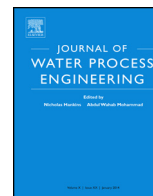




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Utilisation of barium-modified analcime in sulphate removal: Isotherms, kinetics and thermodynamics studies

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ABSTRACT

Analcime and commercial zeolite were employed as a precursor for preparing sorbent material for SO_4^{2-} removal over barium modification. Three sorbents were prepared: barium-modified analcime (ANA-Na-Ba), barium-modified acid-washed analcime (ANA-Ac-Na-Ba) and barium-modified zeolite (ZSM5-Na-Ba). Of the prepared materials, ANA-Ac-Na-Ba was the most efficient sorbent material for SO_4^{2-} removal, with a maximum sorption uptake of 13.7 mg g^{-1} at room temperature. Batch sorption experiments were performed to evaluate the effect of initial pH, initial SO_4^{2-} concentration, sorbent dosage, temperature and contact time of sorption. Several isotherms were applied to describe the experimental results and Bi-Langmuir was found to provide the best correlation for adsorption of SO_4^{2-} on ANA-Ac-Na-Ba. Kinetic studies were applied for the most effective sorbent material, ANA-Ac-Na-Ba, and the results showed that the sorption process follows pseudo-second-order kinetics.

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1. Introduction

Natural zeolites are crystalline-hydrated “tectoaluminosilicate” minerals with cage-like structures [1,2]. Zeolites have a three-dimensional framework consisting of SiO_4 and AlO_4 tetrahedral molecules linked with shared oxygen atoms. Zeolites have a large surface area and high cation exchange capacity (CEC). The isomorphous replacement of Si^{4+} by Al^{3+} produces a negative charge, which is balanced by exchangeable alkali and alkaline-earth metal cations (Na^+ , K^+ , Ca^{2+} etc.). These cations are exchangeable with certain cations in solutions such as Pb^{2+} , Cd^{2+} , Zn^{2+} and Ni^{2+} [2]. Zeolites are usually pretreated with sodium solution before usage, because the ion exchange capacity of zeolite tends to increase if just monovalent cations are present in zeolite materials [3,4]. Zeolites can adsorb variably sized ions, which indicates their use as a selective adsorbent for many pollutants, including dyes [5,6], organics [7,8], ammonium [9,10] and metal ions [3,11] from wastewaters.

Zeolites can be found in volcanic environments (under hydrothermal conditions), salt lakes and sediment layers. The most common types of zeolites are clinoptilolite, mordenite, dachiardite, analcime (ANA), phillipsite and heulandite. Recently,

ANA has also been reported to be an adsorbent in the wastewater treatment [12–14]. ANA ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$) is produced as a waste material in the mining industry, with irregular channels formed from four-, six- or eightfold rings [15]. Because zeolite materials have a low affinity for anions, chemical modification is needed to apply sorbent for anionic sulphate removal [2,16,17]. To remove anions from water, it is possible to modify natural zeolites with cationic surfactants (e.g. tetramethylammonium, hexadecyltrimethylammonium (HDTMA) bromide, tetrabutylammonium bromide (TBAB), *n*-cetylpyridinium bromide (CPB)) [1,18–22]. Surface modification using cationic surfactant can change the surface charge and functionality by adding complex hydrophobic groups for positively charged exchange sites [2].

In addition, it is also possible to modify natural zeolites using inorganic salts (e.g. NaCl , FeCl_3 , BaCl_2), which improves the sorption efficiency for anions [23,24]. The modification has been reported to create for example an oxy-hydroxide adsorption layer on the surface and change the surface charge from negative to positive [17,24]. Due to that, stable complexes with anions in solution are formed. In this study, the BaCl_2 modification was expected to impregnate Ba in the framework structure of zeolites and subsequently enable the surface precipitation or complexation of sulphate.

Sulphate (SO_4^{2-}) anion is a major pollutant that occurs in both natural waters and industrial effluent, such as acid mine drainage and wastes from the chemical industry [25,26]. SO_4^{2-}

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mainly results from the process of chemical weathering of sulphur-containing minerals (e.g. gypsum). In addition, SO_4^{2-} is generated through the oxidation of sulphides and elemental sulphur [27,28]. Sulphur is a necessary element for many kinds of organisms. However, excess SO_4^{2-} can cause an imbalance in the natural sulphur cycle [26–29]. In addition, SO_4^{2-} concentrations higher than 150 mg L^{-1} can damage water pipes [30] and concentrations higher than 600 mg L^{-1} can have laxative effects and affect the taste of the water [26].

SO_4^{2-} is common in drinking water and many countries have not set guidelines for it because it is only mildly hazardous [26,27]. In Finland, the SO_4^{2-} limit in drinking water is set at 250 mg L^{-1} [30]. Environmental agencies in many countries have set maximum SO_4^{2-} values of $250\text{--}1000 \text{ mg L}^{-1}$ in both mine drainage and industrial effluent [26]. Typically, domestic sewage contains less than 500 mg L^{-1} of SO_4^{2-} but especially in industrial wastewater the concentration of SO_4^{2-} can be several thousand mg L^{-1} [29].

Some examples of established methods for the removal of SO_4^{2-} are chemical precipitation, biological treatment, ion exchange, reverse osmosis, electrodialysis and adsorption [26,28,31]. However, these methods suffered from various limitations. For example, biological treatment and ion exchange are expensive while precipitation (e.g. with lime) produces large amounts of sludge [26]. Furthermore, low SO_4^{2-} concentrations cannot be removed by lime precipitation due to the high solubility of the produced CaSO_4 [32]. Among the various available water treatment technologies, adsorption may be preferred for SO_4^{2-} removal because it is a simple and effective technique. In addition, adsorption can be used in a so-called hybrid system with precipitation in which sulphate remaining after precipitation can be removed via adsorption. The success of this technique largely depends on the development of an efficient adsorbent [28,29,31]. Activated carbon [33], minerals [28,34], biomaterials [27,29], zeolites [35] and some industrial solid wastes [36] have been reported as adsorbents for SO_4^{2-} removal. However, there is still a need for alternative and locally available raw materials or industrial by-products with which to make sorbents.

The aim of this study was to investigate the effect of modification of natural analcime (ANA) to the sorption capacity for SO_4^{2-} removal from an aqueous solution. Commercial zeolite (ZSM5) was used as a reference material. Batch sorption experiments were performed to evaluate the influence of initial pH, initial SO_4^{2-} concentration, sorbent dosage, temperature and contact time. The Langmuir, Freundlich, Dubinin–Raduschkevich, Temkin, Bi–Langmuir, Sips, Redlich–Peterson and Toth isotherm models were applied to the experimental data. Kinetic studies were performed using pseudo-first-order, pseudo-second-order and Elovich kinetic models.

2. Materials and methods

2.1. Materials

Analcime (ANA) was obtained from a Finnish mining company. Commercial zeolite ($\text{NH}_4\text{-ZSM-5}$, $30:1 \text{ SiO}_2:\text{Al}_2\text{O}_3$, CAS: 1318-02-1) was used as a reference material (Alfa Aesar). Before use, all materials were dried overnight at 110°C , crushed and sieved to obtain a particle diameter less than $150 \mu\text{m}$ and to ensure a uniform product quality. The barium used in the modification was BaCl_2 . SO_4^{2-} ion stock solutions were prepared by dissolving of Na_2SO_4 (VWR 99.9%) in MilliQ water to generate a concentration of 5 g L^{-1} and the mixture was diluted with distilled water when necessary.

2.2. Characterisation methods

X-ray diffraction (XRD, PanAnalytical Xpert Pro) analysis was done for the untreated analcime and zeolite samples to identify the mineral type. In addition, the produced sorbent materials were characterized by XRD. X-ray fluorescence (XRF, PanAnalytical Minipal 4) analysis was carried out to determine the chemical compositions of untreated samples. Fourier Transform Infrared Spectroscopy (FTIR) spectra of the sorbent were collected using a Perkin Elmer Spectrum One spectrometer equipped with an Attenuated Total Reflectance (ATR) unit. The specific surface areas, pore sizes and pore volumes of samples were determined from nitrogen adsorption desorption isotherms at the temperature of liquid nitrogen (-196°C) using a Micromeritics ASAP 2020.

2.3. Preparation of sorbents

Modification of analcime and zeolite was performed using two different protocols. By the protocol 1, analcime and zeolite were treated with NaCl and after that with BaCl_2 [37]. In the protocol 2, analcime was acid (HCl) washed before NaCl and BaCl_2 treatment.

2.3.1. Protocol 1

Analcime and ZSM-5 (5 g) was mixed with 1 M NaCl solution (50 mL) for 24 h, rinsed with deionised water and dried at 105°C to ensure that all ion exchange sites were in Na form. The barium modification was done by mixing the material (5 g) with 1 M BaCl_2 solution (100 mL) for 16 h, rinsing with deionised water and drying at 105°C . The materials were stored in a desiccator prior to use.

2.3.2. Protocol 2

Analcime (5 g) was acid washed with 2 M HCl (100 mL) for 24 h, rinsed with deionised water and dried 105°C . Next, the analcime was mixed with 2 M NaCl solution (50 mL) for 24 h, rinsed with deionised water and dried at 105°C to ensure that all ion exchange sites were in Na form. The barium modification was done by mixing the material (5 g) with 1 M BaCl_2 solution (100 mL) for 16 h, rinsing with deionised water and drying at 105°C . The materials were stored in a desiccator prior to use.

2.4. Batch sorption experiments

In the sorption experiments, the effects of initial pH, initial SO_4^{2-} concentration, sorbent dosage, temperature and contact time on the removal efficiency of SO_4^{2-} over Ba-modified analcime (ANA-Na-Ba), Ba-modified acid-washed analcime (ANA-Ac-Na-Ba) and Ba-modified commercial zeolite (ZSM5-Na-Ba) were studied. The observed sorption conditions are presented in Table 1. Kinetic studies were performed in a 1 L reactor vessel equipped with a magnetic stirrer with an agitation speed of 1000 rpm.

All sorption experiments were done duplicated. All samples were filtered through $0.45 \mu\text{m}$ filter paper (Sartorius Stedim Biotech) or separated using a centrifuge (3500 rpm, 5–15 min) before measurement of sulphate concentration by ion chromatography (Methrom 761 Compact IC).

2.5. Adsorption isotherms

Adsorption isotherms reveal the nature of the adsorption at varying initial concentrations in pH found to be optimal. The Langmuir, Freundlich, Dubinin–Raduschkevich, Temkin, Bi–Langmuir, Sips, Redlich–Peterson and Toth isotherm models were applied to the experimental data. Isotherm parameters were obtained using nonlinear regression with the Microsoft Excel (GRG nonlinear) solver tool.

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