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Physicochemical study of arsenic removal using iron hydroxide

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Abstract
Iron hydroxide (III) synthesized and applied to remove the As (III) and As (V). The optimum pH on the adsorption is between pH 4 and pH 9. Experiments were performed to study the effect of pH and the contact time (T) on the Co precipitation- sorption of Arsenic (III) and Iron (III) Hydroxides. Several co-precipitation experiments are performed with 120 mg of iron (III), from solutions having a pH ranging from about 4.7 and 9, at time 240 min. In this study, the adsorption of the arsenic (III) on the surface of iron hydroxide (III) is examined by adopting surface complexation model, This model successfully used to describe the adsorption of iron on the metal oxides suppose that this phenomenon occurs through an inner-sphere legend exchange mechanisms with surface functional group (≡ FeOH). The results of the study show that the co-precipitation of arsenic (III) with $Fe(OH)_3$ was more dependent on the concentration of iron and H^+ ions. Complexation in a monodentate area was more important than the bidentate throughout the pH range studied, but the bidentate complex has important role near pH 8.

Keywords: Iron (III) Hydroxide, Arsenic, Adsorption, monodentate, bidentate.

Introduction

Arsenic is an element known to cause several serious complications health. The long-term exposure to low concentrations can lead to cancer and skin diseases, whereas exposure at higher concentrations is fatal, Arsenic can be found in two different oxidation states, As(V) which dominates under oxidative conditions, and As(III), which is the predominant species in reducing environments. The As(III) is considered more toxic and also presents a higher mobility than As(V) in natural systems[1]. The iron oxide materials are very abundant in nature, and it presents a high affinity adsorption of arsenate and arsenite [2, 3]. Various materials are used for the adsorption of arsenic [4, 5]. To have a high adsorption capacity of adsorbent, a large specific surface area is required, which is achieved by reducing the particle size of the nanoparticles throughout [6, 7].

An effective strategy for producing an adsorbent such as iron oxide, having the same time a high adsorption capacity (high surface area), and facilitates the outright separation between solution and the adsorbent, is to coat inert material by iron oxide nanoparticles. The coating of iron oxide nanoparticles can be achieved by rapid precipitation of salts of Fe (III). Studies on sand coated iron oxide have been made [8-10], glass fibers coated with iron oxide [11] and alumina coated with iron hydroxide [12]. The use of zero- valent iron as adsorbent is another alternative with good removal of arsenic from water [6]. The adsorption of arsenic by the iron oxides involves interactions between the adsorbate and the hydroxyl group of the iron oxide [13]. This phenomenon is clearly demonstrated when adsorption of arsenate (III) on the iron oxide was studied by using IR spectroscopy [14]. The surface chemistry of the iron oxides varies with pH. At low pH, the hydroxyl groups at the surface of the iron oxide are doubly protonated ($\equiv Fe(OH)_2$) , and the surface charge of the iron oxide is thus positive. At a certain pH, the hydroxyl group is protonated with only one proton (≡FeOH) and thus the (net) surface charge of the iron oxide is neutral. This pH is called the point of zero charge , for iron oxides, the point of zero charge (PZC) it ranges between 5.5 and 9[13]. At pH values above the PZC, the hydroxyl group is

deprotonated (≡FeO$^-$); and consequently the iron oxide surface bears a negative charge. A maximum adsorption of arsenate has been observed at acidic pH values around 4 [15, 16]. At pH lower than 3, fully protonated arsenate (H_3AsO_4) species are present in solution and electrostatic attraction is impossible, resulting in a lower adsorption. At pH values above the point of zero charge, the iron oxide is negatively charged, therefore repels the negatively charged arsenate. Consequently adsorption is substantially lower at these pH- values [13]. Carbanat et al also showed that the adsorption capacity achieved is about 0.6 mg (As)/g [17].
The Possible chemical bonds that can form between arsenate and iron oxide to the adsorption surface are shown in Figure 1.

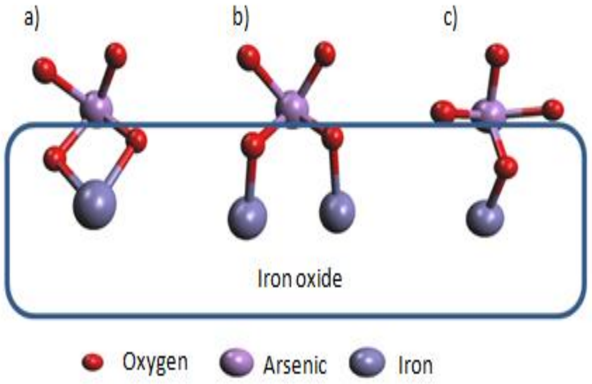


Figure 1: Schematic representation of the different complexes that can form on the surface of the iron oxide. (a) Mononuclear bidentate; (b) bidentate two nuclear; (c) monodentate. Protons and charges are not included in the sketch.

In this work, we have tested the sorption of arsenic(III) on iron hydroxide; and adsorption mechanisms have been proposed. The Analyses were performed at the Laboratory of Nuclear Chemistry from the perspective of well- controlled settings work. The control of technical analysis requires precise knowledge of the mechanisms of interaction between arsenic and iron hydroxide.

2. Materials and methods

2.1. Materials

Arsenic ready for use (1g/L), Ferric chloride hexahydrate $FeCl_3.6H_2O$, nitric acid supra pur, Sodium hydroxide 0.1 M,(MERCK products), and Water Ultra Pur.

2.2. Test sample

It takes polyethylene cups well rinsed with water Ultra Pure, we put 25 ml of the solution of Iron and 10 mg / L of Arsenic. To each cup is adjusted pH with 1% nitric acid or 0.1 N sodium hydroxide while stirring, the solution so as moderate, using a magnetic stirrer according to the chosen pH value analysis. After times 30, 60, 120, 180 or 240 minutes, the two phases of solution separated by means of a glass funnel rinsed with ultra pure water containing a filter paper, then retrieves the solution in a 25 ml vial rinsed well as Ultra Pure water. Finally the solution is acidified recovered added 250 µL Supra Pure nitric acid. Analyses of arsenic are made by the SAA Atomic Absorption Mode "Four Thermo model" analysis technique, in well-defined measuring conditions while respecting the concentration ranges of arsenic. The samples were measured under the same conditions as the calibration solutions and compared to the calibration curve previously drawn. The pH measurement is performed by an Orion model pH meter.

2.4. Determination of concentration of arsenic adsorbed

2.4.1. Atomic absorption Spectroscopique method (Four mode)

The SAA analysis was performed with atomic absorption spectrometer (oven method) Brand Thermo Electron Corporation SAA.

2.4.2. pH Measurement

The pH measurement method was used to determine the charge densities of surface iron oxide (III). in a flask of 1000 ml : 0.6 g of hydrated hydroxide Iron Hexa $FeCl_3.6H_2O$ in powder was dissolved, 10 ml of the solution Arsenic 1 g / L and complete to the mark with the Ultra Pure water. Titration was 0.1 M sodium hydroxide (NaOH). The pH was measured with a digital pH meter (Orion Model 420A pH meter). The 1% solution of nitric acid is used as a reactant in the range of pH 4 to 11.0. The solutions were stirred magnetically. The system was equilibrated at a constant pH.

2.5. Adsorption experiments

2.5.1. Process of adsorption

The adsorption capacity (Qe) was calculated by the equation below Eq. (1):

$$Qe = (C_0 - Ce)\frac{V}{W} \qquad (1)$$

Where Co is the initial concentration of As(III) ion (ppm),Ce is the final concentration of As(III) ion (ppm),V is the volume of As(III) ion solution (mL) and W is the weight of the iron hydroxide (g) used.

3. Results and Discussion

3.1 Chemical structure

3.1.1 Adsorption isotherms of Arsenic (III)

The results of analysis pH and Analysis Atomic Adsorption allow us to plot the curves in **Figures 2, 3, 4, 5, 6,7,8,9,10,11,12 and 13.**

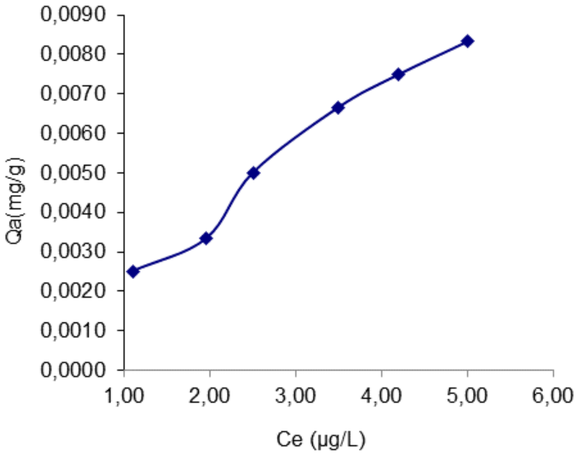


Figure 2: Adsorption isotherms of arsenic (III) ion on the iron oxide at pH=4

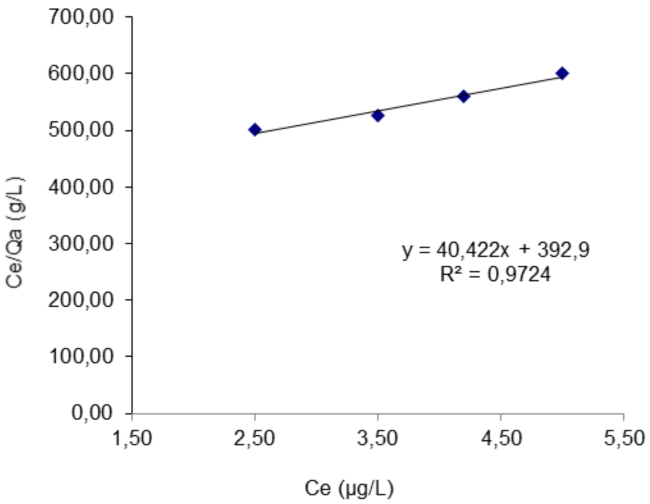


Figure 3: Adsorption isotherms of arsenic (III) ion on the iron oxide at pH=4, linearized according to Langmuir.

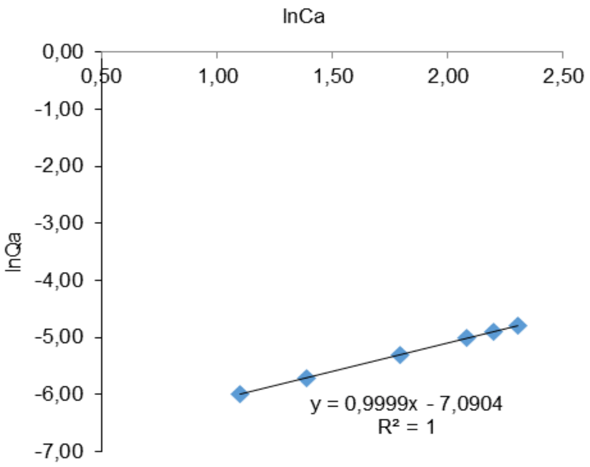


Figure 4: Adsorption isotherms of arsenic (III) ion on the iron oxide at pH=4, linearized according to Freundlich.

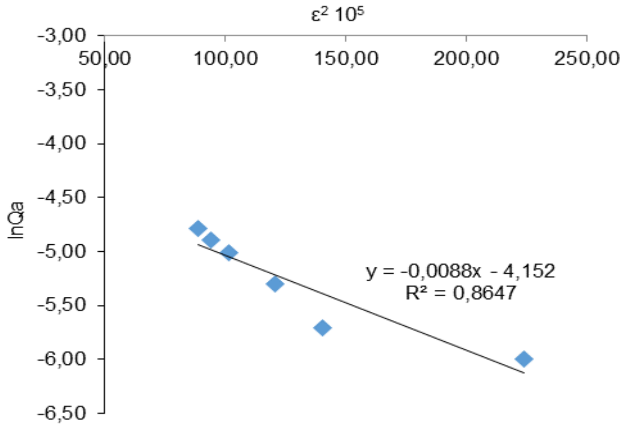


Figure 5: Adsorption isotherms of arsenic (III) ion on the iron oxide at pH=4, linearized according to Dubinnin-Radushkevich equations.

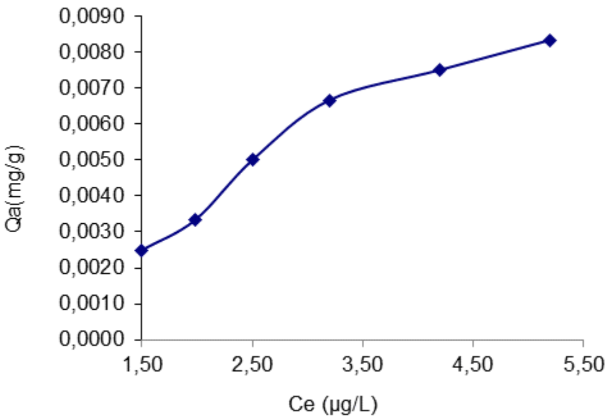


Figure 6: Adsorption isotherms of arsenic (III) ion on the iron oxide at pH=7

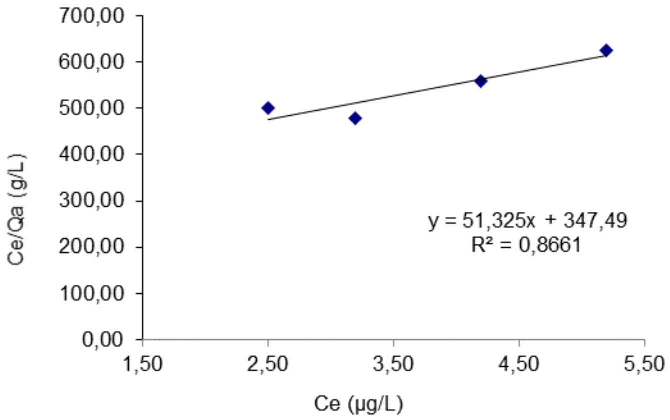
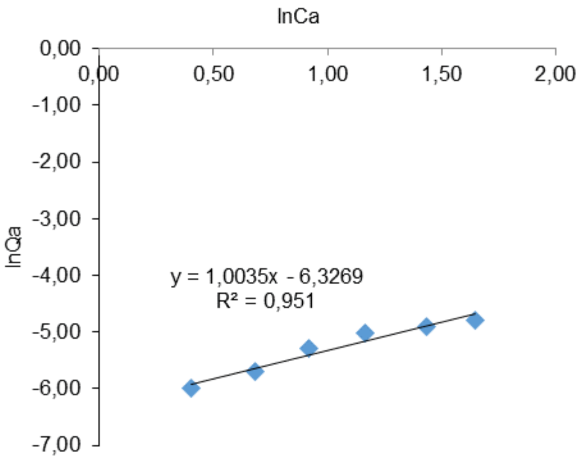


Figure 7: Adsorption isotherms of arsenic (III) ion on the iron oxide at pH=7, linearized according to Langmuir.



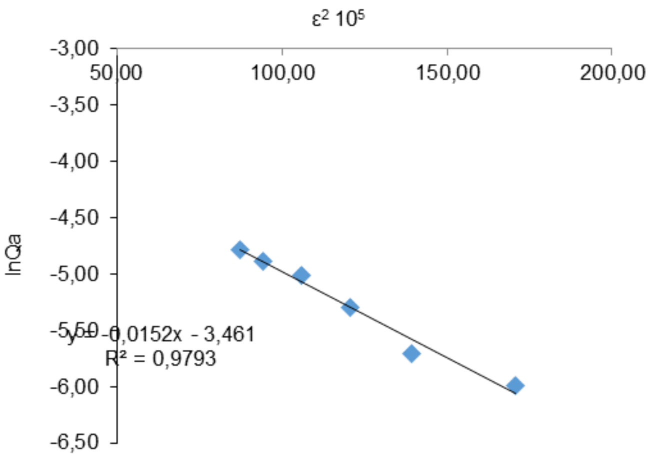


Figure 8: Adsorption isotherms of arsenic (III) ion on the iron oxide at pH=7, linearized according to Freundlich.

Figure 9: Adsorption isotherms of arsenic (III) ion on the iron oxide at pH=7, linearized according to Dubinnin-Radushkevich equations.

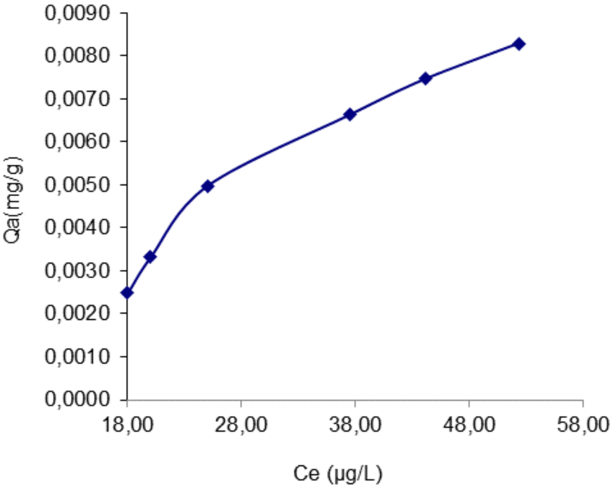


Figure 10: Adsorption isotherms of arsenic (III) ion on the iron oxide at pH=9.

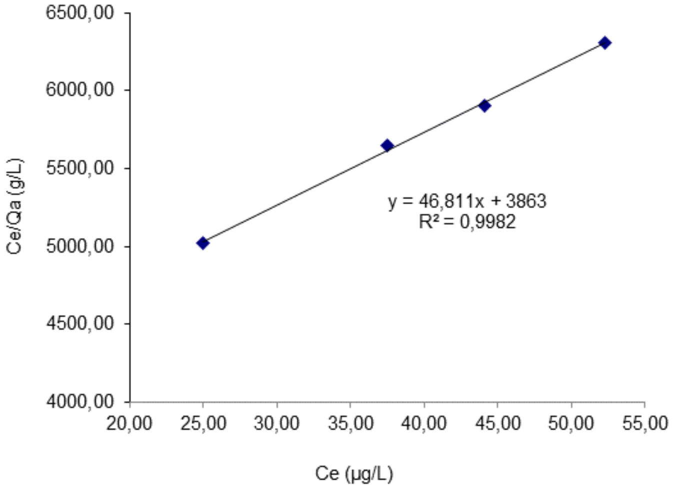
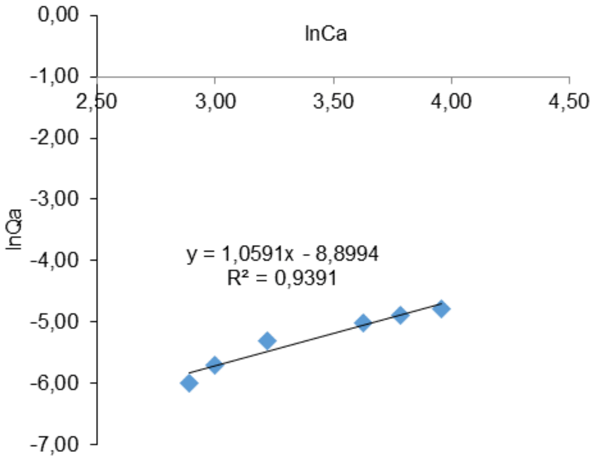


Figure 11: Adsorption isotherms of arsenic (III) ion on the iron oxide at pH=9, linearized according to Langmuir.



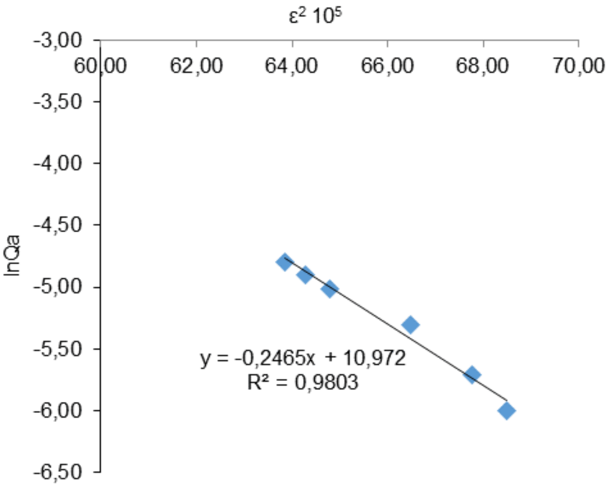


Figure 12: Adsorption isotherms of arsenic (III) ion on the iron oxide at pH=9, linearized according to Freundlich.

Figure 13: Adsorption isotherms of arsenic (III) ion on the iron oxide at pH=9, linearized according to Dubinnin-Radushkevich equations.

The Langmuir isotherm equation is represented by the following Eq. (2) [11]:

$$\frac{Ce}{Qe} = \frac{Ce}{Qm} + \frac{1}{Qmb} \qquad \textbf{(2)}$$

Where Ce is the equilibrium concentration of metal ions (mg/L), Qe is the amount of metal ions adsorbed (mg/g), Qm is the maximum adsorption capacity of metal ions (mg/g), and b is the Langmuir adsorption equilibrium constant (mL/mg). Therefore, the plot of Ce/Qe against Ce gives a straight line with a slope of 1/Qm and an intercept of 1/ (Qmb).

The Freundlich isotherm equation is represented by the following Eq. (3) [11]:

$$\ln Q_e = b_F \ln C_e + \ln K_F \qquad \textbf{(3)}$$

Where Ce is the equilibrium concentration of metal ions (mg/L), Qe is the amount of metal ions adsorbed (mg/g), K_F is the maximum adsorption capacity of metal ions (mg/g), and b_F is the adsorption intensity. Freundlich constants, K_F and b_F, can determined from a linear plot of lnQe versus lnCe.

The Dubinin-Radushkevich isotherm equation, which is more generally used to distinguish between physical and chemical adsorption, is given by the following Eq.(4) [11]:

$$\varepsilon = RT \ln(1+\frac{1}{Ce}) \qquad \textbf{(4)}$$

Our experiment was conducted to study the effect of pH, experiences of co precipitation of Fe (III), are carried out with various concentrations of Arsenic (III) at 120 mg of iron (III) from solutions with pH from about 4,7 and 9 at the 240 min in **Figures 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12 and 13.** From these results, the co-precipitation of arsenic (III) with Fe (OH) is more dependent on the concentration of iron in the hydrogen released. Often, there is no significant change in the removal of As (III) in the pH values <5.

According to the diagram of Fe (III) (figure 7) as a function of pH we found that there are two acidity constants pKa**1**, pKa**2** [10]:

$FeOH_2^+ \leftrightarrow H^+ + FeOH$ pKa**1**= 6.5 **(5)**

$FeOH \leftrightarrow H^+ + FeO-$ pKa**2** = 9.0 **(6)**

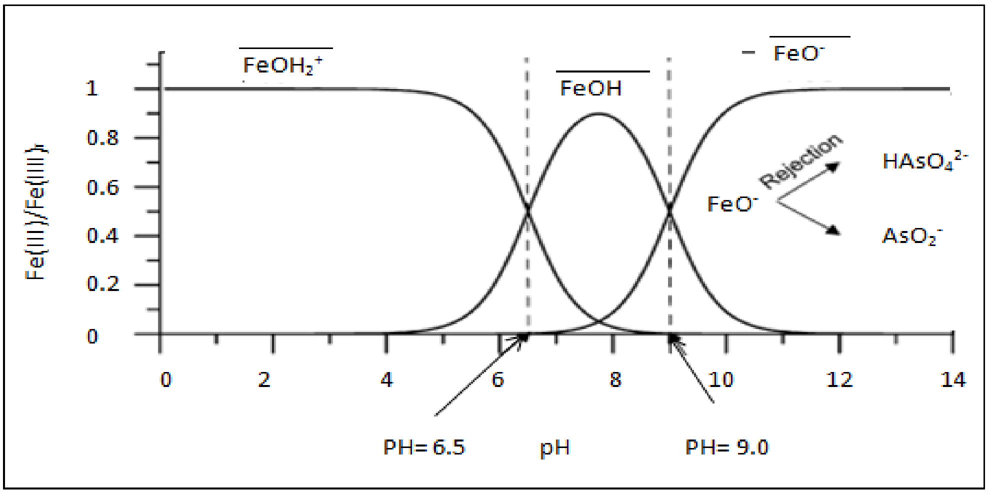


Figure 3: diagram of iron as a function of pH [18].

The value of Qa increases with increasing pH in all cases, and reaches a maximum at a pH of from pH 7 and then decreases sharply to a pH of about pH 9 to pH 12. In addition the effect of pH is more important in conditions of optimum contact time, similar results were obtained showing that adsorption As (III) of hematite, reached a maximum at pH 7.0 [20].

3.2 Theory of adsorption Iron oxide

3.1. Analysis of the concentration of arsenic adsorbed on the iron oxide.

Analyses were performed by the atomic absorption method "Four Mode". The analysis of curves represents with different mass 120 mg of iron, and also a function of the concentrations of arsenic remained after adsorption.

3.1.1. Study of the reaction mechanism

A model is proposed reaction mechanism to explain the phenomenon of adsorption of arsenic (III) on iron oxide. The following shows the reactions bringing into play during the experiment.

SOH = FeOH, $Fe(OH)_2$ or $Fe(OH)_3$

The arsenite ions are essentially fixed to the hydroxide groups of Iron (III) available (Figure 14). The SOH Iron groups may experience protonation to form $S\text{-}OH_2$, mainly depending on the pH of the solution. The pH increases the degree of protonation groups SOH Iron (III) is reduced by acting on the equilibrium equation.

Therefore the density of FeOH complex evolves with increasing pH. Beyond pH = 9, we find that the (Qa) remains almost constant, which explains the interaction between the molecules of arsenic and oxides FeO- predominant in the field of basic pH.

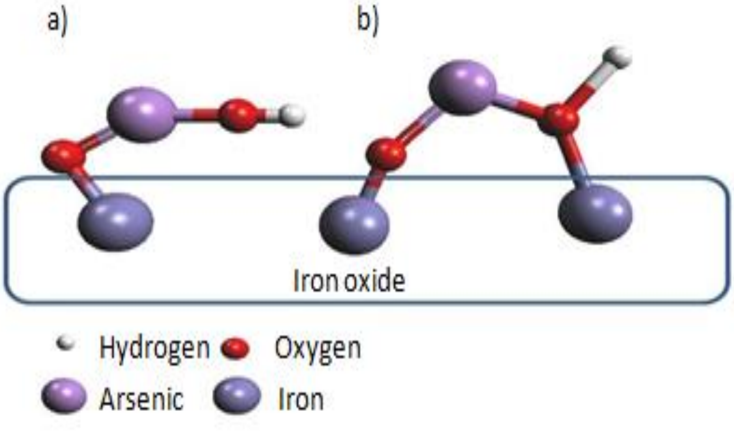


Figure 14: mechanism to explain the phenomenon of adsorption of arsenic on iron oxide (III).

Conclusion

The main findings of this study is that the adsorption reactions between the ions arsenic and iron oxide (III) have been proposed based on the characterization of physical and chemical properties of iron oxide (III) including the release of H^+ ions by the hydroxyl group OH of iron oxide (III), and the nature of the iron complex and also taking account of the properties of the surface charge of adsorption. The adsorption of Arsenic (III) on iron oxide (III) material was investigated, in order study of surface complexation of this element. The properties of the solid phase depends on the adsorption process and the iron oxide type and adsorbed component. The amount adsorbed increased with increasing concentration, according to the three models isotherms of adsorption, the pH variation is independent of evolution of absorption process.

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