



## Research paper

## Study of adsorptive materials obtained by wet fine milling and acid activation of vermiculite



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## ABSTRACT

Wet fine milling, as a pretreatment step to acid activation of vermiculite, was applied in order to decrease the environmental impact of the procedure commonly used to increase the mineral's adsorption capacity. Milling caused fragmentation of the material and several changes in its structure: edges of the flocks became frayed, the surface cracked, cation exchange capacity (CEC) increased, and most of the iron in oligonuclear and bulk form was removed. At the same time the specific surface area, crystallinity, chemical composition and adsorption capacity did not change significantly. Fine ground material was more susceptible to acid activation, which caused a decrease in the crystallinity and CEC, development of meso- and microporosity, an increase in the total volume of pores, in the specific surface and external surface areas. Micropores were developed faster in lower acid concentrations in the rough ground material, while the external surface area and total pores volume increased faster in the fine ground vermiculite. The latter material also had a higher CEC. Application of  $0.5 \text{ mol L}^{-1} \text{ HNO}_3$  to rough ground vermiculite did not change its adsorption capacity, however it changed from  $55 \pm 7$  to  $110 \pm 8 \text{ mg g}^{-1}$  when the material was fine ground. The optimal treatment conditions for both materials were obtained for  $1.0 \text{ mol L}^{-1} \text{ HNO}_3$ , however the adsorption capacity for the fine ground vermiculite increased more (i.e., from  $55 \pm 7$  to  $136 \pm 7 \text{ mg g}^{-1}$ ) than for its rough ground counterpart (i.e.,  $52 \pm 7$  to  $93 \pm 7 \text{ mg g}^{-1}$ ). Concentrations higher than  $1.0 \text{ mol L}^{-1}$  resulted in deterioration of the adsorption capacities in both cases. Considering all the experimental outcomes, it can be concluded that the environmental impact of acid activation of vermiculite may be diminished by application of fine grinding of the material before the chemical activation process. Such treatment resulted in higher adsorption capacity at a given acid concentration compared to the rough ground material.

## 1. Introduction

The global community is becoming increasingly aware of both the environmental presence and the real or potential environmental impact of man-made chemicals (Peake et al., 2016). Continuous contamination of the environment with diverse groups of chemical compounds and their adverse effects on both ecosystem and human health is one of the most relevant environmental issues of today (Kuzmanovic et al., 2013). Decreasing the environmental impact of wastewaters to acceptable levels has become the first and major concern of the uttermost

importance and the demand on efficient, economic and environment friendly technologies of removing pollutants at affordable costs has been rising (Sevekow, 2003; Pereira and Alves, 2011). Dyes are common pollutants generated in various industries such as paper, plastics, food, cosmetics, and textile (Rozada et al., 2003; Angin et al., 2013). They are usually the first to be noticed in water bodies because of their intense color, they exhibit ecotoxicity and by interrupting light penetration in aquatic environments hinder photosynthetic activity (Forgacs et al., 2004; Bhatnagar and Jain, 2005). Adsorption is considered one of the most promising, effective and attractive approach for

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water treatment giving wide control over water pollution (Gupta and Ali, 2012; Teng and Low, 2012; Hadi et al., 2015). Layered materials show promising perspectives in this field to be used as adsorbents (Roy et al., 2006). Vermiculite is a clay mineral that is very abundant and much cheaper compared with other clay minerals, it is also commonly used in agricultural, industrial and environmental applications (Duman and Tunç, 2008). Due to its structural characteristics it exhibits good adsorption properties towards cationic species. Clay minerals can be subjected to various modifications in order to change their properties (Bergaya and Lagaly, 2006; Komadel and Madejova, 2006; Lagaly et al., 2006; Stawiński et al., 2017a). One of the most common modifications is acid activation. It results in an increase of porosity and specific surface area and thus formation of new adsorption centers what increases the maximum adsorption capacity (Komadel and Madejova, 2006; Steudel et al., 2009; Santos et al., 2015; Stawiński et al., 2016). Furthermore, catalytic properties, based on increased materials acidity, may be improved as well (Chmielarz et al., 2012). However, this process might be considered as unsustainable and not fulfilling the premise of Green Chemistry (Anastas and Warner, 1998) as it usually produces highly acidic waste containing metals leached during the procedure. One solution to this problem was using the waste to produce layered double hydroxides, however other ways to reduce the environmental impact to acid activation of clay minerals should be investigated.

The issue of changes in vermiculite upon grinding has been already raised by some authors. Barabaszová and Valášková (2013) characterized that material after different milling techniques, Pérez-Maqueda et al. (2004) carried our studies on ground and sonicated vermiculite, Maqueda et al. (2007, 2009) and Perez-Rodriguez et al. (2011) studied leaching of ground vermiculite. However, to the authors' best knowledge, studies on wet milling, as well as adsorption studies on such prepared materials is lacking.

The aim of this study was to examine the influence of wet milling of vermiculite on its susceptibility to acid activation in order to increase the sustainability of acid activation process, and to investigate adsorption properties on these materials.

## 2. Experimental

### 2.1. Adsorbents preparation

South African raw vermiculite (fraction 0.5–1 mm) was kindly supplied by ROMICO POLSKA Sp. z o.o. Two procedures of particle size reduction were applied prior to chemical activation: a) milling in a grinder with steel blades to obtain fraction below 355  $\mu\text{m}$  (5 g of raw material ground for 30 s, rough ground vermiculite (AV)), b) grinding in a planetary mill (Planetary Mono Mill Pulverisette 6, Fritsch, 27 g of raw materials mixed with 75 mL of distilled water was ground for 6 h at 350 rpm, fine ground vermiculite AVg). Ground sample (AVg) was filtered, washed with distilled water and dried at 50 °C. Acid treatment was performed using 0.5, 1 and 2 mol L<sup>-1</sup> solutions of HNO<sub>3</sub> (analytical grade, Chempur). Portions of 25 g of each material were transferred to round-bottom flasks containing 50 mL of pre-heated to 98 °C acid solution and equipped with a reflux condenser, then stirred for 2 h keeping the temperature constant. In the next step the samples were filtered, washed with distilled water and dried at 50 °C. Acid concentration used in the activation was indicated in samples' names (suffixes N0.5, N1.0, N2.0), suffix c550 indicates calcination at 550 °C.

### 2.2. Material characterization

Particle size distribution was assessed using test sieves with nominal sieve opening varying from 45 to 355  $\mu\text{m}$ . The structure of the materials was studied with X-ray powder diffractometer (Bruker, D2 Phaser) equipped with CuK $\alpha$  radiation source ( $\lambda = 0.154184 \text{ nm}$ ), measurement range: 2–70° 2 $\theta$ , step size: 0.02° 2 $\theta$ , slit width: 0.6 mm, step scan size: 0.02°, counting time: 1 s. Mössbauer spectroscopy measurements

were performed in transmission mode using RENON MsAa-3 spectrometer equipped with the LND Kr-filled proportional detector and He–Ne laser based interferometer used to calibrate velocity scale. A single line commercial <sup>57</sup>Co(Rh) source kept at room temperature was applied for 14.41-keV resonant transition in <sup>57</sup>Fe. Spectra were collected for about 24 h for materials kept at room temperature and fitted within transmission integral approximation by means of the MOSGRAF-2009 software. The coordination and aggregation of iron present in the samples was determined using UV-VIS-Diffuse Reflectance spectroscopy and measured in the range of 200–900 nm with a resolution of 2 nm 600, scan speed: 120 nm min<sup>-1</sup>, band width: 2 nm using an Evolution 600 (Thermo Scientific) spectrophotometer. Infrared spectra of the samples were recorded using Attenuated Total Reflectance technique in the range of 525–4000 cm<sup>-1</sup> with resolution of 2 cm<sup>-1</sup>, number of scans: 50 (Nicolet 6700 FT-IR, DTGS detector, Thermo Scientific). Second derivative methods were used in the case of ATR-FTIR and UV-Vis-DRS analyses for better detection of the peaks. The textural parameters of calcined (550 °C, 6 h) and outgassed (350 °C overnight in high vacuum) samples were determined by adsorption of N<sub>2</sub> at –196 °C using a 3 Flex (Micromeritics) surface characterization analyzer. Cation exchange capacity was determined using the ammonium acetate method (Steudel, 2008). Chemical composition of samples was determined using X-ray fluorescence (XRF) analysis (Skayray Instrument EDX 3600H - Alloy Analyser). The samples' thermal decomposition was determined as the function of weight loss that occurred during the temperature increase. Samples were heated in the Setaram LabsysTM apparatus for thermogravimetric analysis at the constant heating rate of 10 °C min<sup>-1</sup> in the temperature range from 20 °C to 1000 °C and in air atmosphere (gas flow of 100 mL min<sup>-1</sup>). The SEM/EDS analysis was performed using a High resolution (Schottky) Environmental Scanning Electron Microscope with X-Ray Microanalysis and Electron Backscattered Diffraction analysis: Quanta 400 FEG ESEM/EDAX Genesis X4M. Samples were coated with an Au/Pd thin film by sputtering, using the SPI Module Sputter Coater equipment.

### 2.3. Adsorption experiments

Adsorption experiments were conducted at room temperature, without pH adjustment, with a magnetic stirrer (Velp, Multistirrer 15) and a centrifuge (Sartorius, Sigma 2–16) using a cationic dye Astrazon Red FBL 200% (AR), CI 85496-37-3, supplied by Dystar (Fig. S1, Supplementary materials). Concentration of the dye was determined using UV-Vis spectrophotometer (Thermo Scientific, Evolution 220) at 531 nm and the adsorption capacities were calculated using Eq. (1).

$$q_e = \frac{(C_0 - C_{eq}) V}{m} \quad (1)$$

where  $q_e$  adsorption capacity (mg g<sup>-1</sup>),  $C_0$  and  $C$  initial and final concentrations (mg L<sup>-1</sup>) respectively,  $V$  volume of adsorbate (mL),  $m$  adsorbent mass (mg).

In the kinetic studies, 100 mg of each material was placed in a different Erlenmeyer flask with a cap and mixed with 200 mL of 100 mg L<sup>-1</sup> dye solution. While the flasks were constantly stirred (for 2 h) samples were collected at pre-determined time intervals, immediately centrifuged (1 min at 4500 r.p.m.) and concentration of the dye in the supernatant determined.

In the equilibrium studies portions of 20 mg of each material were placed in Erlenmeyer flasks with caps and mixed with 30 mL of the dye solution of concentrations varying from 30 mg L<sup>-1</sup> to 200 mg L<sup>-1</sup>. The flasks were stirred for 2 h, centrifuged and concentration of the dye in the supernatant determined in all samples. A blank test was performed in both studies.

### 2.4. Data analysis

Two kinetics models (i.e., pseudo 1st order (Lagergren, 1898) and

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