Characterisation of electrokinetic properties of clinoptilolite before and after activation by sulphuric acid for treating CSG water

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A B S T R A C T

Clinoptilolite, an abundant and low cost natural zeolite, activated by sulphuric acid has been shown to be useful for treating coal seam gas (CSG) co-produced saline water. This paper aims to further examine the effect of the acid activation on changes in physicochemical properties of clinoptilolite which underpin the treatment of CSG saline water by clinoptilolite. Microelectrophoresis was applied to measure surface (zeta) potential of clinoptilolite particles before and after the acid activation as function of pH. The change in the surface potential was theoretically analysed applying the theory on the electrical double layers at solid-solution interfaces. The proton donor–acceptor reactions occurring simultaneously on amphoteric alumina and silica sites of clinoptilolite were considered. The mass balances were applied to link the zeolite active sites with the zeolite charge and potential. Comparing the model with the experimental data reveals the important role of the dealumination process occurred by the acid activation. The dealumination is the main reason for the increase in the surface charge and cation exchange capacity of clinoptilolite after the acid activation due to the increased defects in the crystal structure/ lattice, which result in increasing numbers of charge vacancies. These results support our previous findings on the effectiveness of the acid activation of clinoptilolite in treating saline CSG co-produced water.

1. Introduction

Zeolites are micro-porous and hydrated alum-silicate crystalline minerals that contain alkali and alkaline earth metals. Their frameworks are composed of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra, which are linked together with a shared corner to form cages connected by pore openings of definite sizes. The pore size of zeolite ranges from 0.3 to 1 nm [1]. Each AlO_4 tetrahedron in the framework bears a net negative charge which is balanced by additional non-framework cations like sodium $[Na^+]$, potassium $[K^+]$, or $[Ca^{2+}]$. The negative charge on the lattice is neutralised by positive charge of the cations located within the material pores. These univalent and/or bivalent metal cations may be replaced via ion-exchange to other ions. Due to electrostatic forces it is not possible to make an Al–O–Al bond. They are made up of "T-atoms" which are tetrahedrally bonded to each other with oxygen bridges. A general formula of zeolite can be written as $M_{2/m}O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$, where M is the charge balance cation, m is

the valence of the metal cation, y is generally valence of the number of water molecular in the voids of zeolites [2]. Chemical composition of zeolites includes an amount of extra frame cations, which stabilise the electrical charge in the aluminium centred tetrahedral units.

Clinopotilolite is the most widely distributed zeolite in nature and is widely used in the world [3]. It has a high Si/Al ratio with high thermal stability, resistance against radiation. It is also relatively stable under acidic conditions. The clinoptilolite samples from several deposits all over the world have shown great capability for cation exchange due to its optimal natural structure [4]. Unlike synthetic zeolites with just one type of non-framework cation, natural zeolites contain several types of cations such as Ca^{2+}, Na^+, K^+, and Mg^{2+} which are also the most common cations in clinoptilolite [5]. The variations in the purity and composition of natural clinoptilolite make a detailed study of their physicochemical properties indispensable to determine the potential applications. This information is also essential for designing pre-treatment and activation options to modify the nature zeolite to improve its sorption and ion exchange properties. For instance, it is shown that the Coal Seam Gas (CSG) co-produced saline water can be

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effectively treated using a natural zeolite of clinopotilolite type [6]. The sodium adsorption ratio of CSG saline water has been found to be significantly decreased using clinopotilolite. Furthermore, the water quality can be improved even further by activating clinopotilolite with sulphuric acid.

This paper aims to investigate how sulphuric acid activation can modify the physicochemical properties of on clinoplilolite which underpin the improved treatment of CSG saline water. The research particularly focuses on electrokinetic properties of fine clinoplilolite particles in an aqueous solution which can play a significant role in our understanding of the adsorption mechanism of organic and inorganic species at the solid-solution interface [7–10]. The related mechanisms can explain how the electrokinetic properties of zeolites control aggregation, coagulation and dispersion of particles in suspensions, and provide detailed information about the clay particles, their interactions with the surrounding medium, and the electrical properties of particles [11]. This paper makes further contribution to general knowledge base on natural zeolite since no reports on surface potential of acid activated clinoplilolite are available in the literature although several studies have been conducted on surface potential of natural zeolite and modified zeolites with inorganic salts and organic molecules [12–17].

2. Experimental

2.1. Materials

The natural zeolite (Escott Zeolite) sample used in this study was provided by Zeolite Australia Ltd (Werris Creek, New South Wales, Australia). The crystal phases of the zeolite samples were analysed by X-Ray Diffraction (XRD) using a Rigaku Miniflex Instrument and cobalt radiation (Rigaku Corp., Japan). The particle size was analysed using a Malvern Mastersizer 2000 size analyser (Malvern Corp., UK). Analytical grade sulphuric acid (H_2SO_4) (Sigma–Aldrich, Australia) was used to treat and activate the natural zeolite sample. The acid concentrations of the solutions were chosen as 0.01 M, 0.1 M, 1 M, 2 M, and 5 M, and prepared with deionised (DI) water which was freshly purified by using a setup consisting of a reverse osmosis (RO) unit and an Ultrapure Academic Milli-Q water system (Millipore, USA). The DI water has a specific resistance of 18.2 MΩcm^{-1} at room temperature (23 °C). Additionally, analytical purity NaCl, NaOH (sigma-Aldrich, Australia), HCl (Sigma–Aldrich, Australia), and NaOH (Sigma–Aldrich, Australia) were used to prepare various salt solutions using the DI water.

2.2. Experimental methods and procedures: acid activation

The acid activation tests of the natural zeolite sample were carried out in a 500 mL of beaker which was mounted on a magnetic stirrer, and a magnetic bar for the agitation. A suspension of 30% by weight in 0.01 M, 0.1 M, 1 M, 2 M, and 5 M H_2SO_4 solutions was prepared, and mixed at 500 rpm for 30 min. This solid concentration was the best concentration for the treatment of CSG saline water [6]. Finally, the suspensions were separated by a suction filter system, and then the modified zeolite samples were dried in an oven at 80 °C for 6 h. All modified zeolite samples were collected for performing the zeta potential measurements.

2.3. Experimental methods and procedures: pH profiles

The pH measurements of the zeolite suspensions were carried out in order to obtain the buffer pH of the zeolite sample. In this regard, the suspensions of 0.5% by weight were prepared to profile the pH of the suspensions at an initial pH of 2 (acidic), 5.6 (near-to-

neutral), and 11.5 (basic) as a function of time. The DI water mentioned above was used in preparing the neutral pH liquid buffer environment. The suspensions were stirred by using a magnetic stirrer at room temperature (23 °C) for 2 h, and the data were collected for every 15 s. Finally, the pH profiles of the suspension at each pH value were obtained until the pH values reached the plateau.

2.4. Experimental methods and procedures: zeta potential measurements

The zeta potential measurements of the natural and the acid-activated zeolite samples were determined using a Zeta Potential Analyser (ZetaPlus, Brookhaven, US), which equipped with an Uzgiris cell. First, the zeolite samples were ground using a ceramic mortar and pestle. Then, the ground samples were screened through a 38 μm sieve, and the undersized fraction was conditioned in DI water (with a solid ratio of 1%). For pH adjustments, the suspension was mixed for about 5 min in order to reach equilibrium after adding the desired amount of 0.1 M HCl or 0.1 M NaOH. Before each experiment, the suspensions were kept for 3 min to allow the coarse particles to settle down. Then, a small amount of suspension was taken from the top of the suspension and transferred to the measurement cell. Finally, twenty measurements at each pH value were performed, and the average value of the measurements was obtained for the zeolite particles. Finally, the Smoluchowski equation of the ZetaPlus built-in software was used to calculate zeta potential, ζ, from the mobility data as follows:

$$\zeta = \frac{\eta}{\varepsilon\varepsilon_0} U \tag{1}$$

where $\varepsilon = 78$ is the solution (water) dielectric constant, $\varepsilon_0 = 8.85418 \times 10^{-12}$ C^2 J^{-1} m^{-1} is the permittivity of vacuum, η is the viscosity, and U is the electrophoretic mobility.

3. Theoretical analysis

3.1. Zeolite surface dissociation versus pH of aqueous solutions

Most of zeolites can be considered as a permanently charged mineral because they usually possess a net negative structural charge resulting from isomorphic substitution of cations in crystal lattice [12]. The most common condition is that Al^{3+} substitutes Si^{4+} as a main element in zeolite structure. Meanwhile, some exchangeable cations such as Na^+, K^+, Ca^{2+}, and Mg^{2+} enter into the zeolite channels to compensate the positive charge deficiencies of zeolite lattice. Therefore, natural zeolites have little or no affinity for anionic species due to this negative charge [16]. Besides, the broken bonds at Si–O–Si (siloxane group) of zeolite particle surface which generated during the grinding process can be also considered the reason of the negative surface charge of zeolite (Fig. 1).

3.2. Linkage of zeolite active sites and surface potential

Traditionally, the surface potential and surface dissociation as a function of solution pH can be linked through the Gouy–Stern–Grahame (GSG) double-layer theory [18]. In this theory, the electrical double layer is divided into two regions: 1) the compact region very near the solid surface, where the ions strongly interact with the solid surface under the restricted conditions imposed by the size and charge of ions and molecules, and 2) the diffuse region, where the distributions of counter-ions and co-ions are controlled by their electrostatic (Coulomb) interactions with the solid surface and their thermal (Brownian) diffusion. The diffuse layer can be