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Characterization of acidic pumice and determination of its electrokinetic properties in water

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ABSTRACT

In this study some characterization tests of acidic pumice were performed using various techniques such as Mercury Intrusion Porosimetry (MIP), Scanning Electron Microscope (SEM), X-Ray Diffraction (XRD), Thermal Analysis (DTA–TG), FTIR and its electrokinetic properties in water such as zeta potential (ZP), isoelectrical point (IEP), indifferent, specifically adsorbing and potential determining ions were determined. The results showed that (i) pore dimensions of the irregular or oval and fibrous cavities of the pumice varied between 0.05 µm and 2 mm depending on its particle size and these cavities usually did not intersect each other; (ii) as the pumice particle size decreases, both total pore volume and total pore surface area significantly decrease as well; (iii) pumice maintained its thermal stability approximately up to 900 °C; (iv) pumice had a negative surface charge between pH 1.8 and 11.4; and (v) Cl^-, Br^- SO_4^{2-}, Na^+, $Al(OH)_2^+$ and Ca^{2+} ions were indifferent, $C_{16}H_{33}(CH_3)_3N^+$, Al^{3+} and $Al(OH)^{2+}$ cations were specifically adsorbing and, H^+ and OH^- ions were potential determining ions for acidic pumice.

1. Introduction

Pumice is an amorphous, porous volcanic rock which is composed mainly of SiO_2 and whose porous structure is formed by dissolved gases precipitated during the cooling as the lava hurtles through the air [1,2]. Having a reserve of nearly 3 billion m^3, Turkey has important pumice deposits. Moreover, after Italy, Greece, China and Iran, respectively, Turkey is the fifth largest pumice producer in the world [3]. There are two kinds of pumice: acidic pumice and basic pumice. Acidic pumice is the most common pumice type both in Turkey and the world [1].

Pumice has high porosity and, as a result, low apparent density (0.35–0.65 g/cm^3) in aggregate form. It is therefore used in the construction industry, particularly in the production of light-weight brick and concrete elements that have thermal/acoustic insulation capabilities [1,4]. Many studies have been conducted to determine possible usage areas of pumice as well as the above-mentioned traditional usage area. In this scope, many researchers have studied the use of natural and/or modified pumice as an adsorbent for organic (i.e. phenol, textile dyes) and inorganic (various heavy metals and radioactive elements) water pollutants [5–9].

The term “electrokinetics” means the relative motions of charged species in an electric field. The field may be applied, or it may be created by the motion of a liquid or adjacent solid phase [10]. However, the term “electrokinetic properties” carry a wider connotation including ZP the structure of electrical double layer (EDL), IEP, potential determining, indifferent and specifically adsorbing ions [11]. ZP is the electrical potential at the hydrodynamic plane of shear (or slipping plane) and is an intrinsic property of a mineral particle in a liquid [12]. That is, ZP is an important concept which is used to explain many physical, chemical and physico-chemical events such as adsorption, coagulation, stability, flotation and viscosity. Therefore, it is encountered in various fields such as environment –particularly in abatement of water pollution–, mining, pharmacy, ceramics and paint [13,14]. Accordingly, many studies in the literature have conducted ZP measurements of natural minerals under different conditions i.e. quartz, corundum, colemanite, calcite, clays, zeolites, coal to synthetic minerals i.e. silicon carbide, silicon, zirconia, carbon (fiber) [11]. Zeta potential measurements require high attention and sensitivity and, at the same time, the definition of the measurement conditions should be well identified because, as known from the literature, there can be very different ZP values and IEP's for the same mineral [15]. This variation is caused by direct effect through ZP values, and; other electrokinetic parameters due to various factors, which can be classified as: (i) pretreatments like washing, leaching, ultrasonic scrubbing, or de-sliming that may be used on a sample before measurement; (ii) impurities originating from the mine deposits or the mining process; (iii) variations in the test-conditions (premixture period, environment temperature, solid/liquid rate, purity of the water used; the type of instrument used for measurement and its application technique, and even the sensitivity of the person

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making the measurement and the hygiene conditions of the measuring location) [15–17].

Fuerstenau [18] studied the ZP of crystallized SiO_2 (quartz) mineral (which has the same metal oxide compound as pumice) and reported that the IEP of quartz was pH 1.8. Huang and Fuerstenau [19] measured ZP of quartz suspension, on which an ultrasonic dispersion had been applied, and determined that its IEP was pH 2. Clark and Cooke [20] performed a detailed study on metal ion adsorption on quartz and pointed out Na^+ ions were indifferent, Ca^{2+} and Mg^{2+} ions were specifically adsorbed and H^+ and OH^- are potential determining ions. Kosmulski [16] investigated the IEP of fused silica using six different zeta-meters and determined that several instruments produced negative ZPs across the entire pH range, while other instruments gave an IEP at pH 2–4. Similarly, Parks [15] reported varying IEPs for quartz (between pH 1.5 and 3.7) as well as other minerals, according to the pretreatments applied to the samples and experimental conditions. Even though many studies have been carried out on quartz, there is only one previous study on the ZP of pumice [21] in the literature. Tunç and Duman [21] examined the effect of different mono and multivalent electrolytes on the ZP of pumice from the Nevşehir region (Turkey). They reported that Li^+, Na^+, K^+, Cl^-, ClO_4^-, NO_3^-, CO_3^{2-}, SO_4^{2-} and PO_4^{3-} are indifferent ions for pumice, and that the divalent cations (Ca^{2+}, Mg^{2+} etc.) are potential determining ions for pumice. The present authors suggest that, according to the results (ZP curves) obtained by Tunç and Duman [21], these cations are most likely indifferent or may be accepted as specifically adsorbing ions. In the present work, the electrokinetic properties (i.e. IEP, indifferent, specifically adsorbed and potential determining ions) of acidic pumice from the Tatvan region (Turkey) were investigated using some ZP measurements. The results were compared with those previously reported by Tunç and Duman [21]. In addition, Tatvan region has nearly half of the total Turkish pumice reserves, thus, the material characteristics of the acidic pumice collected from this region were determined in detail so as to promote this raw material in a better way.

2. Experimental studies

The pumice sample used in this study was collected from the Tatvan region of Turkey. The sizes of the sample as received were between 0.5 and 4 cm. 500 g of sample was ground in a ball mill to reduce its size to −125 μm. Without any further treatments such as washing, ultrasonic dispersing etc. the sample was subjected to ZP, BET, XRD, FTIR, XRF and Thermal Analysis (DTA–TG). Liquid pycnometer was used to measure the true density (2.22 g/cm^3) of the sample. The surface of the pumice in aggregate size was coated with paraffin and then its bulk density (0.39 g/cm^3) was measured according to Archimedes principle. The mineralogical and chemical analyses of the pumice sample were performed using XRD (Rigaku RINT 2200) and XRF (Rigaku ZSX Primus) techniques. FTIR analysis of the powder sample was carried out using Perkin Elmer Spectrum BX-2 having a standart mid-IR DTGS detector. FTIR spectra were recorded, in the range of 400–4000 cm^{-1} at a resolution of 4 cm^{-1} with KBr pellets technique. The KBr powder was prepared by mixing the pumice sample with KBr powder (around 1:100) and using a hydraulic press. In addition, thermal stability of the pumice was checked between 50 and 1200 °C in alumina crucible in nitrogen atmosphere with the heating rate 5 °C/min (Setaram Setsys Evolution).

To see the inner pore structures (and pore morphology) the secondary electron images of fracture surfaces of pumice samples in aggregate size were obtained from a Scanning Electron Microscope (SEM Leo-1430 VP) equipped with an Energy Dispersive Spectrometry (EDS). Before SEM analysis, the fractured surfaces of the samples were coated with carbon. Moreover, to see its pore size distribution, total pore volume etc., the Mercury Intrusion Porosimetry analysis were performed on the pumice samples in different particle size fractions (<125 μm, 1.173–2, 2–4 and 4–8 mm) with Quantachrome Poremaster 60 which generates pressure to 60,000 psia for pore size analysis from 440 μm to 0.0036 μm pore diameter. The mercury porosimeter is based upon the physical principle that a non-reactive, non-wetting liquid will not penetrate fine pores until sufficient pressure is applied to force its entry. The relationship between the applied pressure and the pore diameter into which mercury will intrude is given by the Washburn equation (Eq. (1)):

$$D = (-4\gamma \cos\theta) / P \qquad (1)$$

where P is the applied pressure, D is the pore diameter, γ is the surface tension of the mercury (480 dyn cm^{-1}) and θ is the contact angle between mercury and the pore wall, usually taken as 140°.

The ZP measurements of the pumice as a function of pH and that of salt concentration were carried out with a Malvern ZS90 Zetasizer using He–Ne red laser beam (λ: 633 nm) through M3-PALS (Mixed Mode Measurement Phage Analysis Light Scattering) technique. This instrument measures the ZP of the particle according to the electrophoresis method [11] with high sensitivity. Prior to the ZP measurements pumice powders were dried in an oven at 110 °C for 2 h and stored in a plastic bag and throughout the measurements this sample was used. 2 g of pumice powders (−125 μm) was dispersed into 50 ml of a background electrolyte solution of 1 mM NaCl to ensure a constant ionic strength. The pH was adjusted using 1 M KOH or 1 M HCl and stirred for 1 h with a magnetic stirrer at room temperature (25–26 °C), afterwards, the suspension was centrifuged (Hettich Universal 32) for 10 min at 3500 rpm. Next, an aliquot of 0.75 ml was taken from the supernatant solution and placed in electrophoresis cell, then an appropriate amount of sample from the pumice bed was transferred into the electrophoresis cell, afterwards, ZP was measured. Prior to the ZP measurements, stock solutions of 5×10^{-2} M of NaCl, Na_2SO_4, $CaCl_2$, $AlCl_3$, and CTAB (cethyltrimethyl ammonium bromide, $C_{16}H_{33}(CH_3)_3NBr$ and that of 1.4×10^{-2} M of $CaSO_4\cdot2H_2O$ were prepared with distilled water. All the organic and inorganic chemicals used in this study were purchased from Merck and were of analytical grade. Throughout the experimental work, distilled water was used and for pH adjustments Sartarous pH-Meter with glass electrode was used which has a sensitivity of ±0.01.

3. Results and discussion

3.1. Characterization

According to the results of the XRD analysis of the pumice, there were two peaks: one at 23° and the other at 28° (Fig. 1). These peaks belonged to the mineral dachiardite [(Ca, Na, K, Mg)$_4$, (Si, Al)$_{24}$O$_{48}$, 13H$_2$O)], which is a kind of natural zeolite. In addition, the background line rose in 20°–30° range and formed a broad peak. Since the 100 peak of the quartz is known to be at "$2\theta = 26.65°$", this finding points out amorph quartz substance (i.e. pumice). A similar

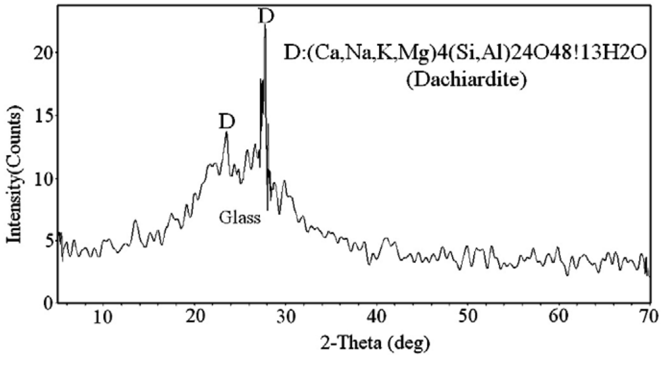

Fig. 1. XRD pattern of the pumice.