

# 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. Iron oxides such as siderite and molysite, which are respectively based on  $\text{FeCO}_3$  and  $\text{FeCl}_3$ , can be found in nature. In this work, their observed performance, raw or roasted at different temperatures, as adsorbents of some inorganic anions is discussed. Roasted 1:1  $\text{FeCO}_3$ :  $\text{FeCl}_3$  mixture was very selective for arsenic and allowed a 100% removal of As from a  $10 \text{ mg L}^{-1}$  As solution. Besides, the 1:1  $\text{FeCO}_3$  and  $\text{FeCl}_3$  mixture roasted at  $500^\circ\text{C}$  showed good selectivity for, in order of preference, arsenate, bromate, phosphate, fluoride and nitrate anions with distribution coefficients of, respectively, 4200, 2800, 2500 0.4 and  $0.03 \text{ L g}^{-1}$ .

**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 ( $\text{AsO}_4^{3-}$ ), bromate ( $\text{BrO}_3^-$ ), fluoride ( $\text{F}^-$ ), phosphate ( $\text{PO}_4^{3-}$ ), nitrate ( $\text{NO}_3^-$ ) and perchlorate ( $\text{ClO}_4^-$ ). 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  $\text{Fe}_3\text{O}_4$  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  $700^\circ\text{C}$ . 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  $100 \text{ mg/g}$  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 molysite and their mixtures (raw or co-roasted at different temperatures) is studied.

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## II. MATERIALS AND METHODS

### A. Point of Zero Charge pH ( $pH_{ZC}$ )

Siderite and molysite are minerals mainly composed of  $FeCO_3$  and  $FeCl_3$ , respectively. These reactants were ground to sizes below 0.5 mm and between 0.5 and 1 mm. Some samples of such grounded 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  $KNO_3$  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  $Al\ K\alpha$  (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  $min^{-1}$ .

### 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 ( $FeCO_3$ ) alone or combined with  $FeCl_3 \cdot 6H_2O$  (in 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  $\mu m$  filter and analysed via inductively coupled plasma atomic emission spectroscopy (ICP-AES).

### E. $AsO_4^{3-}$ , $BrO_3^-$ , $F^-$ , $PO_4^{3-}$ and $ClO_4^-$ Adsorption

A similar procedure was followed for 0.5 mM  $AsO_4^{3-}$ ,  $BrO_3^-$ ,  $F^-$ ,  $PO_4^{3-}$  and  $ClO_4^-$  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 EGC 500KOH 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 ( $pH_{ZC}$ ) 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].  $pH_{ZC}$ s close to neutrality are required to avoid pH alteration of treated water.

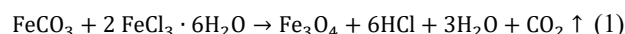
The techniques used to understand the mechanism of adsorption of anions on iron hydroxides along with experimental evidence on the effect of pH have revealed that the adsorption of anionic pollutants occurs mainly through the formation of internal sphere complexes and/or on the surfaces of iron hydroxides.

The initial and final pH values of a mixture of 0.25 g siderite (size 0.5 to 1 mm) with 25 mL of a 0.1 M  $KNO_3$  solution have been plotted in Fig. 1. It can be observed that the S-shaped curve of the experimental points cuts off the diagonal at  $pH_{ZC} = 7.6$ , thus close to the desired neutral  $pH_{ZC}$ . However, no satisfactory removal of As was attained with raw siderite (20-30%) and its roasting was attempted.

XPS analysis reveals that siderite roasting causes a change in its composition and consequently its  $pH_{ZC}$  also changes (Table I). Hence, while  $pH_{ZC}$  for raw siderite was close to neutrality, plain roasted siderite underwent an alkaline reaction. Consequently, the  $pH_{ZC}$  of plain roasted siderite was 11, beyond the desired neutral pH value.

$pH_{ZC}$  values for 400, 500, 600, 700 and 750 °C roasted  $FeCO_3$  and  $FeCl_3$  1:1 mixtures were also determined. The  $pH_{ZC}$  of 1:1  $FeCO_3$  and  $FeCl_3$  mixture roasted at 475-510 °C was in the range of the desired neutral pH: 6-7.5 (Fig. 2). However,  $pH_{ZC}$  experiments for such mixtures did not result on the expected neutral  $pH_{ZC}$  values at  $pH_{ZC}$  experiments probably because Fe (II) at siderite undergoes oxidation when cooling after the roasting process.

In the XPS spectrum of 1:1  $FeCO_3$  and  $FeCl_3$  mixture roasted at 475-510 °C (Fig. 3), the maximum detected Fe  $2p_{3/2}$  and Fe  $2p_{1/2}$  positions for magnetite ( $Fe_3O_4$ ) are 710,6 eV and 724,1 eV respectively [13] can also be observed. The presence of magnetite in the 1:1  $FeCO_3$  and  $FeCl_3$  mixture roasted at 475-510 °C is inferred and the consequent reaction (1) is assumed to occur:



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  $CO_2$  loss and, finally, the peak at 500 °C might be explained by the magnetite formation,  $Fe_3O_4$ .

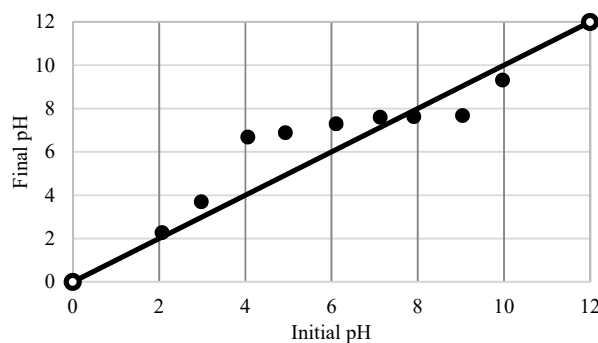


Fig. 1 Initial and final pH values for a 0.25 g siderite and 25 mL of a 0.1 M  $KNO_3$  mixture. Cut off point with diagonal indicates  $pH_{ZC}$  value

Mixtures 2:1 and 1:2  $\text{FeCO}_3$  and  $\text{FeCl}_3$  were also analysed for  $\text{pH}_{\text{ZC}}$ . 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  $\text{FeCO}_3$  and  $\text{FeCl}_3$  mixtures revealed that such mixture showed a high selectivity for As, achieving As 100% removals for a  $10 \text{ mg L}^{-1}$  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  
PHYSICO-CHEMICAL AND STRUCTURAL PROPERTIES OF RAW AND ROASTED SIDERITE

Property	Siderite	Roasted siderite
Crystal	Rhombohedral	-
Formula	$\text{FeCO}_3$	
Composition	Fe 48,3%	Fe 14,1%
	C 10,3%	C 24,2%
	O 41,3%	O 61,7%
	Traces: Mg, Mn, Ca	Traces: Mg, Na, Ca
$\text{pH}_{\text{Zc}}$	7,6	11

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

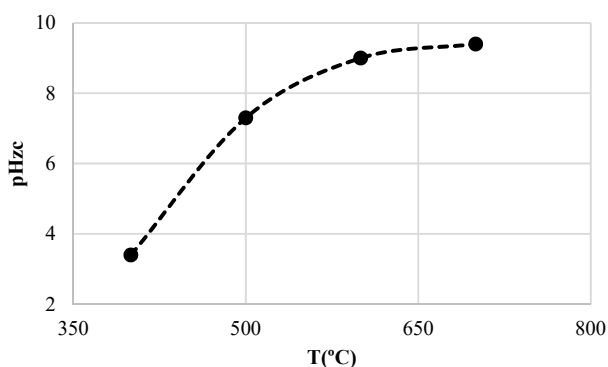


Fig. 2 Effect of roasting temperature on  $\text{pH}_{\text{ZC}}$  values for  $\text{FeCO}_3$  and  $\text{FeCl}_3$  1:1 mixtures

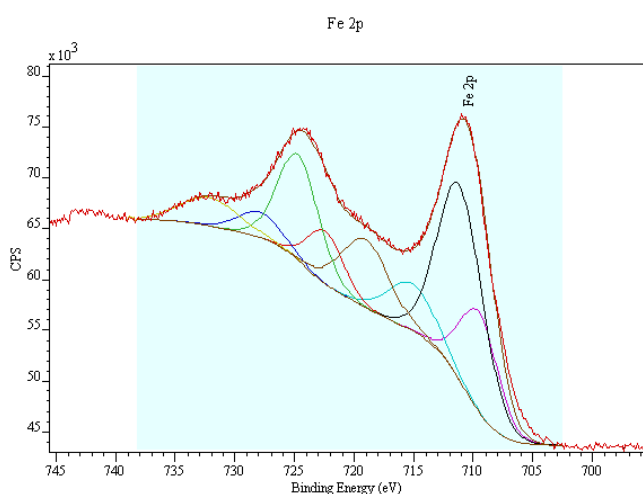


Fig. 3 XPS spectrum of the surface of the fractured siderite sample at  $475 \text{ }^\circ\text{C}$

The adsorption of anions with the 1:1  $\text{FeCO}_3$  and  $\text{FeCl}_3$  mixture roasted at  $500 \text{ }^\circ\text{C}$  from a water containing a high concentration of chloride, was very favourable for  $\text{AsO}_4^{-3}$  (distribution coefficient of 4200). The other anions showed the following selectivity order:  $\text{AsO}_4^{-3} > \text{BrO}_3^- > \text{PO}_4^{-3} \gg \text{F}^- > \text{NO}_3^-$ .

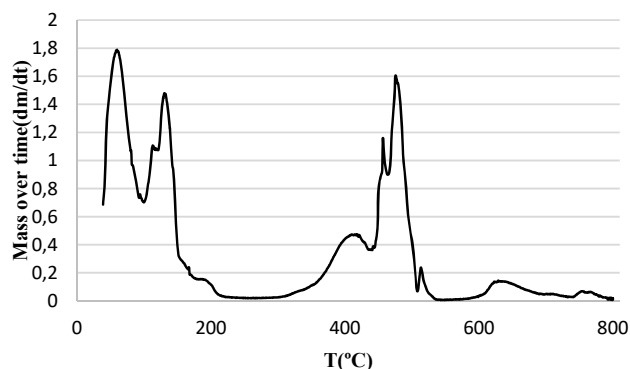


Fig. 4 Thermogravimetric analysis of the 1:1  $\text{FeCO}_3$  and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  mixture

#### IV. CONCLUSIONS

In view of the promising results obtained with the 1:1  $\text{FeCO}_3$  and  $\text{FeCl}_3$  mixture roasted at  $500 \text{ }^\circ\text{C}$  regarding the removal  $\text{AsO}_4^{-3}$  as well as other anions such as  $\text{BrO}_3^-$ ,  $\text{PO}_4^{-3}$ ,  $\text{F}^-$  and  $\text{NO}_3^-$  (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.

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