

## Arsenic removal by adsorption on iron(III) phosphate

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### Abstract

Under natural conditions, arsenic is often associated with iron oxides and iron(III) oxidative capacity towards As(III) is well known. In this study, As(III) and As(V) removal was performed using synthesised iron(III) phosphate, either amorphous or crystalline. This solid can combine (i) As(III) oxidation by iron(III) and (ii) phosphate substitution by As(V) due to their similar properties. Results showed that adsorption capacities were higher towards As(III), leading to  $\text{Fe}^{2+}$  and  $\text{HAsO}_4^{2-}$  leaching. Solid dissolution and phosphate/arsenate exchange led to the presence of  $\text{Fe}^{3+}$  and  $\text{PO}_4^{3-}$  in solution, therefore various precipitates involving As(V) can be produced: with  $\text{Fe}^{2+}$  as  $\text{Fe}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}_{(s)}$  and with  $\text{Fe}^{3+}$  as  $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}_{(s)}$ . Such formations have been assessed by thermodynamic calculations. This sorbent can be a potential candidate for industrial waste treatment, although the high release of phosphate and iron will exclude its application in drinking water plants.

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### 1. Introduction

Arsenic is a ubiquitous element found in the atmosphere, soils and rocks, natural waters and organisms [1]. It is mobilised through a combination of natural processes such as weathering reactions, biological activity and volcanic emissions as well as through a range of anthropogenic activities [2]. Most environmental arsenic problems are the result of mobilisation under natural conditions. However, man has an additional impact through gold mining, combustion of fossil fuels and the use of arsenical pesticides and herbicides [2], or of additives to livestock feed [3]. Although the use of arsenic-containing products such as pesticides and herbicides has decreased significantly in the last few decades, their use for wood preservation is still common [4]. The impact on the environment of the use of arsenic compounds, at least locally, will remain for some years. Of the various sources of arsenic in the environment,

drinking water probably poses the greatest threat to human health and high arsenic concentrations can be found in groundwaters.

Following the accumulation of evidence for the chronic toxicological effects of arsenic in drinking water [5,6], the W.H.O. recommended that many authorities reduce their regulatory limits. In Europe (Directive 98/83/CE), and in the USA (<http://www.epa.gov/safewater/ars/implement.html>) for example, they were lowered from 50 to 10  $\mu\text{g}$  total As/L. Processes to selectively remove the excess arsenic from both drinking water and industrial waste waters or mining discharges are therefore urgently required.

Removal of dissolved arsenic from water is linked to the chemistry of the As(III) and As(V) species and thus to their relative distribution, simultaneously influenced by pH and redox conditions [7,8]. In oxygen-rich environments where aerobic conditions persist, and under natural pH conditions, As(V) (arsenate) is prevalent and exists as a monovalent ( $\text{H}_2\text{AsO}_4^-$ ) or divalent ( $\text{HAsO}_4^{2-}$ ) anion, whereas As(III) (arsenite), the more toxic form, exists as an uncharged ( $\text{H}_3\text{AsO}_3^0$ ) or anionic species ( $\text{H}_2\text{AsO}_3^-$ ) in a moderately

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reducing environment where anoxic conditions persist [1,2].

Under natural conditions, arsenic is associated with iron oxides [9] and the formation of  $\text{Fe}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}_{(s)}$  or  $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}_{(s)}$  can be observed. Arsenic adsorption in soils increases with iron oxide content [10]. Furthermore, Fe(III) oxidative capacity towards As(III) is well known, especially when As(III) is adsorbed on the surface of iron oxide [11].

It is already known that arsenate and phosphate have similar chemical and biological properties [12] and this paper presents an economical, non-conventional material which combines Fe(III) oxidative capacity and the similar chemical properties of phosphate and As(V). A retention mechanism based on the study of phosphate release, to underline a possible exchange between phosphate and arsenate, and the thermodynamic prediction of precipitate formation are discussed.

## 2. Experimental

All chemicals were of analytical grade and used without further purification. All solutions were prepared with high purity de-ionised water (resistivity  $18.2 \text{ M}\Omega \text{ cm}$ ) obtained with a Milli-Q water purification system (Elgastat Prima 1-3). All glassware was cleaned by soaking in 10%  $\text{HNO}_3$  and rinsed three times with de-ionised water. The arsenate stock solution was prepared from sodium heptahydrate salt  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  (Fluka, purity >98.5%). The arsenite stock solution was prepared from sodium (meta)arsenite  $\text{NaAsO}_2$  (Fluka, purity >99%).

### 2.1. Iron(III) phosphate

Iron(III) phosphate was prepared as amorphous or crystallised solids, respectively named thereafter  $\text{FePO}_{4(\text{am})}$  and  $\text{FePO}_{4(\text{cr})}$ . The amorphous  $\text{FePO}_{4(\text{am})}$  was prepared by mixing 50 mL of 0.83 M  $\text{FeCl}_3$  (Prolabo, 29%) and 50 mL of 0.83 M  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$  (Prolabo, 98%), previously acidified to pH 1.2 with concentrated HCl [13]. As pH strongly decreased after mixing, it was fixed again to 1.2 with concentrated NaOH solution. After a standing time of 30 min, the brown precipitate was recovered by centrifugation (Sigma 2.15, Bioblock,  $3215 \times g$  during 10 min), washed with de-ionised water, air-dried for 1 day and ground for homogenisation. The crystalline  $\text{FePO}_{4(\text{cr})}$  was prepared according to the same protocol but using  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  (Prolabo, 99%) instead of  $\text{Na}_3\text{PO}_4$ ; no thermal treatment was needed. The solids were stored in dark flasks and sheltered from light.

### 2.2. Solids characterisation

The solids' structures were analysed using X-ray Diffraction (Siemens D5000, with EVA 8.0 application included in

the package) and Scanning Electronic Microscopy (Philips XL 30 combined to EDS analyser) techniques. Both Differential Thermal Analysis and ThermoGravimetric Analysis measurements were performed on a Setaram Labsys apparatus.

Specific surface areas were measured with the BET protocol (Micromeritics ASAP 2000). Surface charge and  $\text{pH}_{\text{zpt}}$  (pH value at zero point of titration) were determined by potentiometric titrations (PHM 250 Meterlab pH meter) of 1 g/L  $\text{FePO}_4$  in 0.01 M  $\text{NaNO}_3$  with 0.01 M NaOH and 0.01 M  $\text{HNO}_3$  solutions [14]. Cationic exchange capacity (CEC) was established according to the NF X 31-130 standard [15]: a 10 g/L solid suspension was put in contact with a 4 g/L cobaltihexammine trichloride solution for 3 h. The difference in absorbance at 470 nm (measured with an Agilent 8453 spectrophotometer) between cobaltihexammine solution with and without solid led to the CEC value and thereafter to the surface  $\text{p}K_a$  [14].

### 2.3. Arsenic analysis

Total arsenic analyses were carried out using a Varian SpectrAA 800 graphite furnace atomic absorption spectrometer (GFAAS), with Zeeman background correction. All measurements were based on integrated absorbance using a hollow cathode lamp (Varian) at 193.7 nm. A palladium–magnesium mixture modifier was used, pre-treatment temperature was  $1400^\circ\text{C}$  and atomisation temperature was  $2500^\circ\text{C}$ . The calibration range was 20–100  $\mu\text{g As/L}$ , the accuracy was 5%, R.S.D. was  $\pm 7\%$  (repeatability tests,  $n > 100$ ).

### 2.4. Phosphate and iron colorimetric determination

Phosphate determination is based on the formation of an antimonyl-phosphomolybdate complex (Afnor standard NFT 90-023 based on ISO 6878-1: [16]), reduced with ascorbic acid to give a blue complex whose absorbance is measured at 700 or 880 nm according to the desired sensitivity. The use of a reductive mixture (sulphuric acid, sodium metabisulfite and sodium thiosulfate) prior to the antimonyl-phosphomolybdate complex formation prevents arsenate interference.

Iron determination is based on the red  $\text{Fe}^{2+}$ -orthophenanthroline complex formation. Total iron or  $\text{Fe}^{2+}$  determination can be carried out with or without an ascorbic acid-based reductive mixture, respectively. Standards from 0 to 2.5 mg/L  $\text{Fe}^{2+}$  were prepared from a 1 g  $\text{Fe}^{2+}/\text{L}$  iron(II)-sulphate stock solution (Merck, 99.5%). The concentration of  $\text{Fe}^{2+}$  was determined by mixing 2.6 mL of sample to 0.8 mL of 0.05 M orthophenanthroline chlorhydrate (Prolabo, 99.5%) and 2.5 mL of 5 M acetic acid (Prolabo, 100%) in a 25 mL-flask, filled with de-ionised water. Total iron concentration was determined according to the same protocol, but 2.6 mL of 1 M ascorbic acid (Aldrich, 99%) was also added. After a standing time of 1 h, absorbance was measured with an Agilent

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