



Integrated use of magnetic nanostructured calcium silicate hydrate and magnetic manganese dioxide adsorbents for remediation of an acidic mine water



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ABSTRACT

The integrated use of two solid adsorbents with magnetic properties was studied with the aim of decontaminating an acid mine water. The adsorbents were magnetic nanostructured calcium silicate hydrate (mag-NanoCSH) and magnetic manganese dioxide (mag-MnO₂), both of which consist of a crystalline Fe₃O₄ nucleus surrounded by external amorphous layers of calcium silicate and manganese oxide, respectively. They were synthesised using simple, quick, and reproducible methods. Both adsorbents were characterised chemically, physically, and magnetically via different analytical techniques. The particle size of the adsorbents varied between 60 and 200 nm, which led to a tendency to agglomerate, and the surface area varied between 30 and 70 m²/g. The magnetic saturation of the adsorbents was found to be around 57–59 emu/g, which is sufficient to ensure complete separation of these two compounds from an aqueous raffinate using a common magnet. The nanostructure and microstructure of both adsorbents had many available adsorption sites, and their chemical structure permitted efficient and simultaneous removal of cationic and anionic species present in aqueous solutions, following different adsorption mechanisms. The influence of the main variables on the adsorption of the ionic species was studied. Samples of an acid mine water were treated using both magnetic composites consecutively. In the first step, mag-NanoCSH was able to dramatically reduce the contents of many of the ions in the treated water. Then, mag-MnO₂ was added to the re-acidified raffinate produced in the first step, and the resulting final aqueous solution was found to comply with the Chilean environmental regulations.

1. Introduction

Mining and industrial operations are commonly recognised as some of the most polluting human activities. They cause numerous environmental problems, including the generation of solid and liquid wastes as well as the contamination of air by dust and gaseous emissions from pirometallurgical plants. One of the main difficulties in such cases relates to the pollution of surface and underground waters by mining and metallurgical residual effluents or their contamination with natural acid mine drainages [1]. This pollution poses both technical and economic problems. These waters contain diverse toxic contaminants, including suspended or dissolved heavy metals, anions and oxyanions as arsenates and sulphates, acidic and saline compounds, and granular and colloidal-type suspended fine solids, which are quite difficult to remove

[2].

Recently, many technical options have been studied in order to remove these pollutants, mostly metallic ions and some anionic species; however, none of these treatment alternatives can be considered optimal. For example, chemical precipitation [3], ion exchange with solid resins [4], solvent extraction [5], chelation [6], biological methods [7] membranes [8] and electrochemical operations [9], among others, have been tested for removing heavy metals. Some of these alternatives are very specific and thus nearly incapable of removing different contaminants in a single process, whereas others can remove cationic species but cannot remove anionic compounds simultaneously. Moreover, some methods are expensive or impractical for use at the industrial scale.

Unquestionably, adsorption processes are some of the most

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promising options for removal of ionic contaminants from aqueous solutions, as many types of natural and synthetic compounds are potential adsorbents. These compounds are very simple to apply, affordable, and widely available [10–15].

In this sense, a suitable industrial-scale adsorbent used to clean up polluted mining solutions must present important characteristics such as a high capacity to remove cationic and anionic species simultaneously, and easy separation from the treated water after the adsorption process. Various microparticle- and nanoparticle-type adsorbents have been prepared and modified in an attempt to improve the surface area and amount of available active adsorption sites for enhancing their efficiency in water treatment [16–18]. However, because of the tiny size of the solid formed between the adsorbent and the adsorbate species during the adsorption process, it is very difficult to separate it from the resultant raffinate aqueous solution, especially if its nature is colloidal.

A previous communication, presented the synthesis and characterisation of a nanostructured calcium silicate hydrate, unmodified or modified with Fe(III), for evaluation as an adsorbent for removing ionic species from acidic aqueous solutions [19]. The preparation of the adsorbents is simple and reproducible using low-cost commercial raw materials as lime and an industrial aqueous solution of sodium silicate. It was concluded that the presence of iron in the adsorbent structure significantly improved its ability to remove arsenic species by forming highly insoluble and stable double iron and calcium arsenate salts. However, although the solids formed in the adsorption process were very insoluble, their separation from the aqueous raffinate was troublesome. A practical solution to overcome this problem is imparting magnetic properties to the adsorbent because the magnetised structure of the adsorbent, including the composite formed with the removed species, could be easily separated from the aqueous solution by using a simple magnetic process employing a permanent magnet [20,21].

In this study, the remediation of an acid mine water samples originating from Chilean mining activity was investigated, using an integrated method with two adsorbents having magnetic properties. In the first stage, the mine water was treated with a new adsorbent prepared in our laboratory, namely a magnetic nanostructured calcium silicate hydrate (mag-NanoCSH), which can remove the highly concentrated pollutants existing in acid mine water. The preparation, characterisation, and adsorption properties of this adsorbent composite are described in Section 2.1. In the second stage, the raffinate produced during the first stage of mine water treatment with mag-NanoCSH is treated with another adsorbent, magnetic manganese dioxide (mag-MnO₂), in order for the final effluent to comply with the national Chilean environmental regulations for discharge to continental surface water bodies. A previous study reported the synthesis, characterisation, and use of this adsorbent for removing traces or low concentrations of some metallic ions from pure acid aqueous solutions [22]. This adsorbent behaves as a hydrous-oxide adsorbent, which exhibits a point of zero charge (pH_{PZC}), or zeta potential, of around 3.5, allowing efficient adsorption of cationic species at pH levels above this value via an ion-exchange mechanism between the metallic ions in solution and the hydrogen ions dissociated from the surface of the adsorbent.

The adsorption mechanisms of both compounds were studied with regard to the surface area, electric charge, and chemical structure of the adsorbents. The final purpose of this practical study was to clean up the mine water effectively using both adsorbents consecutively.

2. Experimental procedure

2.1. Synthesis of the adsorbents

The synthesis of mag-NanoCSH was conducted by means of a chemical reaction between a sodium silicate solution and Ca(OH)₂ in the presence of HCl, as shown in equation (1). A sufficient quantity of magnetite (Fe₃O₄) was added with the purpose of imparting adsorbent

magnetic properties. The synthesis is based on a procedure employed previously in the preparation of a non-modified and non-magnetic NanoCSH [23].



For the first step in the synthesis, the appropriate amount of Fe₃O₄ was added to an already prepared suspension of Ca(OH)₂ in water and HCl in a batch reactor under vigorous stirring at a velocity of 2000 min⁻¹. Second, sodium silicate solution was added to the reactor, and the mixture was stirred at 1500 min⁻¹ for 2 h. A blackish solid corresponding to a magnetic calcium silicate hydrate was rapidly obtained and separated from the suspension using a neodymium magnet. The product was washed with water and ethanol and dried at 333 K for 12 h. In turn, the magnetic MnO₂ adsorbent was synthesised using an oxidative precipitation method in an already reported alkaline medium, in which a salt of Mn(II) was oxidised by KMnO₄ in the presence of magnetite (Fe₃O₄), according to the following chemical reaction [24]:



The mixture was mechanically stirred at 500 rpm for 30 min at room temperature. The use of KOH allowed it to reach pH 12, which rapidly produced a dark-brownish solid, which was separated from the solution using a neodymium magnet. The final product was washed with water and dried at 40 °C.

Both adsorbent composites, mag-NanoCSH and mag-MnO₂, have been prepared and magnetised using a commercial magnetite or Fe₃O₄ prepared at the laboratory scale [25]. Both adsorbents presented a similar adsorption capacity; thus, in this communication, all the reported results correspond to those achieved utilizing the commercial precursor.

2.2. Characterisation of the adsorbents

Different analytical techniques were used to characterize the synthesised adsorbent composites. Among them, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were obtained using a SEM FEI Inspect F50 apparatus. The specific surface area of the particles and other porosimetry parameters were determined via Brunauer–Emmett–Teller (BET) measurements using an N₂ sorptometer at 77 K with Micrometrics ASAP 2010 equipment. The particles were also evaluated via X-ray powder diffraction (XRD) analysis, employing a Bruker D8 ADVANCE device with the purpose of verifying the crystalline or amorphous character of the solid adsorbents. The zeta potential of the mag-MnO₂ particles was determined by means of a Laser Doppler Electrophoresis method using a Malvern Mastersizer Hydro 2000MU device.

The magnetic properties of the mag-NanoCSH and mag-MnO₂ particles were determined using a vibrating sample magnetometer. The iron, manganese, and calcium contents in the adsorbents and all the metal and arsenic concentrations in the aqueous solutions in the adsorption experiments were determined by atomic absorption spectrophotometry (AAS) using a PerkinElmer PinAAcle 900 F instrument. The same technique was utilised to measure the leached metals from the adsorbent in the chemical stability tests. The Si content was measured through elemental analysis. When necessary, inductively coupled plasma mass spectrometry was used for determining lower or trace concentrations of metals in aqueous solutions.

2.3. Adsorbent stability experiments and adsorption studies

Considering that the adsorbents prepared in this study will be employed in the clean-up of acid mine water or even industrial aqueous solutions, the first experimental tests were designed to check their chemical stability towards acid aqueous solutions. The leachability of the adsorbents was evaluated as follows: 50 mg of mag-MnO₂ and

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