Inorganic Anion Removal from Water Using Natural Adsorbents

A. Ortuzar, I. Escondrillas, F. Mijangos

Abstract—There is a need for new systems that can be attached to drinking water treatment plants and have the required treatment capacity as well as the selectivity regarding components derived from anthropogenic activities. In a context of high volumes of water and low concentration of contaminants, adsorption/interchange processes are appealing since they meet the required features. Inorganic ions such as arsenate, bromate, phosphate, fluoride and nitrate anions with distribution coefficients of, respectively, 4200, 2800, 2500 0.4 and 0.03 L g⁻¹.

Keywords—Drinking water, natural adsorbent materials, removal, selectivity.

I. INTRODUCTION

In recent years, anthropogenic actions such as agricultural and industrial activities have contributed to the generation of a variety of aquatic pollutants that have aroused public concern about the quality of drinking water. Inorganic ions are among those pollutants; they can cause serious environmental problems and might also have an effect on human health even at small concentrations. Such inorganic ions include arsenate (AsO₄³⁻), bromate (BrO₃⁻), fluoride (F⁻), phosphate (PO₄³⁻), nitrate (NO₃⁻) and perchlorate (ClO₄⁻). In spite of the fact that these are common substances and sometimes their presence is necessary, their concentration must be within certain limits to avoid environmental impact and their contribution to the development of various human diseases [1]. Thus, there is a need for new systems which can be coupled to drinking water treatment plants. These should have the required treatment capacity as well as the selectivity regarding components present in water. In this sense, the adsorption/interchange (ADIX) processes might be the most appealing. Within those, there is a wide range of options regarding materials and technologies. Recently, nanoparticles of zero-valent iron supported on anionic resins have been used to eliminate As(III) [2], as well as other metal nanoparticles to remove various anions [3]. Also, iron minerals supported on silica have been used to eliminate As(V) [4] and nanoparticles of iron hydroxide synthesized in the laboratory have also been used to remove arsenic [5]. In fact, aluminium and iron oxides have been frequently used as adsorbents to remove water anions. For example, arsenic has also been removed using Fe₂O₃ nanoparticles followed by magnetic separation from the aqueous stream [6]. The methods for preparing the iron oxide magnetic particles are well defined in the work presented by Hasany et al. [7].

Iron hydroxides are found in nature and play a key role in biological and geological processes such as natural purification and transport of pollutants. Goethite and hematite minerals have been extensively studied and are considered reference models because of their diversity, well defined crystalline structure and because they can be easily synthesized in the laboratory. Other natural adsorbent materials (NAM) such as ferrihydrite, akaganeite, goethite, hematite, lepidocrocite and magnetite have been tested for water treatment. Most of these minerals can be synthesized in the laboratory [8]. Over the last few years, abundant information on the application of iron oxides has been collected for water treatment, and laboratory or pilot plant viability studies are currently required.

Liu et al. [9] have carried out a work in which numerous applications and references to goethite are collected, indicating that the adsorption properties can be improved by a heat treatment that produces a porous hematite structure. Hematite can also be activated by its washing with deionized water and roasting at 700 °C. Natural hematite also exhibits remarkable adsorption properties [10]. Also, nanostructured binary oxide particles are of great practical interest [4], [11]. For example, Zhang et al. [12] prepared iron(II)-copper(II) particles capable of eliminating As(III), showing a high capacity, close to 100 mg/g at pH 7.0. Besides the high capacity, there was no significant dependence of such removal with the sulphate or carbonate concentration. However, the current knowledge is scarce and behavior of adsorbents and ion exchangers for the elimination of anionic pollutants is insufficiently selective, thus the development of NAMs and their study is imperative.

In this work, the adsorption of various anions, especially As species with the NAMs siderite and molybdate and their mixtures (raw or co-roasted at different temperatures) is studied.
II. MATERIALS AND METHODS

A. Point of Zero Charge pH (pHzc)

Siderite and molybdenite are minerals mainly composed of FeCO₃ and FeCl₃, respectively. These reactants were ground to sizes below 0.5 mm and between 0.5 and 1 mm. Some samples of such ground minerals were roasted in an oven at high temperatures (400-750 °C).

0.25 g of both sample-sets, roasted or not, were added to 25 mL of a 0.1 M KNO₃ or KCl solution and their pH was adjusted to values that ranged from 2 to 11 by addition of HCl and/or KOH solutions. The mixtures were then stirred for two hours and their pH was then measured.

B. Analysis of X-Ray Photoelectron Spectroscopy (XPS)

Following the evaluation of the surface hydrolytic reaction, several samples of the dry reaction components were collected and analyzed by XPS on a SPECS (Berlin, Germany) equipped with a Phoibos 150 1D-DLD analyzer and monochromatic radiation source Al Ka (1486.7 eV). An analysis of the elements present was performed (wide scan: step energy 1 eV, dwell time 0.1s, pass energy 80 eV, angle of exit of electrons of 90°). The spectra were adjusted by the software CasaXPS 2.3.16, which models Gauss-Lorentzian contributions, after a subtraction of the background.

C. Thermogravimetry

A thermogravimetric analysis of the ground samples (raw or roasted at different temperatures) was performed in a TGA Q-5000 v3.17 thermogravimetric analyzer in a synthetic air atmosphere from 30 to 800 °C with a slope of 5 °C min⁻¹. This reaction also agrees with the thermogravimetric analysis (Fig. 4), where the loss of mass at 60 °C can be due to dehydration, peaks at 400-465 °C due to CO₂ loss and, finally, the peak at 500 °C might be explained by the magnetite formation, Fe₃O₄.

D. Arsenic Adsorption

0.13 mM As solutions were prepared and manually stirred for 1 hour with 0.1 to 10 g quantities of siderite (FeCO₃) alone or combined with FeCl₃ˑ6H₂O (1:1, 1:2 and 2:1 ratios, raw or roasted at 500 °C). After shaking, the mixture was settled for 24 hours and the supernatant was filtered through an 8 μm filter and analysed via inductively coupled plasma atomic emission spectroscopy (ICP-AES).

E. AsO₄³⁻, BrO₃⁻, F⁻, PO₄³⁻ and ClO₄⁻ Adsorption

A similar procedure was followed for 0.5 mM AsO₄³⁻, BrO₃⁻, F⁻, PO₄³⁻ and ClO₄⁻ solutions. Collected filtered samples were analysed via ion chromatography column guard: Dionex Ion Pac AG 11-HC-4 mm and analytical column: Dionex Ion Pac AS11-HC-4 mm. The eluant came from a Dionex EG-050KOH eluent generator with Dionex CR-ATC 500 Anion Trap column continuously regenerated. KOH concentration ranged from 10 mM to 60 mM.

III. RESULTS AND DISCUSSION

The point of zero charge (pHzc) is the pH value at which a solid submerged in an electrolyte exhibits zero net electrical charge on the surface. Ion retention is usually described in terms of ionization of the surface of the adsorbent and sorbate [14]. pHzc’s close to neutrality are required to avoid pH alteration of treated water.
Mixtures 2:1 and 1:2 FeCO₃ and FeCl₃ were also analysed for pH₉C. The former underwent alkaline reactions and the latter shows no defined trend.

Finally, the ICP-AES results of the arsenic retention on the co-roasted 1:1 FeCO₃ and FeCl₃ mixtures revealed that such mixture showed a high selectivity for As, achieving As 100% removals for a 10 mg L⁻¹ As sample. Gimenez et al. [14], who used natural hematite, goethite and magnetite also reported high adsorption capacities of As, especially for hematite.

### TABLE I

<table>
<thead>
<tr>
<th>Property</th>
<th>Siderite</th>
<th>Roasted siderite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal</td>
<td>Rhombohedral</td>
<td>-</td>
</tr>
<tr>
<td>Formula</td>
<td>FeCO₃</td>
<td>FeCl₃</td>
</tr>
<tr>
<td></td>
<td>Fe 48.3%</td>
<td>Fe 14.1%</td>
</tr>
<tr>
<td>Composition</td>
<td>C 10.3%</td>
<td>C 24.2%</td>
</tr>
<tr>
<td></td>
<td>O 41.3%</td>
<td>O 61.7%</td>
</tr>
<tr>
<td></td>
<td>Traces: Mg, Mn, Ca</td>
<td>Traces: Mg, Na, Ca</td>
</tr>
<tr>
<td>pH₉C</td>
<td>7.6</td>
<td>11</td>
</tr>
</tbody>
</table>

Retentions of As with roasted mixtures in the other proportions rather than 1:1 were smaller.

The adsorption of anions with the 1:1 FeCO₃ and FeCl₃ mixture roasted at 500 °C from a water containing a high concentration of chloride, was very favourable for AsO₄³⁻ (distribution coefficient of 4200). The other anions showed the following selectivity order: AsO₄³⁻ > BrO₃⁻ > PO₄³⁻ >>> F⁻ > NO₃⁻.

![Fig. 2](image-url)

**Fig. 2** Effect of roasting temperature on pH₉C values for FeCO₃ and FeCl₃ 1:1 mixtures

![Fig. 3](image-url)

**Fig. 3** XPS spectrum of the surface of the fractured siderite sample at 475 °C

### IV. CONCLUSIONS

In view of the promising results obtained with the 1:1 FeCO₃ and FeCl₃ mixture roasted at 500 °C regarding the removal AsO₄³⁻ as well as other anions such as BrO₃⁻, PO₄³⁻, F⁻ and NO₃⁻ (with distribution coefficients of 4200, 2800, 2500 0.4 and 0.03 respectively), some other specific NAMs for different anions should also be tested. They would be selected on the basis of their selectivity, efficiency, price, quality and compliance of regulations. On the other hand, optimal operating conditions of ADIX systems should be evaluated to increase water quality via a selective behavior for a small group of anions in competition with innocuous natural anions. In this sense, organic matter needs special consideration for, in the long term, it can be the main inhibitor of the process. Finally, the guidelines for uninterrupted operation through the purge and regeneration of the adsorbent should be established. After the operation with real waters, conventional chemical regeneration techniques and specific oxidative techniques will be used to remove deposited organic matter.

### ACKNOWLEDGMENT

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