_{0.6})O₂₀(OH)₄]Ca_{0.31}Na_{0.26}K_{0.33} and [(Si_{5.98}Al_{2.02})(Mg_{4.17}Fe_{0.77}Ti_{0.16}□_{0.75})O₂₀(OH)₄]Ca_{0.37}Na_{0.97}K_{0.54}, respectively, where □ represents vacancy sites or traces of other elements (Cr₂O₃, MnO, NiO etc) and Fe³⁺ is equal to the total iron content based on wet chemical analysis. The quantity of K⁺ suggests that the sample V* is more pure than the V sample, in agreement with previous study which indicated that the presence of K₂O was reported in non-pure vermiculite (Justo et al., 1989). However, the calculated compositions neglected the co-existence of other minerals. This can altered directly the sample characteristic. For example, the data were compared with the chemical compositions of based-vermiculite materials as illustrated in Table 2. Vermiculite shows nominal positive charge on the octahedral sheet (+0.29 to +1.22), negative on tetrahedral sheet (>2) and negative charge per silicate layer (1.2 to 1.9) (Newman and Brown, 1987). The data of Table 2 show that commercial

Table 1
Percentage of the main elements in the composition of pristine and leached vermiculites.

Sample	Wt.%								
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	TiO ₂	CaO	Na ₂ O	K ₂ O	L.O.I.
V	40.08	12.35	6.83	18.74	1.43	2.32	3.37	2.86	12.02
V0.3	43.47	11.48	6.85	16.04	1.51	2.37	1.02	2.75	14.62
V0.5	44.33	11.13	6.80	15.31	1.62	1.55	0.42	2.65	15.99
V0.8	46.14	9.85	6.36	13.70	1.82	0.58	0.45	2.64	18.41
V1.0	51.15	8.67	5.67	13.87	1.43	0.23	0.34	2.59	16.05
V2.0	69.49	2.23	1.97	2.96	1.58	0.10	0.02	0.51	20.63
V3.0	79.00	0.46	0.56	0.39	1.74	0.11	0.02	0.04	18.41
V4.0	78.05	0.40	0.51	0.32	0.58	0.13	0.02	0.04	19.68
V*	40.11	13.42	5.46	23.56	–	1.98	0.92	1.80	12.75
V1.0*	47.60	7.54	5.29	13.82	–	n.a.	n.a.	n.a.	n.a.
V2.0*	55.80	5.01	4.04	6.94	–	n.a.	n.a.	n.a.	n.a.
V3.0*	58.80	0.88	1.37	0.95	–	n.a.	n.a.	n.a.	n.a.
V4.0*	61.30	0.62	0.79	0.92	–	n.a.	n.a.	n.a.	n.a.

L.O.I. = Loss of ignition, n.a. = not analyzed.

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