# Arsenite Adsorption on some Materials containing Iron. Effect of Anionic Species

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Abstract: The effects of arsenic pollution are serious and dangerous to human life. Especially long-term ingestion of contaminated water can cause various forms of cancer. Therefore, solving these problems raised by water pollution is done by removing of arsenic, ensuring the necessary conditions for consumption, in terms of concentration of arsenic. The main method for the removal of arsenic from water is the physical-chemical treatment. In the present paper is investigated the effect of the presence of some anionic species (nitrate, phosphate, chloride and carbonate) in arsenic containing water on the adsorption of arsenic (III) on two iron containing materials: a waste material and a synthetic material. The waste material used for arsenic adsorption experiments was a sludge resulting from hot-dip galvanization. The synthetic material was  $Fe_2O_3$  obtained through annealing of  $Fe(COO)_2 \cdot 2H_2O$  at 800°C. For the studies a synthetic solution containing 100 µg As(III)/L has been used. It has been separately studied the influence of each anionic species at two concentrations: 10 mg/L and 100 mg/L, respectively. It has been also studied the influence of all mixed anionic species at two total concentrations: 10 mg/L and 100 mg/L, respectively. The adsorption experiments have been carried out at different contact times (1, 2, 3, 4, 8 and 24 h). The experimental results showed that when the sludge is used as adsorbent material the increase of anionic species concentration has a positive influence on arsenic adsorption. In the case of the synthetic material this influence is negative. When the synthetic solution contained a mixture of all studied anionic species, regardless their concentration, the waste material presented a higher efficiency of arsenic removal process in comparison with the synthetic material.

Keywords: arsenic, adsorption, sludge, iron oxide, nitrate, phosphate, chloride, carbonate

## **1. Introduction**

The Environmental Protection Agency from USA classified the inorganic arsenic in the Group A – Known human carcinogenic substances. The classification of arsenic in group A is based on the higher incidence at humans in pulmonary cancer through inhalation and the higher risk of the skin, bladder, liver and lung cancer through drinking water [1, 2].

In the environment, arsenic occurs in rocks, soil, water, air, and in biota. Through erosion, dissolution, and weathering, arsenic can be released to ground water or surface water. Geothermal waters can be sources of arsenic in ground water. Other natural sources include volcanism and forest fires [1]. Anthropogenic sources of arsenic relate to its use in the lumber, agriculture, livestock, and general industries. Arsenic is emitted as an air pollutant from external combustion boilers, municipal and hazardous waste incinerators, primary cooper and zinc smelting, glass manufacturing, cooper ore mining, and primary and secondary lead smelting [1-3].

According to World Health Organization (WHO) the maximum permissible limit of arsenic in drinking water is of 10  $\mu$ g/L [4]. Therefore, the development of removal methods for inorganic arsenic from drinking water and underground water is very important. A large variety of methods proposed to reduce arsenic level below the tolerance value have been investigated; these include oxidation-reduction, precipitation, co-precipitation,

adsorption, electrolysis and cementation, solvent extraction, ion-exchange, ion flotation, and biological processing. Methods based on adsorption proved to be very effective in arsenic removal, even from very low concentration solutions [5-17] According to literature data, iron compounds in general and iron hydroxides particularly are very efficient for arsenic removal from water [5-13].

A large number of studies have characterized As(V) adsorption at different oxyhydroxide surfaces, but fewer have dealt with As(III) which is more toxic and generally predominates in ground water. Arsenic adsorption process is influenced by several factors such as: pH, ionic strength, temperature, presence of competing ions, the type of sorbent phases. Regarding the influence of competing ions, the effect of phosphate, nitrate, sulfate and chloride has been investigated. The competing sorption between arsenic and the anions can inhibit arsenic adsorption. The literature data indicate that phosphate, As(V) and As(III) have similar behaviors, these anions competing for adsorption sites on the surfaces of the adsorbents. Sulfate, nitrate, carbonate and chloride have lower competitive effect [12, 13, 18-20].

In the present paper is investigated the effect of the presence of some anionic species (nitrate  $NO_3^-$ , phosphate  $PO_4^{3-}$ , chloride Cl<sup>-</sup> and carbonate  $CO_3^{2-}$ ) in arsenic containing water on the adsorption of arsenic (III) on two iron containing materials: a waste material and a synthetic material.

The waste material used for arsenic adsorption experiments was a sludge resulting from hot-dip galvanization. The synthetic material was  $Fe_2O_3$  obtained through annealing of  $Fe(COO)_2$ · 2H<sub>2</sub>O at 800°C.

## 2. Experimental

The batch As(III) adsorption experiments were carried out using two iron containing materials: a waste material and a synthetic material.

The waste material used for arsenic adsorption experiments was a sludge resulting from hot-dip galvanization. The sludge was grinded and sieved. The < 500  $\mu$ m fraction has been used after drying at 105°C. The sludge was analyzed in order to establish its chemical composition. A sample of material was brought into solution by boiling until almost dry with a mixture of concentrated hydrochloric acid and concentrated nitric acid HCl : HNO<sub>3</sub> = 1 : 3. The residue was treated with water and filtered. The concentrations of Fe<sup>n+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup> and Ca<sup>2+</sup> in the filtrate was determined by means of atomic absorption spectrometry, using a VARIAN SPECTR AA 280 FS spectrophotometer. The concentration of chloride was determined by silver nitrate titration, in presence of K<sub>2</sub>CrO<sub>4</sub> as indicator.

The synthetic material used as sorbent was  $Fe_2O_3$  obtained through annealing of analytical grade  $Fe(COO)_2$ ·  $2H_2O$  at 800°C.

For the studies 100  $\mu$ g As(III)/L synthetic solutions without or with anionic species (NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, Cl<sup>-</sup> and CO<sub>3</sub><sup>2-</sup>) have been used. It has been separately studied the influence of each anionic species at two concentrations: 10 mg/L and 100 mg/L, respectively. It has been also studied the influence of all mixed anionic species at two total concentrations: 10 mg/L and 100 mg/L, respectively. All reagents used to prepare the solutions were in analytical reagent grade. Samples of 0.1 g sorbent material were treated with 100 mL synthetic solution and left at laboratory temperature (23°C) at different contact times (1, 2, 3, 4, 8 and 24 h). After contact time elapsed the suspensions were filtered and the residual concentration of arsenic in the filtrate was determined through atomic absorption spectrometry with hydride generation, using a VARIAN SPECTR AA110 VGA 77 spectrophotometer.

## 3. Results and Discussion

The experimental data regarding the composition of the sludge resulting from chemical analysis are: Fe - 31.6%, Zn - 1.91%, Pb - 0.03%, Ca - 15.6% and Cl - 24.3%. The major component of the sludge is iron, which makes it suitable for arsenic removal from water, due to the high affinity of arsenic towards iron [5-13]. The difference up to 100% is represented by hydrogen and oxygen, because metallic ions are present in the sludge mainly as oxides, hydroxides and chlorides.

During the adsorption experiments the pH of the suspensions was maintained at a constant value due to the buffer capacity of the sorbent materials. In the case of the sludge this value was  $pH_{pzc} = 6.7$  (pzc = "point of zero charge") for initial solutions having pH values in the range 4-9. For the iron oxide  $pH_{pzc} = 6.1$  in the initial pH range 6-9.5 [21].

#### 3.1. Influence of contact time

Experimental data regarding the influence of contact time on the residual concentration of As(III) at two anion concentrations are presented in Figs. 1 and 2. One may notice that in all situations the residual concentration of As(III) decreases as contact time increases. In most cases the decrease becomes slower after an 6 h contact time and one may consider that the equilibrium was reached. Figs. 1 and 2 also show that the residual concentration of As(III) is influenced by the composition of the solutions.

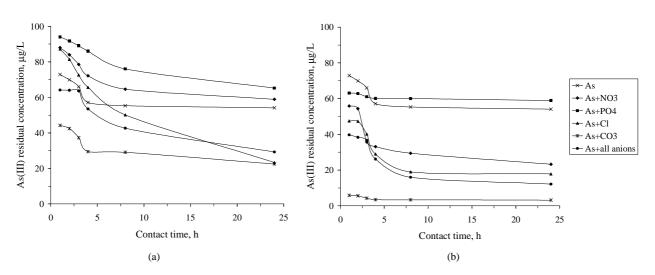


Figure 1. Influence of contact time on the residual concentration of As(III); sorbent – sludge; concentration of anionic species: (a) 10 mg/L; (b) 100 mg/L

Fig. 1 shows that when using sludge as sorbent, residual concentration of arsenic depends on the nature of the anionic species present in the solution and their concentrations, and increases as follows:  $CO_3^{2-} < Cl^- <$  $NO_3^-<\ PO_4^{3-}$  for both concentrations (10 and 100 mg/L). One may notice that the presence of phosphate anions has a negative influence on As(III) adsorption on the sludge, leading to higher residual concentrations than in its absence. This observation is consistent with literature data which indicate that arsenic adsorption is strongly decreased by the presence of phosphate, because of the competition for the binding sites of the sorbent material between arsenic and phosphate [12, 13, 18-20]. The individual presence of other anions  $(CO_3^{2-}, CI^- \text{ and } NO_3^-)$  has a positive effect on As(III) adsorption, leading to residual concentrations lower than those reached in their absence. The residual concentrations in the individual presence of these anions are lower when their concentration is higher (100 mg/L). The lowest residual concentration of As(III) was of 3.2  $\mu$ g/L and was reached for 100 mg/L CO<sub>3</sub><sup>2-</sup>.

The simultaneous presence of all anions has a positive effect on arsenic adsorption, but the residual concentrations were somehow higher than in the presence of  $CO_3^{2-}$  alone,

due to the negative influence of  $PO_4^{3-}$ .

From Fig. 2 one may notice that when the anions are individually present in the sample matrix at concentrations of 10 mg/L, only Cl<sup>-</sup> has no evident influence on As(III) adsorption on Fe<sub>2</sub>O<sub>3</sub>. In this case the residual concentration of As(III) is slightly lower (1.3  $\mu$ g/L) than the value reached in the absence of any anion (2.1 µg/L), but this difference is not significant. All other anions have a negative influence and the residual concentrations are higher, increasing as follows:  $CI^- < CO_3^{2-} < NO_3^- <$  $PO_4^{3-}$ . The negative competitive effect of all studied anions is more evident at higher concentration (100 mg/L), when higher residual concentration of As(III) are reached. When all anions are present together in solution, their negative effect on arsenic adsorption remains and arsenic residual concentrations are slightly higher than for the anions individual presence.

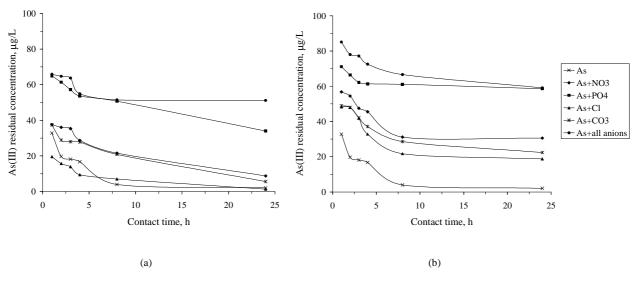


Figure 2. Influence of contact time on the residual concentration of As(III), sorbent - Fe<sub>2</sub>O<sub>3</sub>; concentration of anionic species: (a) 10 mg/L; (b) 100 mg/L

#### 3.2. Influence of sorbent nature

In order to compare the efficiency of the two studied sorbents the data regarding the residual concentrations of As(III) reached after a 24 h contact time are presented in Fig. 3. One may notice that in the absence of the studied anions Fe<sub>2</sub>O<sub>3</sub> is a more efficient sorbent for As(III) leading to a lower residual concentration than the sludge. The same observation is true for the individual presence of the studied anions in the samples, in a concentration of 10 mg/L.

One can also notice that when the anions are individually present in the solutions, but in concentrations 10 times higher (100 mg/L), the residual concentrations of As(III) are lower when the sludge is used as sorbent than in the case of  $Fe_2O_3$ .

At the same time, if the As(III) solution contains simultaneously all anions, regardless their concentration, the sludge is a more efficient sorbent for As(III) than Fe<sub>2</sub>O<sub>3</sub>.

For this reasons we recommend using as adsorbent material in the process of elimination of arsenic the sludge containing iron, because in natural underground water is unlikely to find the studied anions individually. Using the sludge is also advantageous from the economic and environmental protection point of view, since this turns into account a waste resulting from another technological process.

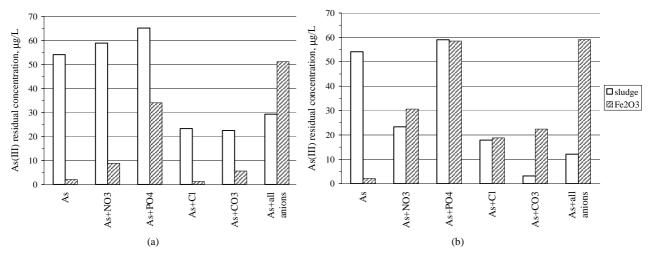


Figure 3. Influence of sorbent nature on the residual concentration of As(III); contact time – 24 h; concentration of anionic species: (a) 10 mg/L; (b) 100 mg/L

# 4. Conclusions

In the present paper is investigated the effect of the presence of some anionic species ( $NO_3^-$ ,  $PO_4^{3-}$ ,  $CI^-$  and  $CO_3^{2-}$ ) in arsenic containing water on the adsorption of arsenic (III) on two iron containing materials: a waste material (a sludge resulting from hot-dip galvanization) and a synthetic material (Fe<sub>2</sub>O<sub>3</sub> obtained through annealing of Fe(COO)<sub>2</sub>· 2H<sub>2</sub>O at 800°C).

For the studies a synthetic solution containing 100  $\mu$ g As(III)/L has been used. It has been separately studied the influence of each anionic species at two concentrations: 10 mg/L and 100 mg/L, respectively. It has been also studied the influence of all mixed anionic species at two total concentrations: 10 mg/L and 100 mg/L, respectively. The adsorption experiments have been carried out at different contact times (1, 2, 3, 4, 8 and 24 h).

The experimental results showed that when the sludge is used as adsorbent material the increase of anionic species concentration has a positive influence on arsenic adsorption. In the case of the synthetic material this influence is negative. When the synthetic solution contained a mixture of all studied anionic species, regardless their concentration, the waste material presented a higher efficiency of arsenic removal process in comparison with the synthetic material.

Since in natural underground waters is likely to find these anionic species together, the iron containing sludge should be more efficient for the removal of arsenic than the iron oxide. The use of the sludge is also advantageous from the economic and environmental protection point of view, since this turns into account a waste resulting from another technological process.

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