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Influence of different pore-forming agents on wollastonite microstructures and adsorption capacities

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ABSTRACT

In this study, porous macro- and micro-cellular wollastonite-based ceramics was synthesized. A ceramic precursor, methylhydrocyclosiloxane, together with micro-sized $CaCO_3$, was used as a starting material. After 20 min of ultrasound treatment, and calcination at 250 °C for 30 min, different pore-forming agents were added to the as-obtained powders. Differential thermal analysis was used to determine characteristic temperatures of processes occurring within powders during heating. Based on the obtained results, the sintering regime was set up. The prepared mixtures were pressed into pallets and sintered at 900 °C. During the sintering regime, porous wollastonite-based ceramics was obtained. The phase composition of the sintered samples, as well as the microstructures, were analyzed by using X-ray diffraction and SEM. A two-phase system was detected in all samples, $CaSiO_3$ wollastonite and Ca_2SiO_4 larnite, and their ratio varied with each pore-forming agent. It was observed that the addition of different pore-forming agents resulted in significantly different microstructures. In a batch test, the influence of pH, the contact time and the initial ion concentration on the adsorption efficiency of As^{+5}, $Cr^{+6}$and phosphate ions on the synthesized adsorbents were studied. Time-dependent adsorption is best described by the pseudo-second-order kinetic model and the Weber-Morris model, which predict intra-particle diffusion as a rate-controlling step of the overall process. High adsorption capacities, 21.93, 23.88, and 27.29 mg g^{-1}, were obtained for the $CaCO_3$-siloxane-nanocellulose sorbent, and similar/lower capacities were obtained for the $CaCO_3$-siloxane-PMMA and $CaCO_3$-siloxane-cotton wool adsorbents.

1. Introduction

In the CaO-SiO_2 system, four types of compounds can be formed: monocalcium silicate, known as wollastonite ($CaSiO_3$), dicalcium silicate (Ca_2SiO_4), tricalcium silicate (Ca_3SiO_5), and tricalcium disiliconheptaoxide ($Ca_3Si_2O_7$). Depending on the molar ratio of the starting materials (molar ratios of CaO:SiO_2 can be 1:1, 2:1, 3:1 and 3:2), different calcium silicate will be synthesized [1].

As far as its properties are concerned, such as low dielectric constant, low dielectric loss, thermal stability, low thermal expansion and low thermal conductivity, wollastonite is widely used in ceramic fabrication, as a high-frequency insulator, filler in resins and plastics, civil construction, metallurgy, paint and frictional products [2–4]. It has also been demonstrated that wollastonite shows biocompatibility, bioactivity and degradability. This indicates that it may be suitable living bone repair and replacement and, accordingly, applied as a medical material for artificial bones and dental roots [5,6]. Another important application of wollastonite is the removal of heavy metal ions, such as As^{+5} and Cr^{+6} [7,8]. Chromium is released into the environment through metal finishing, petroleum refining, leather tanning, iron and steel manufacture, inorganic chemicals' production, textile manufacture, pulp and paper producing processes, etc. It has been reported that chromium is carcinogen and mutagen for humans and animals; therefore its removal from water and wastewater is an issue of significant interest. Several methods for Cr^{+6} removal are known. The most frequently used one is adsorption onto activated carbon [9]. Due to its high cost, new materials that could be used for this purpose are being developed. One of the promising candidates is wollastonite.

Due to all mentioned potential applications of wollastonite, its

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preparation is a very important scientific terms. It has been synthesized using several techniques, such as precipitation, sol-gel, solid-state reaction, etc. All of them require relatively high sintering temperatures – 950 to 1400 °C [10–13]. Another very useful method for obtaining wollastonite ceramics is synthesis from preceramic precursors. Siloxanes, as a source of silicon, are a widely investigated type of preceramic polymers. Polymers transform into ceramics during heat treatment [14]. This method offers some advantages, such as the possibility to easily combine the shaping and the synthesis of ceramics in wollastonite preparation under lower temperatures, up to 900 °C.

Porous materials find nowadays many applications both as final products and materials in technological processes due to their special properties and features that cannot usually be achieved when they are in the conventional dense phase. Macro-porous materials have a wide application in many segments of human life, e.g. porous ceramics for water purification. There is an increasing need for porous ceramics, especially in environments where high temperatures, extensive wear and corrosive media are involved. Porous ceramics have many advantages, such as a high melting point, tailored electronic properties, and high corrosion [15]. One of the ways to obtain porous ceramics is the addition of pore-forming agents, i.e. sacrificial agents, which can be inorganic or organic. Inorganic pore-forming agents are ammonium carbonate, ammonium bicarbonate and ammonium chloride salts or other high-temperature decomposable inorganic carbons such as graphite, coal ash, etc.; organic pore-forming agents include natural fibers, polymers, such as sawdust, shell flour, starch, polystyrene (PS), poly(methyl methacrylate) (PMMA) [16].

In this study, porous macro- and micro-cellular wollastonite-based ceramics, synthesized by adding various organic, pore-forming agents, were investigated. The aim of this paper is to demonstrate the influence of different pore-forming agents on the phase composition, microstructure and, finally, the adsorption capacity of wollastonite-based ceramics for the removal of heavy metals As^{+5}, Cr^{+6}, and phosphates.

2. Experimental procedure

2.1. Materials

All chemicals used in this study were reagent grade and used as received. Deionized water (DIW), resistivity 18 MΩ cm, was used as a solvent. The As^{5+}, Cr^{6+} and phosphate stock solutions were prepared with DIW using $Na_2HAsO_4{\cdot}7H_2O$, $K_2Cr_2O_7$ and K_2HPO_4 (Sigma-Aldrich). Ultra pure HNO_3 acid was supplied from Fluka. Cotton wool used as pore-forming agent, as well as for crystalline nanocellulose isolation was supplied from A.D. Niva, Serbia (Turkish origin). Nanocellulose was obtained from cotton by acid hydrolysis with H_2SO_4 supplied from Sigma-Aldrich. For wollastonite preparation, $CaCO_3$ (Sigma-Aldrich, p.a.), isopropyl alcohol (Sigma-Aldrich, p.a.) and methylhydrocyclosiloxane (ABCR, 100 g) were used. Pore-forming agent, PMMA was supplied from Sigma-Aldrich.

2.2. Adsorbents preparation

2.2.1. Nanocellulose isolation

Acid hydrolysis of cotton was done according to the procedure described earlier in detail [17,18]. In an Erlenmeyer flask of 1 l, 20*g* of cotton and 200 ml of 64% H_2SO_4 solution were added drop-wise keeping an appropriate temperature (40 °C). Afterwards, the cotton dispersion was washed with DIW using repeated centrifugation (n=6000 rpm) and sonication cycles. The centrifugation step was repeated until the pH value of 4 was reached. The last wash was conducted using dialysis with deionized water until the wash water maintained at constant pH value of 5.5.

2.2.2. Synthesis of wollastonite based adsorbent

Wollastonite-based adsorbents were synthesized in a two-step process. In the first step, an amount of 7.7905 g of siloxane (methylhydrocyclosiloxane) was dissolved in 100 ml isopropyl alcohol at magnetic stirrer for 10 min. An amount of 12.9220 g of micro-sized $CaCO_3$ was added and mixed for another 10 min, followed by ultrasound treatment for 20 min and drying overnight at 80 °C. The obtained paste was calcined in furnace at 250 °C during 30 min, with a heating rate of 5 °C/min. The second step was the mixing of the as-prepared powder with organic pore-forming agents: PMMA, cotton wool, and nanocellulose.

2.2.3. Sintering process

The binder-free powders were compacted using uniaxial double-action pressing in an 8 mm diameter tool (Hydraulic press RING, P-14, VEB THURINGER). The applied pressure was 392 MPa, and an amount of 0.5 g of powders was used for each pressed sample. The compacts were placed in an alumina boat and heated in a tube furnace (Lenton Thermal Design Typ 1600). The compacts were sintered isothermally at 900 °C in air atmosphere for 60 min (RT–300 °C with 5 °C/min heating rate, 300–600 °C with 1 °C/min heating rate, 600–900 °C with 3 °C/min heating rate, 900 °C 1 h).

2.3. Adsorption and kinetic experiments

The batch adsorption experiments of As^{+5}, Cr^{+6} and phosphate ions, under magnetic mixing, were applied to evaluate the effect of diffusion processes on the performance of wollastonite-based adsorbents. The adsorbent material, m/V=200 mg l^{-1} suspension, was placed in vials containing 10 ml of the standard solutions of As^{+5}, Cr^{+6} and phosphate ions at different initial concentrations, C_i, namely 0.1, 0.5, 1.0, 2.5, and 5.0 mg l^{-1}. The effect of pH was studied in the range from 3 to 10. Adsorption and kinetic experiments were performed at 25 °C. The adsorption kinetics were studied by changing the contact time of the solution of As^{+5}, Cr^{+6} and phosphate ions in the 5–1440 min range at C_i=5 mg l^{-1}. The mean value from three determinations was used for the processing of experimental data. The percentage of adsorbed As^{+5}, Cr^{+6} and phosphate ions was calculated by using Eq. (1):

$$q = \left(\frac{C_i - C_f}{m}\right)\cdot V \quad (1)$$

where q is the adsorption capacity in mg g^{-1}, C_i and C_f are initial and final As^{+5}, Cr^{+6} and phosphate ions concentration in mg l^{-1}, respectively, V is the volume of the solution in l, and m is the mass of the adsorbent in g.

2.4. Characterization methods

The Fourier transform infrared (FTIR) spectra of the wollastonite-based adsorbents were recorded in the absorbance mode using a Nicolet™ iS™ 10 FT-IR spectrometer (ThermoFisherSCIENTIFIC) with the Smart iTR™ Attenuated Total Reflectance (ATR) Sampling accessories, within the 400–4000 cm^{-1} range, at the resolution of 4 cm^{-1} and in 32 scan mode.

The thermal behavior and characteristic temperatures were determined by simultaneous TG–DTA (Setsys, SETARAM Instrumentation, Caluire, France) in the temperature range between 25 and 1100 °C, under the air flow of 20 ml/min, in an Al_2O_3 pan. The X-ray powder diffraction patterns were obtained using a Philips PW-1050 diffractometer with λCu–K_α radiation and a step/time scan mode of 0.05°/s. The measurements were taken at room temperature in air atmosphere. The morphology of the sintered samples was characterized by scanning electron microscopy (JEOL JSM-6390 LV). The pallets were crushed and covered with gold in order to perform these measurements.

The As^{+5}, Cr^{+6} and phosphate ion concentrations in the solutions after the adsorption and kinetic experiments were analyzed by induc-