ISABELA CRISTINA FILARDI VASQUES

ARSENITE AND ARSENATE REMOVAL FROM CONTAMINATED WATER BY PRECIPITATION OF ALUMINUM, FERROUS AND FERRIC (HYDR)OXIDES

Dissertação apresentada à Universidade Federal de Viçosa, como parte das exigências do Programa de Pós-Graduação em Solos e Nutrição de Plantas, para obtenção do título de *Magister* Scientiae.

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BIOGRAFIA

Isabela Cristina Filardi Vasques nasceu em Barbacena, filha de Maria José e Donizetti, no dia 5 de junho de 1990. Morou em Barbacena até completar o ensino fundamental e médio na cidade.

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SUMMARY

ABSTRACT

VASQUES, Isabela Cristina Filardi, M.Sc., Universidade Federal de Viçosa, June, 2017. **Arsenite and arsenate removal from contaminated water by precipitation of Aluminum, Ferrous and Ferric (hydr)oxides**. Adviser: Jaime Wilson Vargas de Mello. Co-adviser: Walter Antônio Pereira Abrahão.

Arsenic is a metalloid commonly found in mining sites and can be mobilized in water following acid mine drainage. Due to severe consequences of As contamination, the World Health Organization (WHO) recommended 10 µg L^{-1} as a threshold concentration for As in drinking water. To face As toxicity, several methods to remove it from water have been considered, including co-precipitation with Fe and Al (hydr)oxides. Such compounds have been considered a good alternative to remove As from contaminated water due to strong bindings between them. However, not only the water needs to be efficiently clean, but also the waste generated must be safe to disposal. In this study three Fe:Al molar ratio (100:0, 80:20 and 60:40) were used to synthesize ferrous and ferric (hydr)oxides by precipitation in water containing high concentrations (50 and 500 mg L^{-1}) of As (III) and As (V). Mineralogical phases detected by XRD were goethite, lepidocrocite, magnetite, maghemite, gibbsite and bayerite for precipitates from Fe (II) and ferrihydrite, hematite and gibbsite for synthesis with Fe (III). BCR extractants were used in order to evaluate As remobilization from precipitates, including acid soluble, reducible and oxidizable phases. Arsenic associated to Al and adsorbed phases were also assessed by extractions with NH_4F and KH_2PO_4, respectively. Arsenic adsorbed to iron (hydr)oxides represented the major phase among all other extracted phases. It was found that the method was highly efficient for all treatments (> 93 %) in the beginning of the experiment, but efficiency was somewhat lower for treatments in which lepidocrocite and gibbsite were identified in the precipitated phases. In spite of the high efficiency, however, the threshold for drinking water was not attained to the higher concentration of As (III and V). At this high concentration, even the required threshold for effluent discharge was not attained for arsenite in some treatments. In general, the sludges resulting from treatments were considered safe for disposal, except for treatments with arsenite, which were considered hazardous by leaching test. In general, the presence of Al increased the efficiency as well as the stability of the sludge resulting from treatments with Fe (II), but was unfavorable for treatments with Fe (III). In summary, precipitation of Fe (III) in the absence of Al was more efficient to remove As, therefore, treatments in which

precipitation of hematite is favored are the most effective to treat As contaminated water ensuring a safe sludge disposal.

RESUMO

VASQUES, Isabela Cristina Filardi, M.Sc., Universidade Federal de Viçosa, junho de 2017. **Remoção de arsenito e arsenato de água contaminada a partir da precipitação de (hidr)óxidos de Alumínio, Fe ferroso e Fe férrico**. Orientador: Jaime Wilson Vargas de Mello. Coorientador: Walter Antônio Pereira Abrahão.

Arsênio é um metaloide comumente encontrado em áreas de mineração e por isso pode ser solubilizado em água pela formação de drenagem ácida. Devido às severas consequências da contaminação por arsênio, a Organização Mundial de Saúde (OMS) recomendou como sua concentração limite em água potável o valor de 10 $\mu g\ L^{-1}$. A elevada toxicidade do As requer o desenvolvimento de métodos para remoção de As solúvel, incluindo a co-precipitação com (hidr)óxidos de Fe e Al. Esses compostos têm sido considerados uma boa alternativa para remoção de As de águas contaminadas devido às fortes ligações entre eles. Além da qualidade da água, há também a necessidade de avaliar a estabilidade do rejeito formado para fins de deposição. Nesse estudo, três relações molares Fe:Al (100:0, 80:20, 60:40) foram usadas para sintetizar hidróxidos de Fe ferroso e férrico a partir da precipitação em água com altas concentrações (50 e 500 mg L^{-1}) de As (III) e As (V). As fases mineralógicas identificadas pela difratometria de Raios-X nos tratamentos com Fe (II) foram: goethite, lepidocrocita, magnetite, maghemita, gibbsita e bayerita e para os tratamentos com Fe (III) foram: ferridrita, hematita e gibbsita. Os extratores BCR foram usados para avaliar a remobilização do As presente no precipitado, incluindo as fases solúveis em ácido, reduzíveis e oxidáveis. Arsênio associado com Al e as fases adsorvidas foram avaliadas pela extração com NH_4F e KH_2PO_4, respectivamente. Arsênio adsorvido aos (hidr)óxidos representa a maior fase extraída entre todas as outras. A remoção de As pelos precipitados foi altamente eficiente (> 93%) no início do experimento, mas a eficiência foi ligeiramente menor para tratamentos onde foram identificados lepidocrocita e gibbsita. Apesar da alta eficiência, a concentração limite para água potável não foi satisfeita nas maiores concentrações iniciais de As (III e V). A essa concentração, nem mesmo o limite de concentração de As para descarte de efluentes foi satisfeito em alguns tratamentos. Em geral, o lodo resultante dos tratamentos foi considerado seguro para deposição, com exceção dos tratamentos com arsenito, que foi considerado perigoso pelo teste de lixiviação. Em geral, a presença do Al aumentou a eficiência de remoção assim como a estabilidade do lodo gerado dos tratamentos com Fe (II), mas foi desfavorável para os tratamentos com Fe (III). Resumindo, a precipitação de Fe (III) na ausência de Al foi mais eficiente para a remoção de As e portanto, os tratamentos que

favoreceram a precipitação de hematita foram considerados os mais eficientes para o tratamento de água contaminada com As e para disposição segura do rejeito.

1. Introduction

Arsenic is a natural metalloid which can pose concern to human health due to its toxicity. Countries as Bangladesh are known to have many people contaminated with arsenic from drinking water.

Anthropogenic sources of arsenic are related to mining activities mainly those ones associated to sulfides as arsenopyrite. Arsenic has no much uses, so that As bearing minerals are rejected during the ores processing and remain stocked in piles as much as possible in mines (Coussy et al., 2011). Mining of ores associated to sulfides is also related to acid mine drainage arising, responsible for lowering the pH of wastewater.

According to the Brazilian Mining Institute, iron mining production in Minas Gerais State is more than 180 million tons per year. The state has the biggest production of iron, gold, zinc, phosphate and niobium in Brazil (IBRAM, 2015). Considering these numbers, mitigation of environmental impacts is crucial for the development of mining operations in Brazil.

Many techniques have been developed in order to attenuate environmental impacts due to arsenic contamination. Adsorption of As onto Fe (hydr)oxides has been widely considered to treat contaminated water due to its low cost and high efficiency. Notwithstanding, the mechanisms involved in the co-precipitation of Al-Fe (hydr)oxides as well as the stability of arsenic in sludge resulting from water treatment still require studies.

Considering the environmental importance of this concern, this work aimed to evaluate co-precipitation of synthetic aluminum and iron hydr(oxides) in order to immobilize soluble arsenic from contaminated water.

2. Literature Review

Acid mine drainage (AMD) is an important environmental impact generated by mining processes which can contaminate surface and underground water sources with metals and metalloids such as arsenic. Oxidation of sulfides, like pyrite, when exposed to air and water, is the main reaction responsible for AMD formation. Acidification of water can occur in mine pits and in tailings as well. The drainage water is acidified due to the following reaction (Equation 1) (Johnson & Hallberg, 2005):

$$4FeS_2+15O_2+14H_2O \rightarrow 4Fe(OH)^3+8SO_4^{-2}+16H^+ \quad (1)$$

When present, arsenic can be mobilized by AMD. This mettaloid is the 20th most abundant element on Earth, with atomic number 33 and atomic mass 74,92. There are approximately 200 different As bearing minerals: 60% are arsenates, approximately 20% are sulfides and sulfo-salts and the rest are silicates and native As (Sarkar & Paul, 2016).

In addition to the inorganic forms of As: arsenate (As (V)) and arsenite (As(III)), organic forms can occur in nature as: monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), trimethylarsine oxide (TMAO), arsenobetaine (AsB), arsenocholine (AsC), arsenosugars (AsS) and others (Singh et al., 2015). Among the inorganic forms, As (V) occurs as $H_2AsO_4^-$ and $HAsO_4^{-2}$ ions, while As (III) appears as H_3AsO_3 in environmental conditions (Figure 1) (Wang & Giammar, 2015). It can be seen from Figure 1 that at low pH values, the Eh values that distinguishes the occurrence of As (III) and As (V) are close to 0.6 V and as pH increases, Eh decreases, showing an indirect proportional relation between Eh and pH. Inside the black square, it can be seen the more common values for pH and Eh in nature.

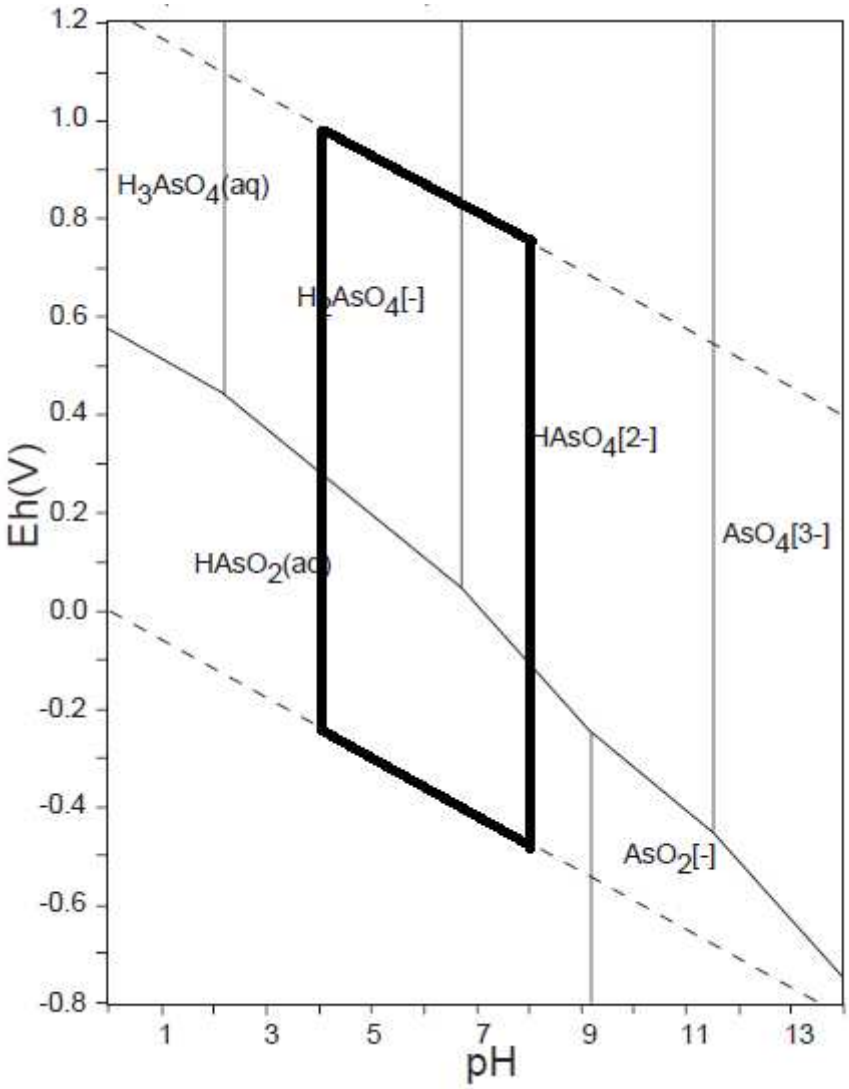


Figure 1. Arsenic speciation according to Eh and pH (Adapted from Takeno, 2005)

Higher toxicity of As (III) relative to As (V) can be due to the rate of uptake by living cells. The neutral form of As (III) crosses the cell membrane faster than As (V) (Rossman, 2003). Besides, As (III) is able to bind to sulfihydryl groups in proteins (Ociński D., 2014) while As (V) affects the biomolecules that depend on phosphate by replacing it for arsenic (Sarkar & Paul, 2016).

Arsenite is more mobile that arsenate in soils and sediments, which constitutes a further environmental issue related to underground water contamination. Arsenate is less mobile due to the specific adsorption onto colloids of soils and sediments, via inner sphere surface complex. On the other hand, As (III) can form both inner and outer sphere complex, which is a weaker interaction with colloids (Ociński et al., 2016).

Effluents containing arsenic have to be treated before being discharged, irrespectively of arsenic form. The threshold for drinking water recommended by World Health Organization (WHO, 2011) is 10 μg L^{-1}, but this limit does not take into account the speciation of arsenic.

In the environment, arsenic can be attenuated by using Fe and Al (hidr)oxides, involving co-precipitation and/or adsorption of As. Co-precipitation takes place when the metal is already in solution following the iron oxides precipitation and adsorption occurs when the iron oxides are previously precipitated (Crawford et al., 1993).

Arsenic mobility is controlled by sorption processes in soils. Hydroxyl groups represent the most reactive sites of the iron (hydr)oxides (Silva et al., 2010). The affinity between As and surface hydroxyl groups is the main reason for using iron (hydr)oxides in treatment of wastewater.

The mechanisms to remove As from acid mine drainage involving Fe (hydr)oxides was already reported by Adra et al. (2013 and 2015). It was also studied the impact of Al in the structure of natural ferrihydrites, which increased the rate of As (III) oxidation to As (V) and helped to maintain the As oxidation state after disposal.

According to Ko et al. (2015), the acid mine drainage also play a different important role on As immobilization. For instance, Ko et.al (2015) aimed to evaluate the use of sludge from acid mine drainage treatment to immobilize As in a contaminated soil due to its high Fe (hydr)oxides content and reached good results for its purpose.

Iron hydr(oxides) are characterized by their substantial surface area which depends on the environmental conditions for crystal growth. The main advantage of an expressive surface area is the high reactivity and interactions with other compounds (Schwertmann & Cornell, 2003).

The ligand exchange is the mechanism associated to As adsorption, which is specifically adsorbed as oxyanions onto Fe and Al (hydr)oxides surfaces. The complexes formed can be monodentate mononuclear, bidentate mononuclear or bidentate binuclear (Figure 2), being the latter the strongest one (Jacukowicz-Sobala et al., 2015).

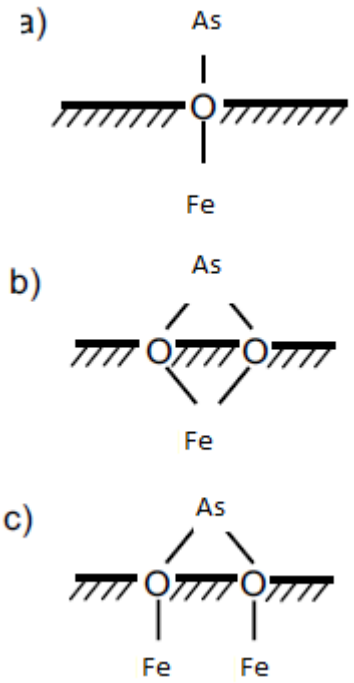


Figure 2. (a) Monodentate mononuclear complex, (b) Bidentate mononuclear and (c) Bidentate binuclear.
(adapted from Jacukowicz-Sobala et al., 2015)

One factor that affects the arsenic adsorption onto Fe and Al (hydr)oxides is pH, because it directly influences the surface charge and the As speciation (Jacukowicz-Sobala et al., 2013). Considering an acidic pH, there are more positive surface charges, which favor anion adsorption. As pH increases, negative charges increase, and cation adsorption increases. Considering that As is present in natural environment mainly as oxyanion, it can be concluded that its optimum adsorption is in acidic pH (Jacukowicz-Sobala et al., 2015). Comparing the main inorganic As species, the adsorption of As (V) is more sensitive to variations of pH than As (III) (Ociński et al., 2016).

Isomorphic substitution for Al in iron oxides has been widely reported in nature. The decrease in the unit cell size is a consequence of isomorphic substitution of Fe by Al inside the oxide structure (Schulze & Schwertmann, 1984). It is well known that the smaller the cell size, the bigger the specific area, which leads to a higher adsorption capacity.

Different (hydr)oxides show different capacities to accept Al in their structure. According to Cornell and Schwertmann (2003), goethite can have Al in a maximum of 33% mol , hematite

18% mol and maghemite and lepidocrocite with a lesser capacity of 10% mol. Also, ferrihydrites were studied by Cismassu et al. (2012) and the Al isomorphic substitution reached proportions between 20-30% mol.

According to Silva et al. (2010), goethites with 13% of structural Al showed higher As (V) adsorption capacity in relation to other goethites with no Al. Goethites with 20% and 23% of Al were not so efficient than those with 13% of Al. It means that there is an ideal proportion of structural Al in goethites for As removal from water.

Arsenic adsorption can also be affected by the presence of other anions in solution, as phosphate, because arsenate and phosphate oxyanions compete for adsorption sites of iron (hydr)oxides. Therefore, the arsenic fraction specifically adsorbed onto Fe (hydr)oxides is evaluated by extraction with phosphate (Antelo et al, 2005). Both arsenic and phosphorus are in group 5A in the periodic table which explains their similarities on chemical properties.

So, this study aimed to understand the mechanisms involved in As removal from water by precipitation of Fe and Al (hydr)oxides and the stability of the resulting precipitates, considering the role of isomorphic substitution. It is expected that the results could be useful on treatment of contaminated water and on sludge disposal.

3. Materials and Methods

3.1. Synthesis of Fe and Al (hydr)oxides

Iron and aluminum (hydr)oxides were synthesized in laboratory following guidelines of Schwertmann & Cornell (2000) methods with some modifications. Ferrous and ferric sulfates were used together with Al sulfates to precipitate the (hydr)oxides at pH 8.0 in water containing different concentrations of As. Sulfates were chosen in order to approach acid mine drainage environment. The treatments consisted of three Fe:Al molar ratios (100:0; 80:20 and 60:40) combined with two concentrations (50 and 500 mg L^{-1}) of arsenate or arsenite (Table 1).

Table 1. Fe:Al molar ratio and concentrations of arsenate and arsenite in treatments.

Fe:Al ratio molar	100:0			80:20			60:40		
[As] (mg L^{-1})	0	50	500	0	50	500	0	50	500
Fe(II) and As(III) treatments		T1.1	T1.2		T1.3	T1.4		T1.5	T1.6
Fe(II) and As(V) treatments		T2.1	T2.2		T2.3	T2.4		T2.5	T2.6
Fe(III) and As(III) treatments		T3.1	T3.2		T3.3	T3.4		T3.5	T3.6
Fe(III) and As(V) treatments		T4.1	T4.2		T4.3	T4.4		T4.5	T4.6
Fe (II) Blanks	B1			B2			B3		
Fe (III) Blanks	B4			B5			B6		

Arsenic solutions were prepared with di-sodium hydrogen arsenate heptahydrate ($Na_2HAsO_4.7H_2O$), as a source of As (V), and arsenite trioxide (As_2O_3), for As (III). Only analytical reagents grade and Milli-Q water were used. The solutions were stored in polyethylene bottles previously clean with HCl 1:1.

The synthesis started by adding ferrous (Fe II) or ferric (Fe III) sulfates (0,646 and 0,323 mol L^{-1}, respectively) and aluminum sulfates (0,498 mol L^{-1}), to the arsenic solutions in order to obtain the corresponding molar ratios (Table 1). Sodium concentration was adjusted for all treatments with Na(OH) based on the concentration in treatments with 500 mg L^{-1} of $Na_2HAsO_4.7H_2O$. Afterwards, the pH was adjusted to 8 by addition of KOH 5 mol L^{-1} in order to promote precipitation of Fe/Al (hydr)oxides. Then, supernatants samples were periodically collected following the (hydr)oxides precipitation: after two hours and 1, 4 and 7 days and then every week, until 35 days, every other week, until 63 days, and finally at the

end of the incubation period (84 days). By using this time frame, it was possible to precipitate a different range of (hydr)oxides, poorly and well crystallized.

The supernatants samples (around 2 ml) were stored in ependorffs until analysis. During the incubation time, bottles containing the suspensions (Figure 3) were oxygenated daily by pumping air during one hour.

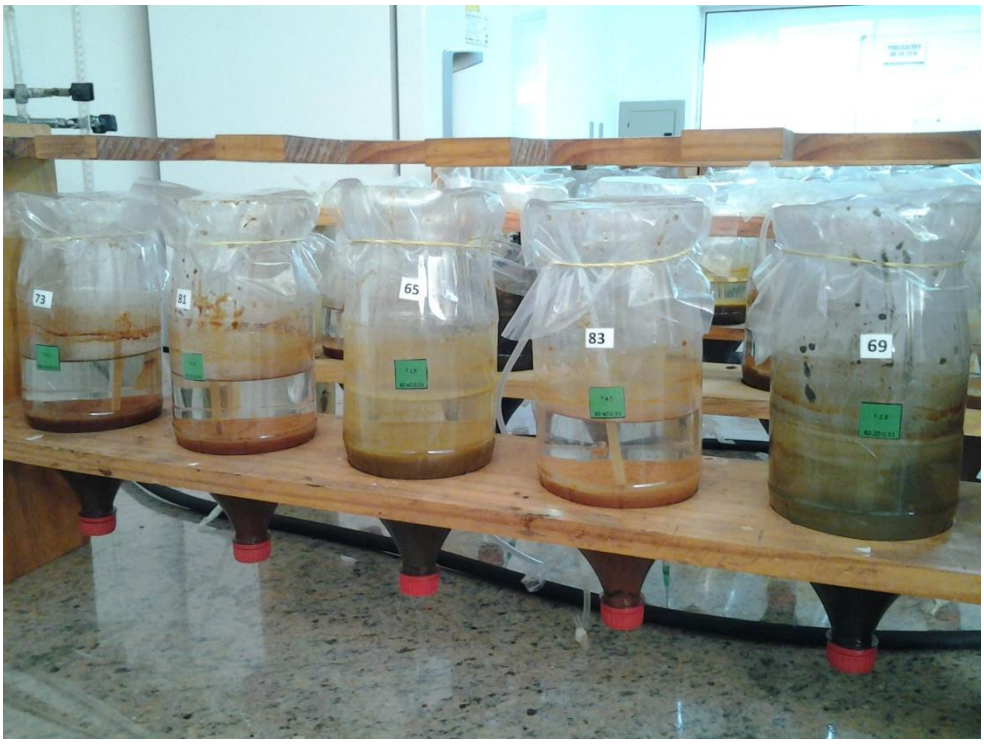


Figure 3. Overview of the experiment (bottles containing the precipitates)

3.2. Precipitates Analysis

Supernatants were siphoned at the end of the incubation period and the remaining suspensions were transferred to vessels: one part was oven dried at 40 ^{0}C, for evaluating the stability of As in precipitates, and another part was freeze-dried for mineralogical characterization. Dried samples were ground in agate mortar and sieved in 100 mesh (oven-dried) or the 200 mesh (freeze-dried).

Freeze-dried samples were dialyzed in 30 mL 3,5kD cassettes with K_2SO_4 solutions at decreasing concentrations (from 0.04 to 0.000002 mol L^{-1} approximately) in order to remove soluble salts that precipitated during drying. Dialyses were held until the electrical conductivity drop to values between 3 μS cm^{-1} and 4 μS cm^{-1}.

The crystalline phases in freeze-dried precipitates were identified by X-ray diffraction with Cu ka (λ = 0.1540 nm) radiation, from 4 to 90º 2θ, at 1° s^{-1} and room temperature. Diffractograms were identified according to Chen (1977).

The stability of As in precipitates was evaluated through discrete extractions using the BCR method solutions (Baig et al., 2009) on oven dried samples. From these results, it was possible to assess the As associated water soluble, acid soluble, reducible and oxidizable phases in the precipitates, simulating different environmental conditions. Arsenic adsorbed and associated to Al were also evaluated, as follows.

(1) Water soluble As: 2 g of samples were washed twice with 25ml of Mili-Q water in a 1:25 solid to solution ratio, shaken for 2 hours and centrifuged at 1006 G.
(2) Acid soluble As: 0.1 g of washed samples were shaken overnight (16 h) in a 1:40 solid to solution ratio with acetic acid 0,11 mol L^{-1} and centrifuged at 3095 G.
(3) Reducible As: 0.1 g of washed samples were shaken overnight in a 1:40 solid to solution ratio with hydroxylammonium chloride 0,5 mol L^{-1} and centrifuged at 3095 G.
(4) Oxidizable As: 0.1 g of washed samples were digested with hydrogen peroxide in a 1:40 solid to solution ratio (8,8 mol L^{-1}) in water bath at 90º C until almost drying. Afterwards samples were shaken for 16 hours with ammonium acetate 1 mol L^{-1} and centrifuged at 3095 G.
(5) As associated to Al: 0.1 g of washed samples were shaken overnight with ammonium fluoride 0,5 mol L^{-1} solution at pH 8.2 in a 1:60 solid to solution ratio and centrifuged at 3095 G.
(6) Adsorbed As: 0.1 g of washed samples were shaken for 8 h with potassium phosphate 0,5 mol L^{-1} solution at pH 8.0 in a 1:80 solid-solution ratio centrifuged at 3095 G.

A leaching test was performed in order to evaluate the hazards associated to the precipitated phases. It was done following the NBR 10005 protocol described by the Brazilian Association of Technical Standards (ABNT, 2004), adapted from USEPA SW 846- Method 1311.

Semi-total contents of As was determined by digestion, using 4ml of HCl: HNO_3 (3:1 v/v), both double-distilled, and 0,1 g of precipitates. The samples were left on pre-digestion overnight (16 h) and heated on a digester block for 2 hours at 120^0C. The suspensions were then filtered and the volume was completed to 50 mL with Mili-Q water.

3.3. Supernatant analysis

Eleven supernatants sampling were performed during the incubation time. Arsenic concentrations in supernatants were analyzed by Atomic Fluorescence Spectrometry (AFS), (Model 10.033 Excalibur PSA Analytical) and Fe and Al were analyzed by ICP-OES, Optima DV8300, Perkin Elmer.

Efficiency of arsenic removal (E) was calculated as follow (Equation 2):

$$E = \frac{Co - Cf}{Co} \; x\,100 \qquad (2)$$

where: Co = initial As concentration, before precipitation, and Cf = As concentration, 2 h and 84 days after precipitation.

Arsenic species were also analyzed in samples of supernatants collected in the end of incubation period, by HPLC-HG-AFS (Table 2).

Table 2. Summary of conditions for As speciation by HPLC-HG-AFS

HPLC	
Column	Hamilton PRP-X100 (250mm x 4,1 mm i.d., Column 10 µm particle size)
Mobile phase	15 mmol L^{-1} of potassium phosphate (KH_2PO_4, K_2HPO_4), pH 6
Sample loop	200 Ml
Flow rate	1,4 mL min^{-1}
HG	
$NaBH_4$/NaOH	1.9% (w/v) $NaBH_4$ in 0.2% (w/v) NaOH; 1 ml min^{-1}
Acid solution	12.5% (v/v) HCl; 2 mL min^{-1}
AFS	
Detector	Excalibur (PS Analytical, model 10.055)
Lamp	Arsenic (193.7 nm)
Primary current	27.5 mA
Boost current	35.0 mA
Carrier gas	Argon, 400 mL min^{-1}
Drying gas	Argon, 1 L min^{-1}

3.4. Statistical Analysis

Results from supernatants and extractions were both conducted in triplicates and the mineralogical phases were analyzed after the homogenization of the three samples. The triplicates were organized in three randomized blocks design distinguished by three different time frames.

Analysis of variance were conducted in order to evaluate the factorials that were significant at 5%. Interactions between the factorials were also conducted and the significant results were evaluated through a Tukey Test.

4. Results and Discussion

4.1. Solid phase characterization

4.1.1. Mineralogical Phases

An assembly of different Fe and Al (hydr)oxides was identified in precipitates by X ray diffraction, depending on the treatment (Figures 4 to 7). Magnetite and maghemite were the dominant phases in Fe (II) treatments without Al and lower concentration of As (50 mg L^{-1}). The highest Fe soluble concentrations were also obtained in these treatments, which is in agreement with the higher solubility of these compounds in relation to other Fe (hydr)oxides, as reported by Cornell & Schwertmann (2003). Precipitation of lepidocrocite and goethite was favored by the presence of Al or higher concentration of As (500 mg L^{-1}) in Fe (II) treatments (Figures 4 and 5). Only increasing As, in the absence of Al, was enough to favor precipitation of lepidocrocite. Segregation of Al (hydr)oxides (gibbsite and bayerite) occurred at a higher amount of Al (60:40 Fe:Al molar ratio). Barcelos (2014) found similar results, but for lantanium (La) at low and high concentrations.

Treatments with Fe (III) showed a small peak for hematite in the absence of Al and at lower As concentration (50 mg L^{-1}), but it disappeared at higher concentration of As and in the presence of Al (Figures 6 and 7).

Ferrihydrite was the dominant (hydr)oxide in Fe (III) treatments. This Fe hydroxide is poorly ordered and it is considered a precursor of hematite that precipitates following the Fe (III) hydrolysis (Schwertmann et al. 1999) This result explains the faster decrease of soluble Fe in supernatants to values that are below the detection limit (0.004 mg L^{-1}), compared to Fe (II) treatments.

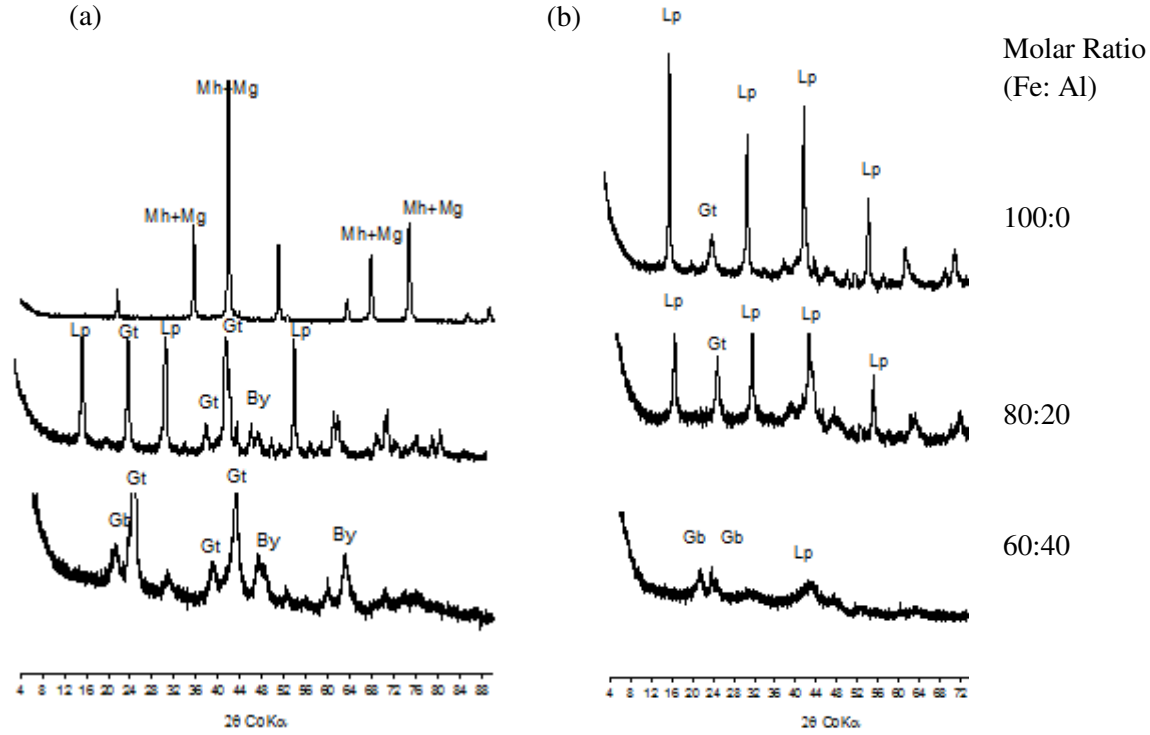


Figure 4. X ray patterns for Fe (II) treatments at (a) 50 mg L^{-1} and (b) 500 mg L^{-1} of As (III). By:Bayerite; Gb:Gibsite; Gt:Goethite; Lp:Lepidocrocite. Mh: Maghemite; Mg: Magnetite.

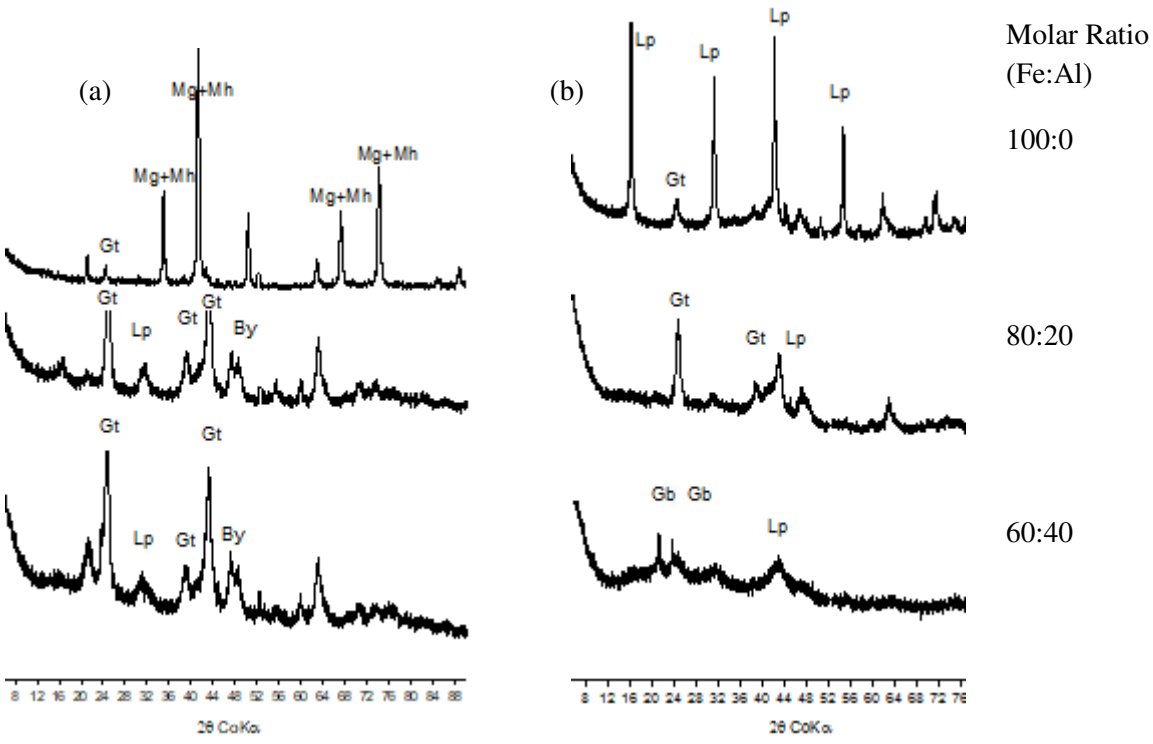


Figure 5. X ray patterns for Fe (II) treatments at (a) 50 mg L^{-1} and (b) 500 mg L^{-1} of As (V). By:Bayerite; Gb:Gibsite; Gt:Goethite; Lp:Lepidocrocite; Mh:Maghemite; Mg: Magnetite.

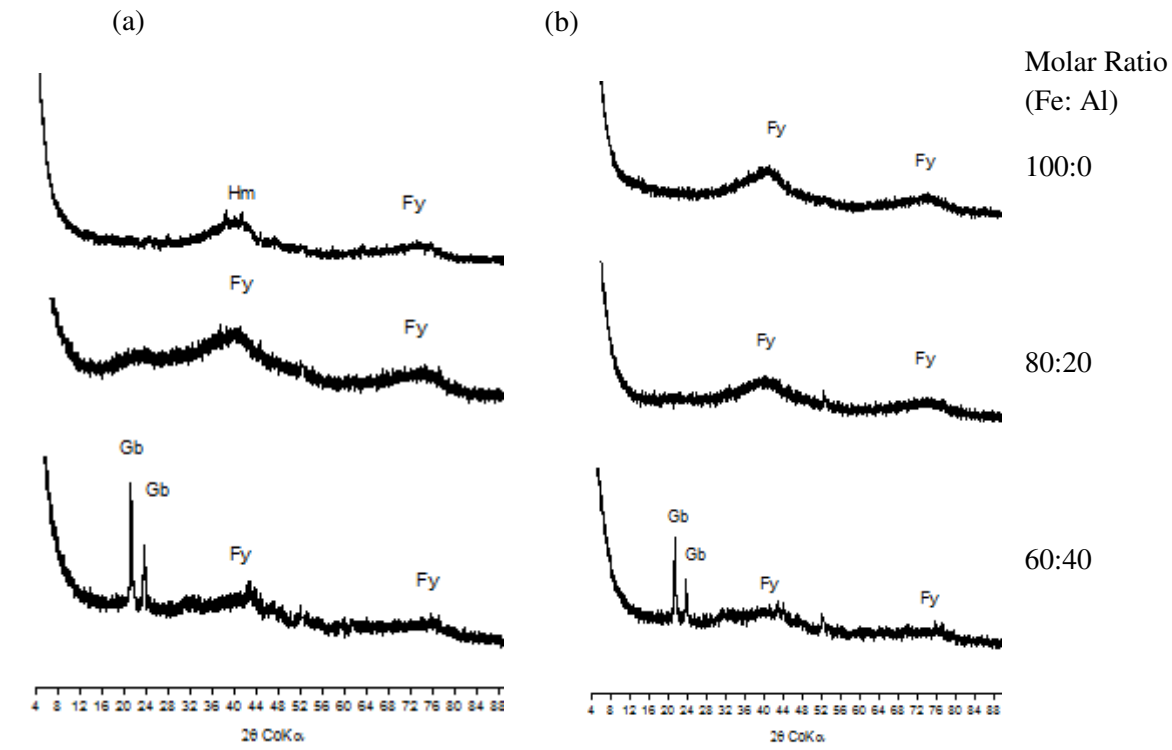


Figure 6. X ray patterns for Fe (III) at (a) 50 mg L^{-1} and (b) 500 mg L^{-1} of As (III). Fy: Ferrihydrite; Gb:Gibsite; Hm: Hematite.

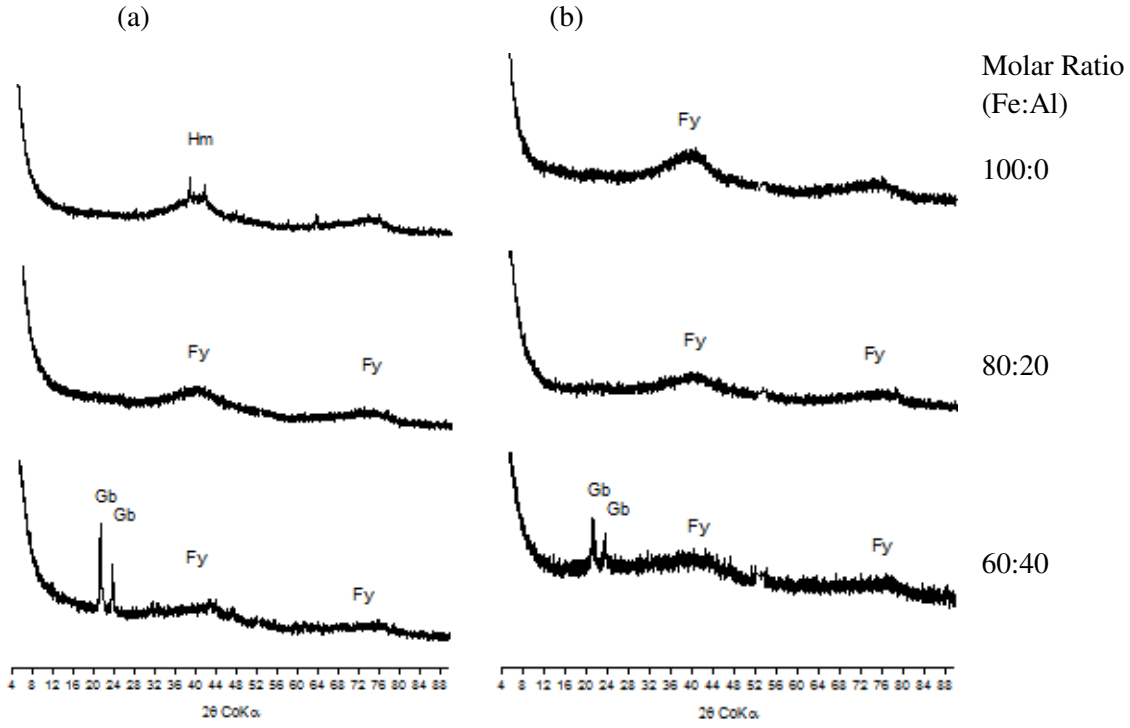


Figure 7. X ray patterns for Fe (III) treatments at (a) 50 mg L^{-1} and (b) 500 mg L^{-1} of As (V). Fy: Ferrihydrite; Gb:Gibsite. Hm: Hematite

The crystallinity of ferrihydrites also seems to decrease due to the presence of Al, with broader and smaller peaks as the Fe:Al molar ratio decreases. This is in line with findings from Violante et al (2009). According to Freitas et al. (2015), Al-ferrihydrite could be the first step of Al-hematites formation. They also suggest that Al-goethites could be an intermediate step in the process of ageing and transformation of Al-ferrihydrite into Al-hematite. According to these authors the arsenic trapped in Al-hematites would be a result from Al-ferrihydrite ageing, as the closed packed structure of hematite wouldn't allow arsenic entrapment.

Freitas et al. (2016) identified magnetite as a result of syntesis from a Fe:Al molar ratio of 1:0.3 after 120 days of incubation period under similar conditions ot the present work. However, in presence of Al, magnetite was not detected in the present study. According those autors, the presence of Al increased As stability into precipitates slowing down or preventing further phase transformations. Association of As with magnetite is desirable due to the magnetic properties of this oxide that could be useful for its recovery after water treatment.

Arsenic bearing phases were not found segregated from Fe and Al (hdr)oxides in precipitates (Figure 8). However, the presence of arsenic promoted differences between mineralogy of precipitates from Fe (III) treatments. Bayerite was identified in in precipitates from treatments without As at a 60:40 Fe:Al molar ratio, but only gibbsite was found in Fe (III) treatments with As at the same molar ratio.

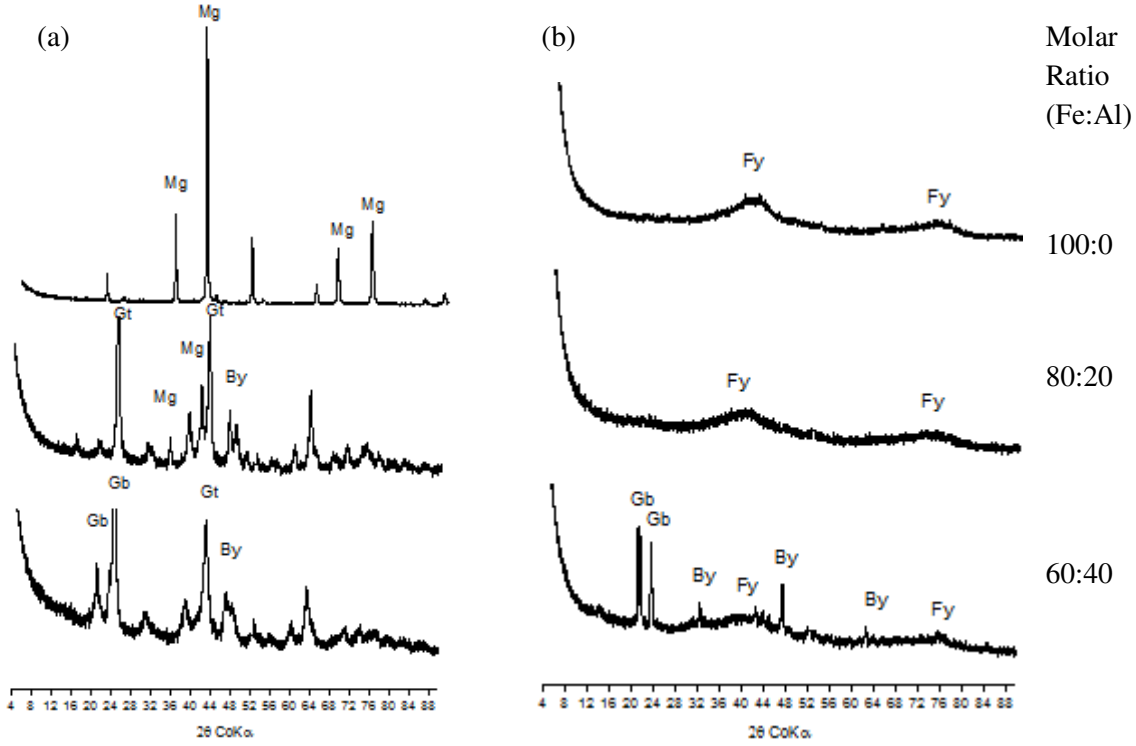


Figure 8. X ray patterns of precipitates in the absence of As for (a) Fe (II and (b) Fe (III) treatments. By: Bayerite; Fy: Ferridryte; Gb: Gibsite; Gt:Goethite; Mg:Magnetite

4.1.2. Leaching Test

Results of leaching tests revealed higher concentrations of As in leachates from all treatments with 500 mg L^{-1} of As (III), reinforcing higher mobility of arsenite compared to arsenate (Table 3). These results indicate that only precipitates from treatments with 500 mg L^{-1} of As (III) were classified as hazardous materials according to NBR 10004 ([As] >1 mg L^{-1}). On the other hand, the sludge resulting from all other treatments were considered safe for disposal independent on the initial concentration of As (V) in water. Therefore, As (III) oxidation to As (V) is warranted to increase the stability of the sludge from water treatment.

Table 3: Arsenic concentration in leachates following NBR 10005 leaching test of leachates from different treatments

Fe:Al	[As]	Fe(II) treatments		Fe(III) treatments	
		As(III)	As(V)	As(III)	As(V)
		mg L^{-1}			
100:0	50	<DL	0.04(0.03)	0.06(0.02)	0.05(0.01)
	500	7.15(0.76)	0.26(0.06)	3.83(0.32)	0.07(0.008)
80:20	50	0.05(0.01)	0.02(0.005)	0.36(0.04)	0.04(0.005)
	500	2.00(0.60)	0.16(0.09)	11.29(1.10)	0.14(0.01)
60:40	50	0.15 (0.02)	0.07(0.004)	0.32(0.17)	0
	500	3.60(0.19)	0.10(0.01)	9.43(1.5)	0.10(0.01)

DL : As: 0.02 mg L^{-1}

Leaching tests also confirmed that the presence of Al provided higher stability of As in precipitates from Fe (II) compared to Fe (III) ($p<0.05$). This is in line with findings from Freitas et al. (2016), who showed that the presence of structural Al in iron oxides precipitated from Fe (II) sulfates can favor the As stability. According to the authors this is because Al favors the oriented attachment of nanocrystals to promote the imprisonment of arsenic inside the mesocrystals. However, the highest As concentration was obtained in leachate from precipitates with 80:20 Fe (III):Al molar ratio and As (III), which was considered the least stable treatment. This imply that Al did not favor the As stability in precipitates from Fe (III) treatments.

Previous results from our group (Mello et al., submitted) have also shown that precipitates produced by similar treatments were considered safe for disposal based on Toxicity Characteristic Leaching Procedure (TCLP). Such studies however were performed for lower initial concentrations of soluble As ($\leq$ 5 mg L^{-1}). It is worth of noticing that all reagents and procedures of TCLP, reported by United States Environmental Protection Agency (EPA 1311), is quite similar to the leaching test based on NBR 10005 Brazilian regulation. Therefore, the main contribution of the present study is to state a safe limit for treatment of As contaminated water based on precipitation of Al-Fe (hydr)oxides. This limit can be considered between 50 and 500 mg L^{-1} of As, i.e. a Fe:Al:As molar ratio between 100:0:0.5 and 100:0:5, for both arsenate and arsenite. Probably such limit is lower for As (III) compared to As (V).

Concentrations of Fe and Al in leachates were also low (Table 4). There is no maximum allowed concentrations for Fe and Al in leachates established by ABNT NBR 10004 but

according to Brasil (2011), the maximum values for soluble Fe in effluent discharge is 15 mg L^{-1} and all of treatments are below this threshold.

There was a decrease in Al concentration in leachates from Fe (II) compared to Fe (III) treatments at the 80:20 Fe:Al molar ratio. It is also clear that leached Al decreased as the Fe:Al molar ratio decreased (Table 4). These apparently contradictory results can be explained by the mineralogy of precipitates. It has been observed that goethites were the main (hydr)oxides precipitated from Fe (II) treatments in the presence of Al (Fig. 4 and 5), but ferrihydrite was the main phase in Fe (III) treatments. Due to the structural defects of ferrihydrites, Al could form clusters of Al amorphous (hydr)oxides on the surface of this (hydr)oxides, which occurs in a less extent on well crystalized (hydr)oxides as goethites. This was suggested by Cismassu et al. (2012).

Table 4. Fe and Al concentration for leaching test

Fe:Al	[As]	Fe(II) treatments				Fe(III) treatments			
		As(III)		As(V)		As(III)		As(V)	
		Fe	Al	Fe	Al	Fe	Al	Fe	Al
		mg L^{-1}							
100:0	50	0.54(0.19)	0	0.96(0.21)	0	0.35(0.01)	0	0.28(0.07)	0
	500	<DL	0	0.95(0.66)	0	2.13(0.11)	0	0.28(0.05)	0
80:20	50	0.10(0.02)	0	1.54(0.85)	0.16(0.04)	1.10(0.61)	31.10(1.75)	1.12(0.13)	30.63(0.75)
	500	0.49(0.25)	0	1.10(0.86)	0	0.42(0.03)	25.66(0.69)	0.24(0.02)	25.62(2.25)
60:40	50	0.36(0.13)	0.95(0.10)	<DL	0.86(0.03)	0.14(0.05)	0.33(0.10)	0.15(0.04)	0.22(0.02)
	500	0.34(0.07)	0.09(0.004)	<DL	0.14(0.04)	0.25(0.05)	0.34(0.01)	1.12(1.60)	0.40(0.14)

DL: Fe: 0.013 mg L^{-1}; Al: 0.08 mg L^{-1}

4.1.3. Extractable arsenic phases

The Community Bureau of Reference (BCR), now Standards, Measurements and Testing Programme SM&T, developed a sequential extraction method to assess different available forms of trace elements in sediments. Such method is based on the solubility of compounds in acidic, reducible and oxidizable environment. It comes up with a sequential use of different extractants in the same sample. Notwithstanding, Baig et al. (2009) showed similar results for discrete extractions compared to the sequential scheme. The main advantage of the discrete

extractions is to avoid samples losses. Therefore, the discrete extractions procedure was preferred in this study.

The samples were initially washed twice with Mili-Q Water. The results indicated that water soluble As is negligible in relation to the total As concentration (Tables 5 and 6). This indicates that the water leaching of precipitates does not represent risks for As contamination.

Hydroxylammonium chloride was supposed to be the most effective among the BCR extractants because it would reduce the Fe (hydr)oxides. Then, the expected Fe:As molar ratios should be about the same of the treatment. The results, however, show Fe:As molar ratios much higher than expected in the reducible phases. This suggest that As was not associated to easily reducible Fe, implying that it was preferably attached to more stable Fe (hydr)oxides. It can also be interpreted that As attached to Fe phases protect them from the reductive dissolution. The same was reported by Mello et al. (1999) for phosphorus associated to Fe-Al ((hydr)oxides.

The acetic acid extracted phases would address for arsenic associated to carbonates, but they only represents weakly soluble phases in the absence of carbonates (Larios et al., 2012), which is the case of the present study. Treatments of water with 500 mg L^{-1} of As (III) produced precipitates with higher concentrations of acid soluble As ($p < 0.05$). This result is comparable to the leaching test, which is expected, as the extractant solutions used in both procedures are similar.

Table 5. Percentage of As extracted by BCR, KH_2PO_4 and NH_4F solutions from precipitates of Fe (II) treatments relative to pseudo total contents (digestion with HCL:HNO_3 3:1)

Fe (II): Al	[As]		Percentage (%)					
			Water soluble	BCR Procedure			Phosphate Extraction	Fluoride Extraction
				Acid soluble	Reducible	Oxidizable		
100:0	50 mg L^{-1}	As (III)	0	0.12	0.14	0.01	0.42	0
80:20			0	0.19	0	0.01	0.86	0.04
60:40			0	0.21	0	0.02	2.97	0.05
100:0	500 mg L^{-1}		0	1.05	0	0.06	9.58	0.65
80:20			0	0.35	0.01	0.05	7.92	0.74
60:40			0	0.57	0.03	0.10	11.46	0.38
100:0	50 mg L^{-1}	As (V)	0	0.04	0.17	0.02	0.60	0.12
80:20			0	0.42	0	0.01	2.01	0
60:40			0	0.39	0	0.02	2.63	0.21
100:0	500 mg L^{-1}		0	0.01	0.02	0.01	6.88	0.13
80:20			0	0.05	0.01	0.01	7.29	0.10
60:40			0	0.07	0.03	0.07	13.33	0.31

Table 6. Percentage of As extracted by BCR, KH_2PO_4 and NH_4F solutions from precipitates of Fe (III) treatments relative to pseudo total contents (digestion with HCL:HNO_3 3:1).

Fe(III):Al	[As]		Percentage (%)					
			Water soluble	BCR Procedure			Phosphate Extraction	Fluoride Extraction
				Acid soluble	Reducible	Oxidizable		
100:0	50 mg L^{-1}	As (III)	0	0.08	0.01	0.04	1.27	0
80:20			0	0.11	0	0.42	1.29	0
60:40			0	0.27	0.03	0.34	0.99	0.13
100:0	500 mg L^{-1}		0	0.18	0.05	0.02	1.88	0.05
80:20			0	0.56	0.04	0.03	2.79	0.04
60:40			0	1.32	0.02	0.05	3.79	0.1
100:0	50 mg L^{-1}	As (V)	0	0.06	0.03	0.07	6.04	0
80:20			0	0.07	0	0.10	6.41	0
60:40			0	0.09	0	0.17	5.97	0
100:0	500 mg L^{-1}		0	0.06	0.02	0.01	15.60	0.06
80:20			0	0.08	0.01	0.08	12.99	0.14
60:40			0	0.07	0.01	0.06	12.33	0.37

Larios et al. (2012) also found low concentrations for reducible phases in Fe rich sediments. The authors ascribed these results to the high Fe content that would require a higher ionic strength to dissolve the Fe (hydr)oxides. In this case, arsenic bounded to Fe (hydr)oxides is underestimated due to the low efficiency of hydroxylammonium chloride solution.

The extraction with hydrogen peroxide of the BCR procedure aims to assess oxidizable fraction, which is the arsenic bound to organic material and sulfides. The highest amount of oxidizable As was found in precipitations from Fe (II) treatments of water contaminated with arsenite at a 60:40:5 Fe:Al:As. This is in line with previous results (Mello et al., submitted) that found oxidizable fractions of As just in precipitates from treatments with Al. Larios et al. (2012) also found high As concentrations in sediments without organic matter or sulfides. According to these authors the oxidizable phases of As can be overestimated due to the low specificity of hydrogen peroxide. Such results, therefore, cannot be ascribed to the presence of As associated to organic compounds or sufides, but can be due to a higher mobility of As associated to gibbsite or bayerite.

Potassium phosphate was able to extract more arsenic from precipitates of water contaminated with arsenate ($p < 0.05$). Considering that phosphate is an oxyanion that competes with arsenate for adsorption sites on iron oxides, the possible reason for that is a higher adsorption of As (V) on iron oxides. This hypothesis is feasible because the treatments of water with arsenate were in general more efficient compared to water with arsenite, as shown before. Campos et al (2013) observed a decrease on As adsorption, from 65% to 21%, in the presence of phosphate in a soil sample that showed the highest rate of As adsorption.

Adsorption of As onto amorphous or low crystalinity Fe (hydr)oxides is known to be higher than onto well crystallized oxides due their higher specific area (Ociński et al., 2016). Therefore it is expected higher amounts of As adsorbed onto ferrihydrite than onto goethites (see fig. 12 to 15) and this can be a reason for higher phosphate extractable As (V) on precipitates from Fe (III) treatments ($p < 0.05$) (Tables 5 and 6). However, this was not observed for As (III) treatments, probably due to the oxidation of As (III) to As (V) coupled to iron oxidation in Fe (II) treatments (Fig. 11).

According to Larios et al (2012), NH_4F is used to determine As associated to Al (hydr)oxides likewise than for phosphorus (Alleoni et al, 2012). Higher fluoride extractable As was found

in precipitates from Fe (II) treatments, especially for arsenite ($p < 0.05$), suggesting that association between Al and As is favored in these treatments. Actually, there is no apparent reason for that.

In general, all extractions mobilized low concentrations of As compared to the total contents precipitated. The As percentage that wasn´t extracted by these procedures represent the As so strongly associated to Fe and Al (hydr)oxides that is very unlikely to be mobilized under environmental conditions.

4.2. Supernatants Analysis

4.2.1. Efficiency of As removal from contaminated water

Arsenic removal occurs in a higher extent just after the precipitation of (hydr)oxides, due to the co-precipitation. Therefore, the efficiency of As removal will be calculated with the samples from 2h after pH adjustment and after the 84 days of experiment. Percentages of As removal were above 90%, corroborating the efficiency of the Fe and Al (hydr)oxides precipitation in treatment of As contaminated water. The Tukey test detected one treatment significantly different ($p<0.05$) from the others, with a slightly lower efficiency for As removal (Table 7). This treatment is related to the use of As (III), corroborating that arsenate is easier removed from water than arsenite as previously observed by several researchers (Pierce & Moore (1981), Adra et al. (2015). This implies that in the beginning of the experiment, Al did not enhance As removal in Fe (II) treatments. In this treatment, Al (hydr)oxides were identified and therefore, this lower efficiency could be related to the their presence in detriment of Fe (hydr)oxides.

The above-mentioned results partially disagree with statements from other authors. Mello et al. (2006), for example, observed that presence of gibbsite prevented As mobilization due to Fe (hydr)oxides reductive dissolution in soils from a gold mining area. According to Ladeira et al. (2001) and Duarte et al. (2011) gibbsite can also form inner-sphere complexes with adsorbed As (V) and As (III), which are very stable, much like the As-Fe (hydr)oxides complexes. However, according to Vithanage et al (2007), the adsorption isotherms for arsenite showed a lower adsorption for gibbsite compared to goethite, which is in agreement with results of the present study.

Fe (III) treatments were more efficient to remove As ($p<0.05$), probably due to the faster precipitation compared to Fe (II). Such results imply that the co-precipitation is more efficient to remove As in treatments which favor the precipitation of hematite and ferrihydrite, identified in Fe (III) treatments, compared to magnetite, maghemite, lepidocrocite and goethite, identified in Fe (II) precipitates.

Table 7. Arsenic removal efficiency from different treatments

Treatments	Efficiency mean after 2h	Efficiency mean after 84 days
T 2.2	99.98 a	99.93 a
T 4.2	99.98 a	99.99 a
T 3.2	99.98 a	99.97 a
T 4.4	99.98 a	99.97 a
T 4.6	99.98 a	99.97 a
T 3.4	99.96 a	99.93 a
T 1.2	99.93 a	99.78 a
T 3.6	99.90 a	99.84 a
T 2.4	99.89 a	99.98 a
T 2.6	99.89 a	99.97 a
T 2.1	99.80 a	99.98 a
T 4.3	99.80 a	99.99 a
T 1.3	99.80 a	99.81 a
T 1.1	99.80 a	99.98 a
T 4.5	99.80 a	99.99 a
T 3.1	99.80 a	99.99 a
T 3.5	99.80 a	99.86 a
T 2.5	99.80 a	100.00 a
T 3.3	99.80 a	99.97 a
T 4.1	99.80 a	99.99 a
T 1.4	99.33 a	99.74 a
T 1.5	98.44 a	100.00 a
T 2.3	97.99 a	99.99 a
T 1.6	93.49 b	99.90 a

* Treatments followed by the same letter did not differ significantly according to Tukey test ($p< 0.05$)

4.2.2. Arsenic concentration in supernatants

In spite of high removal efficiencies, after 2h all treatments with As (III) did not reach the limit concentration for drinking water (<10 µg L^{-1}), but for As (V) even treatments with

higher As initial concentration (500 mg L^{-1}), namely the ones with 100:0 Fe (II):Al and 60:40 Fe (III): Al molar ratio attained this threshold. Other treatments with As (V) and lower As concentration (50 mg L^{-1}) also attained this value as 100:0 and 60:40 Fe (II):Al and all treatments with Fe (III).

After the 84 days, treatments with initial As concentration of 500 mg L^{-1} did not reach the recommended threshold for drinking water (<10 µg L^{-1}), especially that ones with arsenite (As III). On the other hand, all treatments with initial 50 mg L^{-1} of As were suitable to accomplish with that threshold, reaching As concentrations bellow the detection limit (5,19 µg L^{-1}) at the end of the experiment (Figures 9 and 10).

According to the Environmental National Council (CONAMA), the maximum As concentration for effluents discharge is 0,5 mg L^{-1}. Therefore, if supernatants are considered effluents, after 2 hr of precipitation all treatments with Fe (III) could be discharged without other processing. However, some Fe (II) treatments did not attain this threshold, especially for As (III). For As (V), only 60:40:5.1 Fe:Al:As molar ratio treatments would not be suitable to be discharged. For Fe (II) and As (III) treatments, only one treatment with low As initial concentration did not reach 0.5 mg L^{-1}, 60:40 Fe:Al molar ratio, the others were from treatments with higher initial As concentration.

Only some treatments with high initial concentration of arsenite (500 mg L^{-1}) would require additional care previously to effluent discharge after the 84 days of experiment, namely the ones with Fe:Al molar ratios of 100:0 for Fe (II) and 60:40 for both Fe (II) and Fe (III). All other treatments would be suitable for effluent discharge at the end of the experiment (84 days).

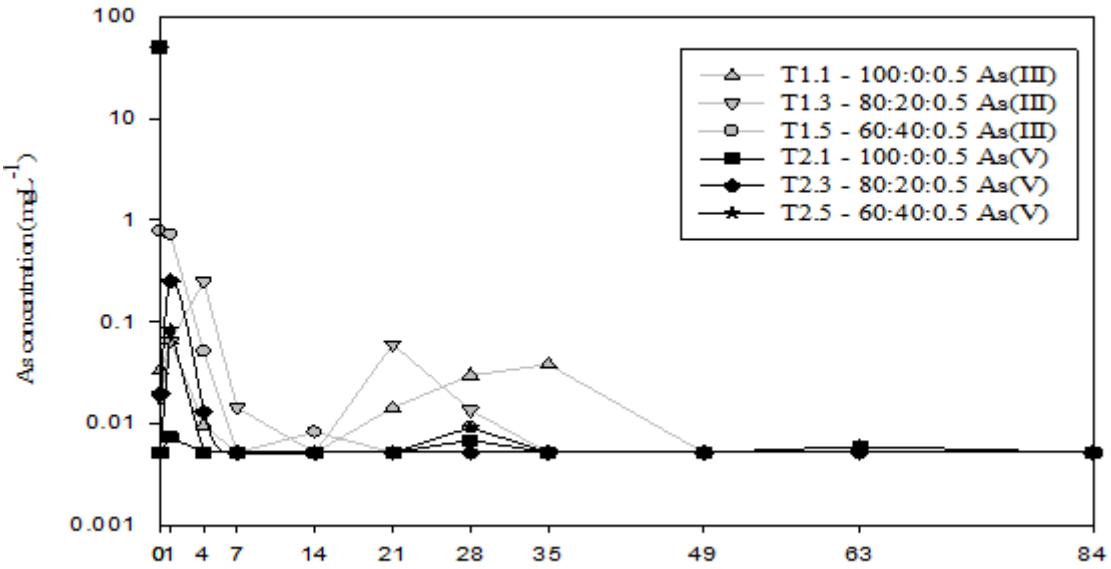
As mentioned earlier, all treatments were suitable to accomplish with the threshold for drinking water when the initial concentration of As was 50 mg L^{-1}. Nevertheless, the time lapse necessary to attain that limit was different for As (V) and As (III). Treatments of water contaminated with arsenite (As III) lasted 35 to 49 days to reach that threshold while for As (V) the limit was reached earlier, just seven days as much.

The role of Al on As immobilization by Fe (hydr)oxides is rather controversial. Some authors suggest that isomorphic substitution of Fe for Al favor the As adsorption (Silva et al., 2010) and immobilization (Freitas et al., 2015). On the other hand, Mello et al. (submitted)

suggested that presence of Al slows down As immobilization by Fe (hydr)oxides. At the beginning of the experiment, 2 h after precipitation, it was shown before with the analysis of removal efficiencies that lower efficiencies for As removal were observed for treatments with Al, mainly the ones with 60:40 Fe:Al molar ratio. This behavior suggests that higher percentages of Al in precipitates can delay the removal of As from solution. This is in agreement with previous results from Mello et al. (submitted). However, by the end of the experiment, presence of Al increased the As removal from water for Fe (II) treatments ($p<0.05$). For Fe (III) treatments, the opposite was observed, however, statistically, the presence of Al did not influence.

In summary it can be seen that Fe (III) treatments were somewhat more efficient to remove As from water than Fe (II) ones, especially for As (III) ($p < 0.05$). As discussed earlier, there were three Fe (II) treatments and only two Fe (III) treatments with lower efficiency for As removal. Also, just one out of the three treatments that did not reach the As concentrations limit for effluents discharge was with Fe (III).

(a)



(b)

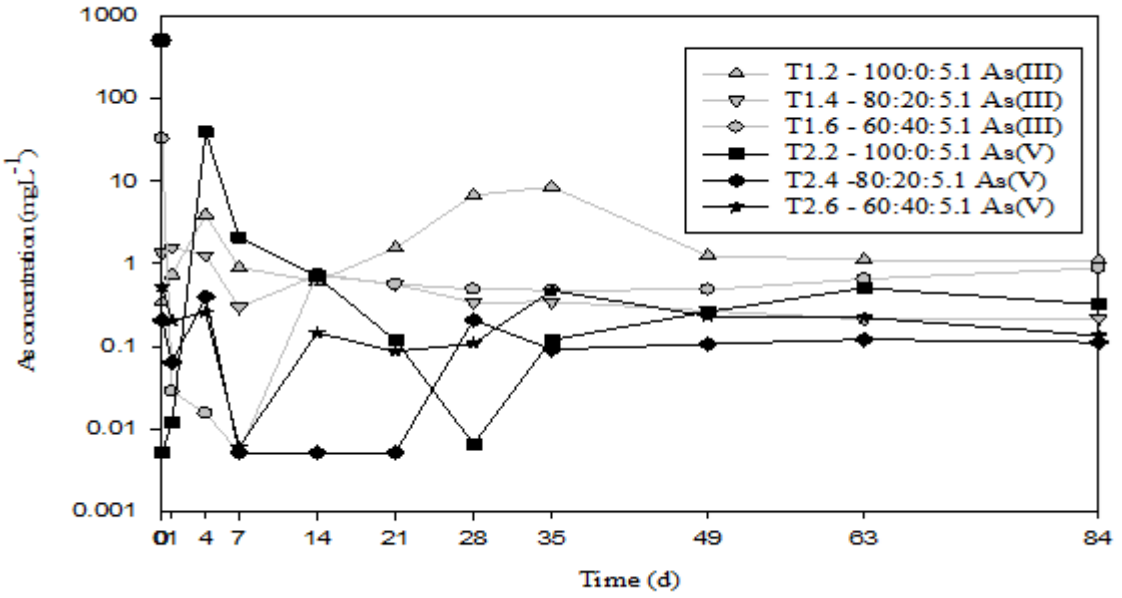
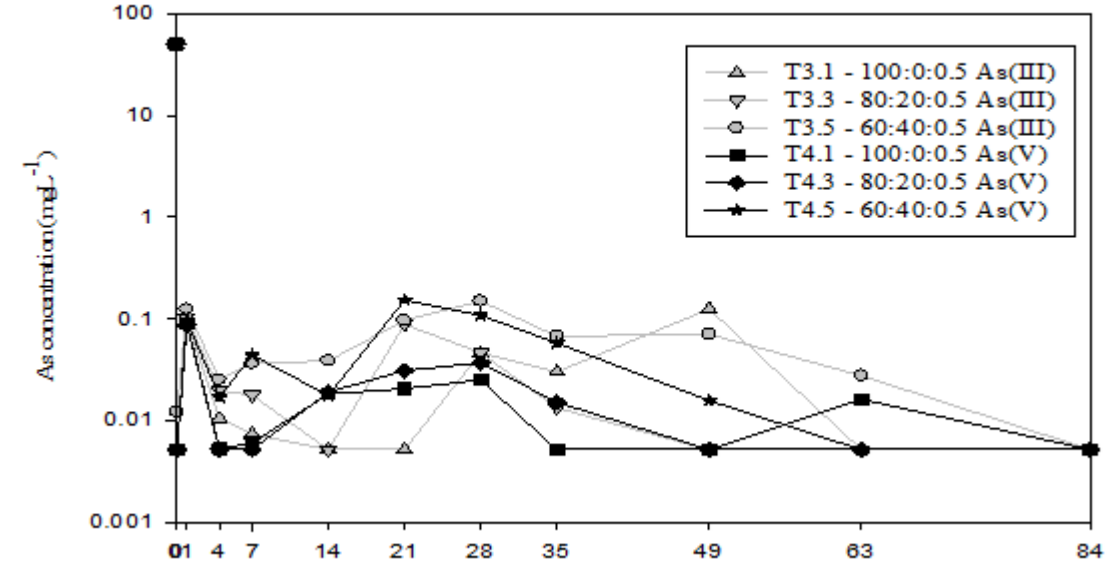


Figure 9. As concentration in Fe (II) treatments with As initial concentration of (a) 50 mg L^{-1} and (b) 500 mg L^{-1} during the incubation period

(a)



(b)

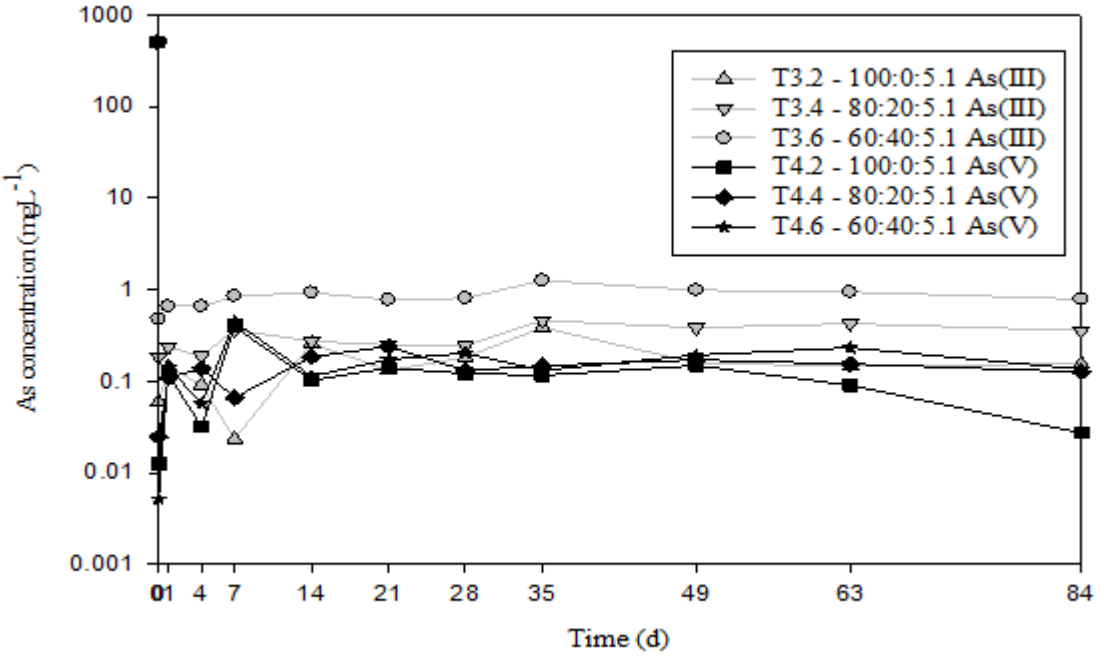
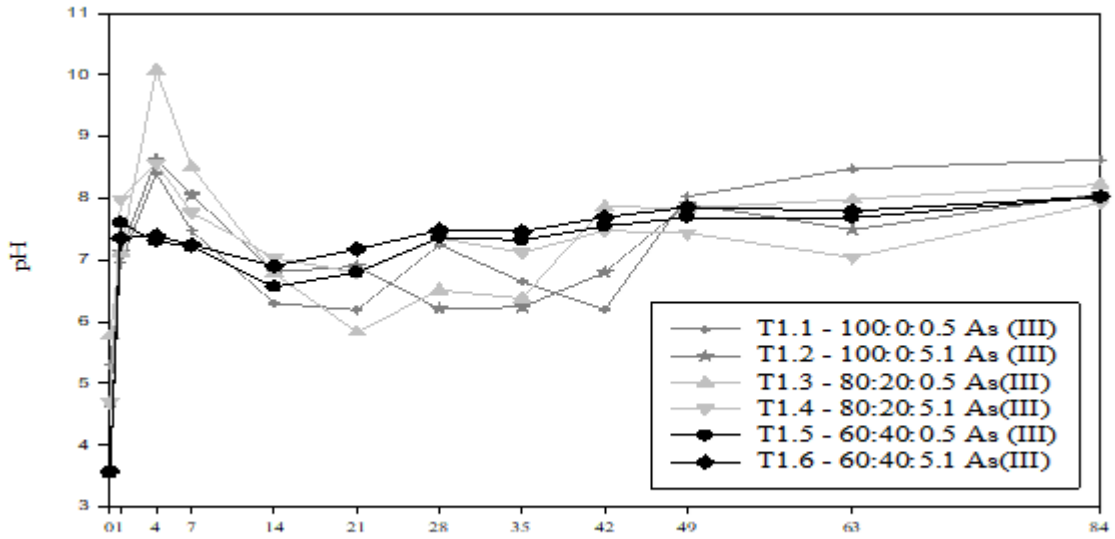


Figure 10. As concentration in Fe (III) treatments with As initial concentration of (a) 50 mg L^{-1} and (b) 500 mg L^{-1} during incubation period.

(a)



(b)

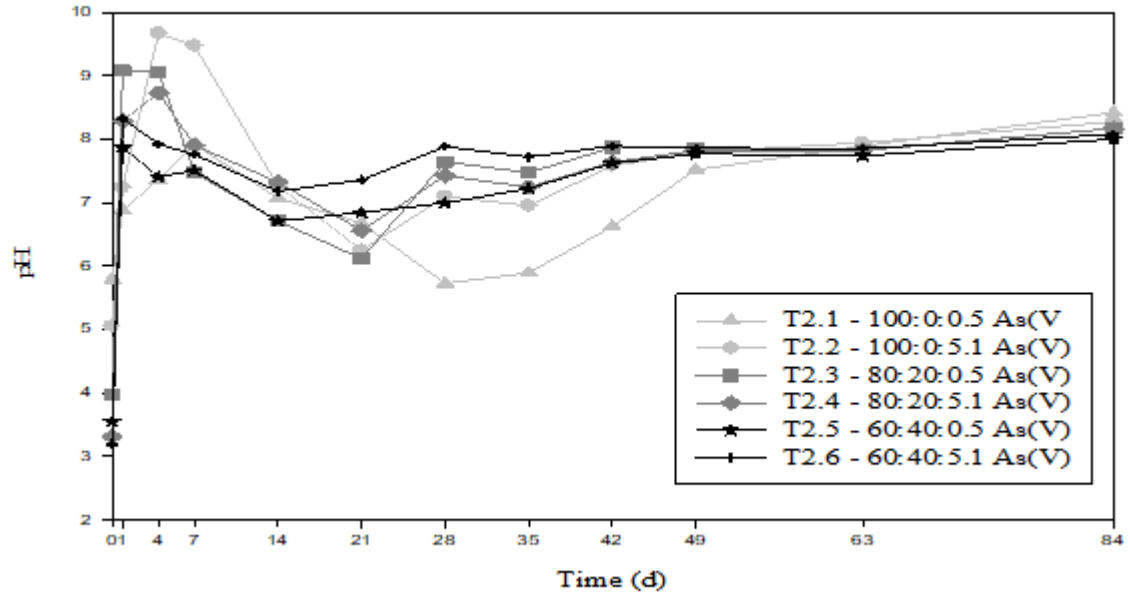
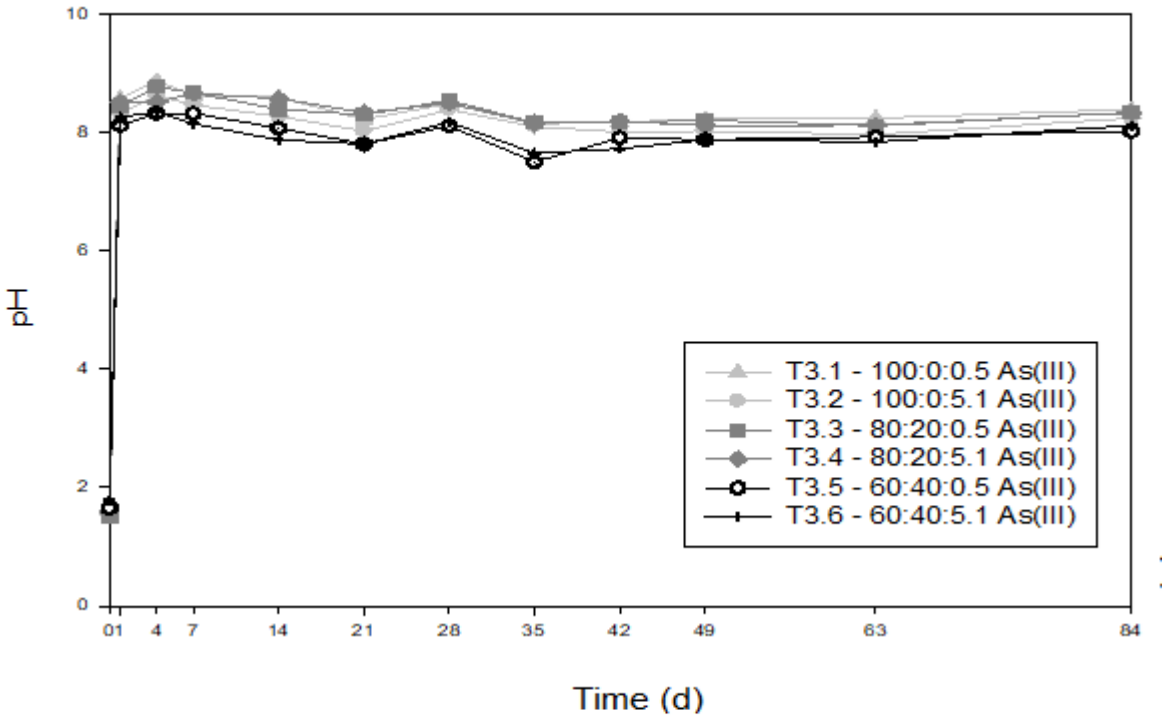


Figure 11. pH values in (a) Fe (II) and As (III) treatments and (b) Fe (II) and As (V) treatments during incubation period.

It can be also seen that soluble As (V) concentrations varied in a higher range during the experiment for Fe (II) compared to Fe (III) treatments. The same can be observed for pH values of supernatants (Figures 11 and 12).

Therefore such variations can be related, due to effects of pH on soluble Fe and then on soluble As (especially in higher As concentrations), which will be discussed in the following section. The effect of pH on arsenite removal is not so evident as shown by Ociński et al. (2016), who identified negligible variations on arsenite removal from solution with manganese and iron oxides when pH varies.

(a)



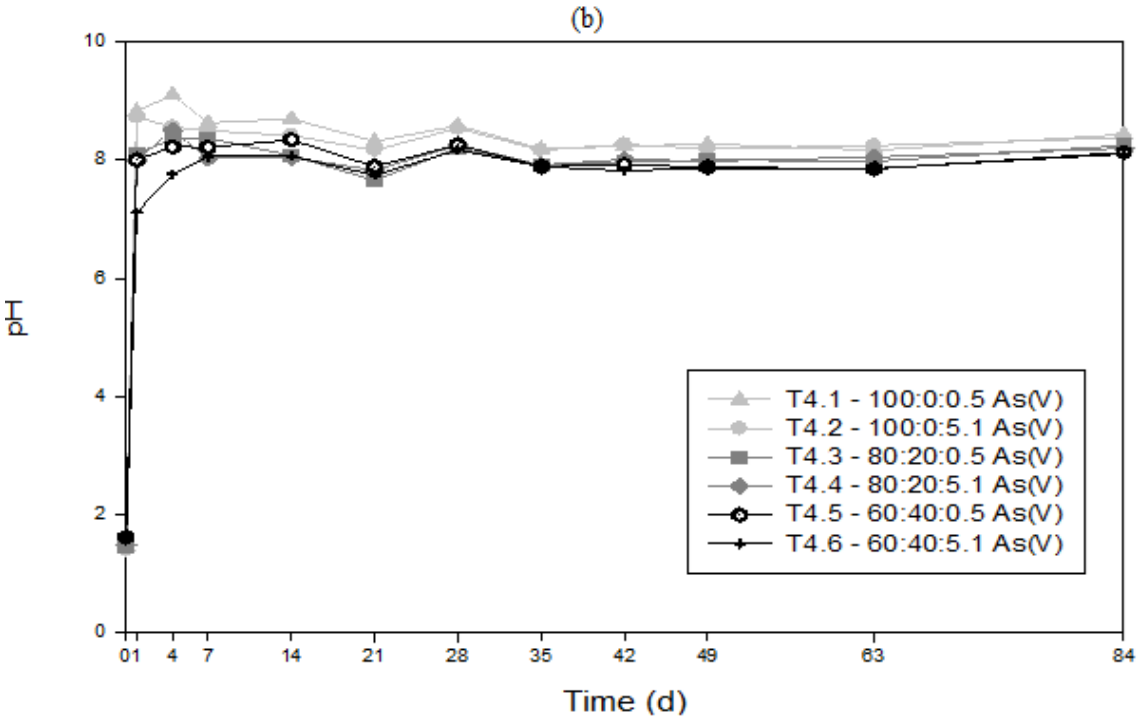


Figure 12. (a) pH variation in Fe (III) and As (III) treatments and (b) Fe(III) and As (V) treatments.

4.2.3. Iron concentrations in supernatants

Fe and Al precipitation occurred immediately after the pH increasing to 8. Even though the pH has been periodically buffered by addition of KOH, the (hydr)oxides precipitation itself also buffers the pH, as shown below by the global reaction (Equation 3) for iron oxidation and hydrolysis (Schwertmann & Cornell, 2010). The equilibrium clearly shows that increasing pH decreases soluble Fe^{2+} and vice versa, occurring the same with Fe^{3+}.

$$4Fe^{+2} + 6H_2O + O_2 \rightarrow 4FeOOH + 8H^+ \qquad (3)$$

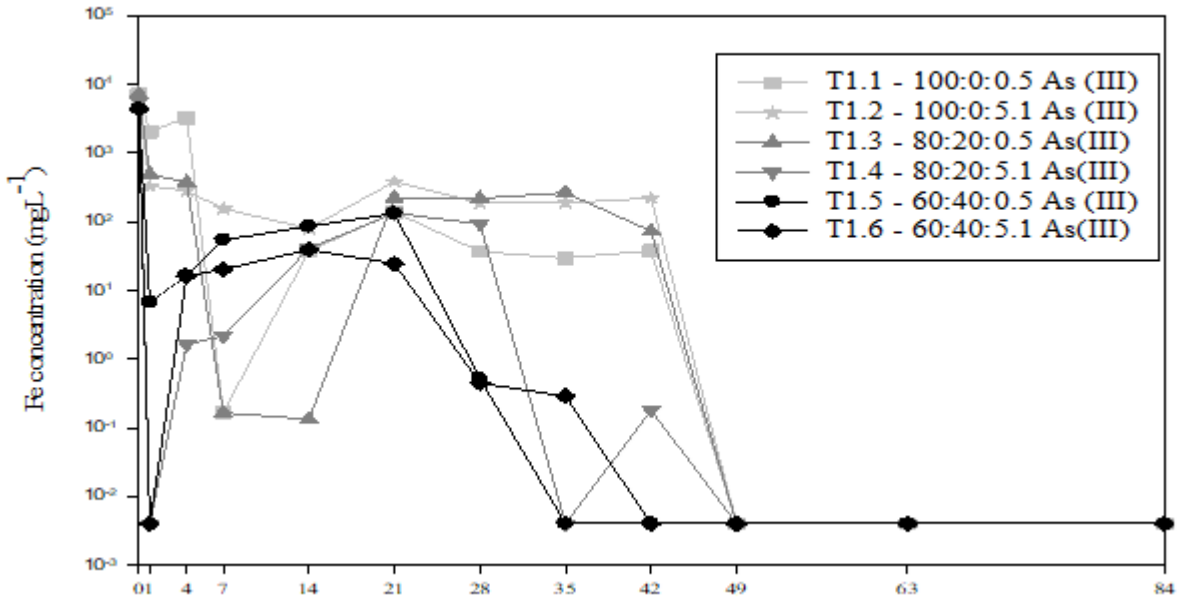
The concentrations of soluble Fe during the experimental period varied in a much higher range for Fe (II) treatments, about 7 orders of magnitude (Figure 13) compared with just 2-3 orders of magnitude for Fe (III) treatments (Figure 14). This is probably due to a delay in oxidation of Fe^{2+} previously to precipitation of Fe (hydr)oxides which does not occur in Fe^{3+} system. The important role of Fe on buffering pH is also shown by the smaller variation on

pH values with increasing Al (Figures 11 and 12). pH values for higher Fe:Al molar ratios were somewhat less constant compared to other treatments.

The above-mentioned postulate is consistent with the slower decrease in soluble Fe due to the presence of Al. It can be seen that the higher the Fe:Al molar ratio, the faster the decrease in soluble iron concentrations for Fe (II), but the same is not observed for Fe (III) treatments. Such considerations justify the variations in soluble As (V) and pH, as discussed earlier.

According to Brasil (2011), the maximum value of Fe concentration for effluents discharge is 15 mg L^{-1}. Therefore, the effluent generated from all treatments could be discharged without previous treatment regarding Fe concentration.

(a)



(b)

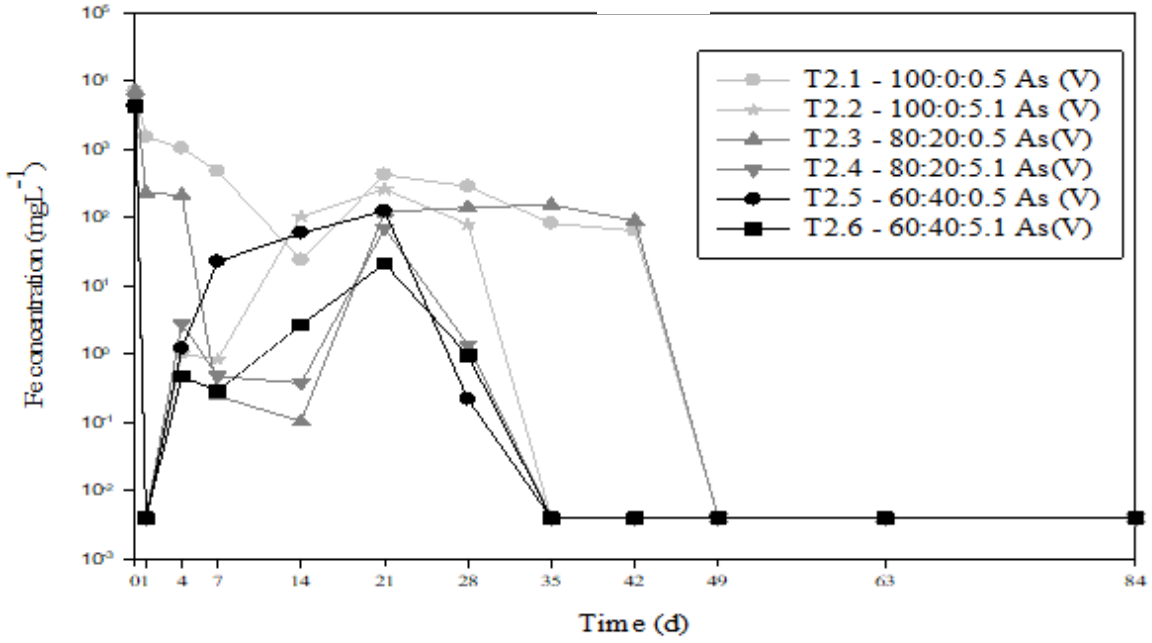
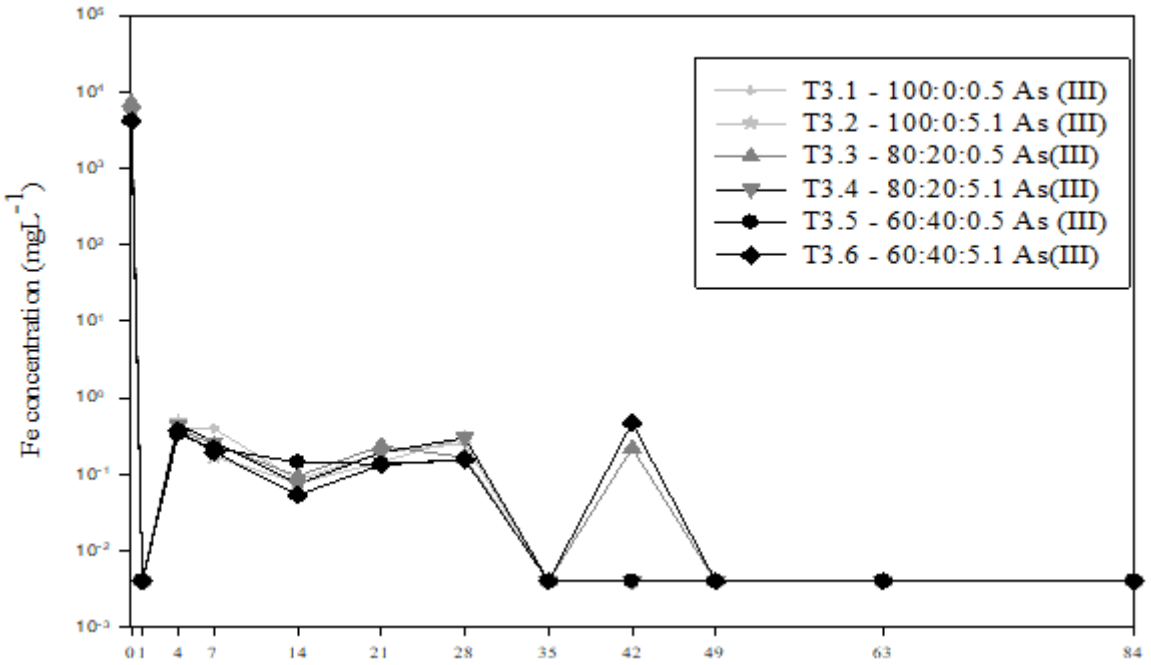


Figure 13. Fe soluble concentration in (a) Fe (II) treatments with As (III) and (b) Fe (II) with As (V) during the incubation period. Detection limit: 0.004 mg L^{-1}

(a)



(b)

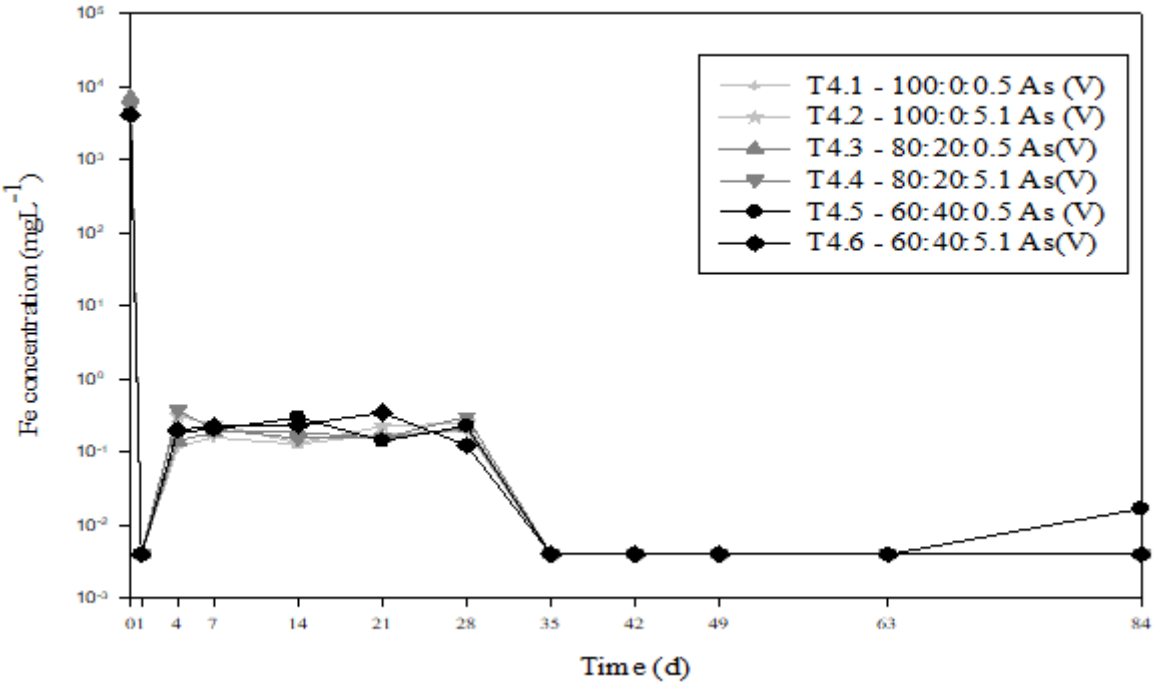


Figure 14. Fe soluble concentration in (a) Fe (III) treatments with As (III) and (b) Fe (III) with As (V) during the incubation period. Detection limit: 0.004 mgL^{-1}

4.2.4. Arsenic Speciation

Arsenic speciation in supernatants collected at the 84th day of experiment was performed only in treatments with higher initial As concentration (Figure 15). This was because the concentrations in treatments with initial 50 mg L^{-1} of As were all below the detection limit by that time.

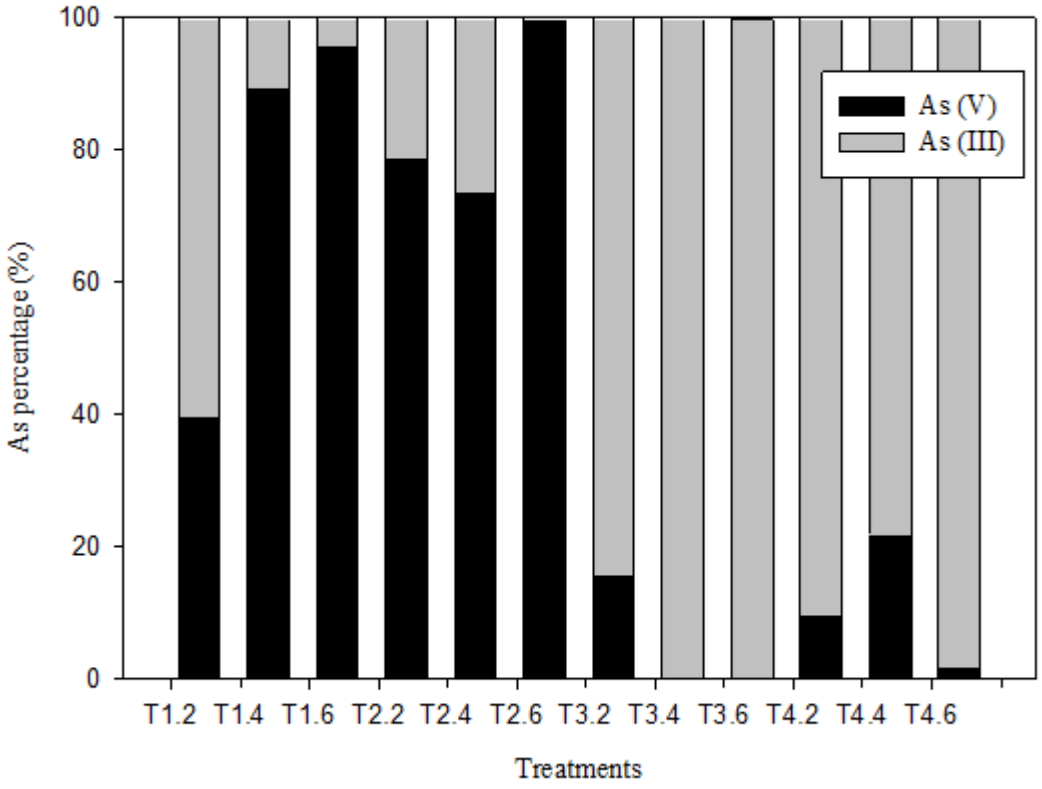


Figure 15. Arsenic (III) and As (V) percentage in solution

The most part of the final As concentration was arsenate in Fe (II) treatments (T1 and T2). This suggests that the As^{3+} that was initially in the T1 treatments was oxidized to As^{5+}. However, in T2 treatments, with initial Fe (II) and As (V), part of arsenate was reduced to arsenite, which can be ascribed to the oxidation of Fe (II) coupled to As^{5+} reduction. On the other hand, treatmens with Fe (III) (T3 and T4) presented most part of the soluble As concentration as arsenite. This means that the initial As (V) in T4 treatments, was partially

reduced to arsenite and the treatments with initial As (III) in T3 treatments did not oxidize even with the daily air injection in the vessels.

These results suggest that Fe (II) prevented the reduction of arsenate, but did not inhibit the oxidation of arsenite. However, Fe (III) prevented the oxidation of arsenite but allowed the reduction of arsenate. Similar findings were obtained by Ona-Nguema et al. (2010) who observed that Fe (II) works as a catalyzer for As (III) oxidation in the presence of soluble O_2, but the same did not happen for Fe (III) system, even in the presence of soluble O_2. This was due to what is called Fenton reactions.

5. Conclusions

1. The treatment for water contaminated with As by precipitation of Fe and Al (hydr)oxydes has its effectiveness affected by As species, As concentration, Fe species and, in a lesser extent, by Fe:Al molar ratio.

2. The leaching test showed that precipitates are safe for disposal only from treatments of water contaminated with lower As concentrations. Higher As concentrations in the sludge would require previous As (III) oxidation to be disposed without contamination risks.

3. The most part of extractable arsenic is specifically adsorbed to Fe (hydr)oxides , which could be concluded from the higher percentage of As extracted from this phase.

4. Precipitation of Al and Fe (hydr)oxides is highly effective to remove soluble As from water, irrespective of the Fe:Al molar ratio. A slightly lower efficiency in the beginning of the experiment is due to the precipitation of lepidocrocite and gibbsite from Fe (II) sulphates and arsenite.

5. As (III) removal to attain the threshold for drinking water is more time-consuming than As (V). Precipitation of Fe and Al (hydr)oxides was not efficient to reach that limit for high As concentrations (500 mg L^{-1}) after 84 days of experiment.

6. All treatments with lower As concentration (50 mg L^{-1}) were able to accomplish with the threshold for effluents discharge by the end of experiment. However, that limit was not attained just for water contaminated with a higher concentration of As (III), at Fe:Al molar ratios of 100:0 for Fe (II) and 60:40 molar ratio for both Fe (II) and Fe (III) treatments.

7. The presence of Al slowed down the As removal from water for all treatments. However, co-precipitation of Al with Fe (hydr)oxides showed to be helpfull for As removal at the end of the experiment in Fe (II) treatments. On the other hand, it was not beneficial for Fe (III) treatments.

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7. Appendix

Table A1: As supernatants concentration for Fe (II) treatments until 21st day

Fe(II):Al ratio	Initial(As) (III) (mgL^{-1})	02 hours	1 day	4 days	7 days	14 days	21 days
		---------- μgL^{-1} ----------					
100:0	**50**	33.5(12.2)	66.1(54.5)	9.7(2.9)	<DL	<DL	14.4(13.6)
80:20	**50**	17.8(10.2)	64.3(53.1)	248.3(197.0)	14.4(12.6)	<DL	60.2(55.0)
60:40	**50**	780.3(510.4)	721.3(445.9)	51.4(13.7)	<DL	8.3(4.5)	<DL
100:0	**500**	341.0(267.4)	738.1(237.8)	3885.3(1662.3)	896.4(458.1)	612.6(191.8)	1545.2 (1139.1)
80:20	**500**	1344.7(834.4)	1565.4(854.4)	1260.4(269.4)	297.4(185.2)	724.9(417.3)	571.3(350.1)
60:40	**500**	32529.3(10950.1)	28.6(3.6)	15.6(6.8)	2.3(1.5)	742.3(235.5)	564.44(147.5)

DL: 5.19 µg L^{-1}. Standard deviation in brackets

Table A2: As supernatants concentration for Fe (II) treatments until 21st day

Fe(II):Al ratio	Initial As (V) (mgL^{-1})	02 hours	1 day	4 days	7 days	14 days	21 days
		----------μgL^{-1}----------					
100:0	**50**	<DL	7.4(4.8)	4.5(4.2)	<DL	<DL	<DL
80:20	**50**	20.0(20.3)	252.0(107.3)	13.1(7.7)	<DL	<DL	<DL
60:40	**50**	<DL	85.1(73.4)	<DL	<DL	<DL	<DL
100:0	**500**	<DL	11.9(8.3)	38708.49(22925.9)	2089.5(2083.6)	698.3(349.3)	118.6(95.0)
80:20	**500**	207.5(67.6)	64.1(60.3)	397.6(209.7)	<DL	<DL	<DL
60:40	**500**	519.4(492.0)	203.6(88.3)	257.7(221.0)	6.1(3.2)	145.5(62.7)	86.9(13.7)

DL: 5.19 µg L^{-1}. Standard deviation in brackets

Table A3: As supernatants concentration for Fe (III) treatments until 21st day

Fe(III):Al ratio	Initial As (III) (mgL^{-1})	02 hours	1 day	4 days	7 days	14 days	21 days
		---------- $\mu g\ L^{-1}$ ----------					
100:0	**50**	<DL	95.3(76.5)	10.6(11.6)	7.4(3.7)	<DL	<DL
80:20	**50**	<DL	103.1(62.1)	19.9(1.2)	17.8(22.3)	<DL	88.5(58.2)
60:40	**50**	12.2(0.5)	124.9(81.0)	25.2(24.1)	36.5(28.2)	38.9(30.2)	96.9(82.4)
100:0	**500**	59.5(41.0)	142.9(31.2)	91.4(100.4)	23.3(7.1)	258.8(252.8)	131.8(124.1)
80:20	**500**	183.0(2.6)	236.6(119.1)	186.2(35.0)	360.2(338.6)	273.7(46.8)	247.5(57.7)
60:40	**500**	478.0(85.9)	652.5(83.1)	653.5(229.1)	849.7(60.6)	922.0(273.0)	772.0(213.9)

DL: 5.19 $\mu g\ L^{-1}$. Standard deviation in brackets

Table A4: As supernatants concentration for Fe (III) treatments until 21st day

Fe(III):Al ratio	Initial As (V) (mgL^{-1})	02 hours	1 day	4 days	7 days	14 days	21 days
		---------- $\mu g\ L^{-1}$ ----------					
100:0	**50**	<DL	89.2(60.5)	5.3(2.4)	6.1(6.1)	18.3(18.3)	20.6(20.6)
80:20	**50**	<DL	86.9(72.7)	<DL	<DL	19.2(19.2)	31.3(30.2)
60:40	**50**	<DL	97.3(80.2)	17.1(19.6)	44.2(33.8)	17.7(3.4)	153.6(89.0)
100:0	**500**	12.6(2.0)	117.4(91.1)	31.8(16.5)	391.7(160.0)	102.1(77.5)	138.8(78.0)
80:20	**500**	24.7(13.4)	108.6(76.9)	137.2(96.9)	65.7(61.8)	185.0(85.1)	238.6(166.2)
60:40	**500**	<DL	140.7(21.1)	57.1(19.5)	445.9(448.4)	113.2(46.1)	172.2(66.4)

DL: 5.19 $\mu g\ L^{-1}$. Standard deviation in brackets

Table A5: As supernatants concentration for Fe (II) treatments until 84th day

Fe(II):Al ratio	Initial As (III) (mgL^{-1})	28 days	35 days	49 days	63 days	84 days
		---------- µg L^{-1} ----------				
100:0	**50**	29.9(28.3)	38.2(38.9)	<DL	6.0(4.7)	<DL
80:20	**50**	13.6(13.6)	<DL	<DL	<DL	<DL
60:40	**50**	9.2(8.2)	<DL	<DL	<DL	<DL
100:0	**500**	6712.5(5238.0)	8516.8(2245.1)	1245.2(481.4)	1108.9(411.9)	1100.5(469.5)
80:20	**500**	339.0(64.9)	345.8(54.1)	268.4(24.2)	212.3(42.6)	217.9(3.8)
60:40	**500**	491.8(34.2)	479.0(27.1)	483.4(43.5)	651.1(153.6)	882.1(518.8)

DL: 5.19 µg L^{-1}. Standard deviation in brackets

Table A6: As supernatants concentration for Fe (II) treatments until 84th day

Fe(II):Al ratio	Initial As (V) (mgL^{-1})	**28 days**	**35 days**	**49 days**	**63 days**	**84 days**
		---------- µg L^{-1} ----------				
100:0	**50**	<DL	<DL	<DL	<DL	<DL
80:20	**50**	<DL	<DL	<DL	<DL	<DL
60:40	**50**	6.9(6.1)	<DL	<DL	6.0(4.1)	<DL
100:0	**500**	6.6(1.0)	120.1(48.2)	262.9(211.6)	508.8(623.1)	321.1(198.4)
80:20	**500**	208.6(79.9)	91.8(30.4)	107.1(27.3)	121.3(86.1)	111.7(153.4)
60:40	**500**	108.4(21.4)	472.9(302.5)	232.9(121.2)	223.4(18.9)	134.9(24.5)

DL: 5.19 µg L^{-1}. Standard deviation in brackets

Table A7: As supernatants concentration for Fe (III) treatments until 84th day

Fe(III):Al ratio	Initial As (III) (mgL^{-1})	28 days	35 days	49 days	63 days	84 days
		---------- $\mu g\ L^{-1}$ ----------				
100:0	**50**	46.7(21.8)	30.2(28.9)	125.2(100.3)	<DL	<DL
80:20	**50**	46.5(25.2)	13.4(12.2)	5.1(3.7)	<DL	<DL
60:40	**50**	149.9(54.7)	67.7(56.0)	70.6(57.8)	27.8(12.5)	<DL
100:0	**500**	182.1(109.4)	384.8(325.2)	158.2(41.7)	145.5(13.2)	155.0(30.8)
80:20	**500**	244.8(119.1)	458.8(70.7)	383.1(63.1)	423.4(43.5)	356.2(15.8)
60:40	**500**	803.0(182.1)	1253.7(404.7)	983.7(270.0)	937.7(58.7)	786.4(215.8)

DL: 5.19 μgL^{-1}. Standard deviation in brackets

Table A8: As supernatants concentration for Fe (III) treatments until 84th day

Fe(III):Al ratio	Initial As (V) (mgL^{-1})	28 days	35 days	49 days	63 days	84 days
		---------- $\mu g\ L^{-1}$ ----------				
100:0	**50**	25.2(12.5)	<DL	<DL	16,3(16,0)	<DL
80:20	**50**	37.1(27.2)	15.2(12.6)	<DL	<DL	<DL
60:40	**50**	109.0(89.2)	58.0(41.2)	15.8(13.4)	<DL	<DL
100:0	**500**	121.1(20.8)	115.9(52.3)	148.1(94.7)	90.2(51.6)	27.2(3.0)
80:20	**500**	130.8(10.1)	146.6(18.7)	171.2(25.7)	153.9(7.3)	126.0(51.2)
60:40	**500**	202.3(75.2)	130.8(20.0)	191.8(75.1)	231.9(112.7)	134.5(21.0)

DL: 5,19 $\mu g\ L^{-1}$. Standard deviation in brackets

Table A9: Easily soluble phase in Fe (II) treatments

			Extraction with water (mg kg^{-1})					
			As		Fe		Al	
	Fe(II):Al	[As]	Mean	Stand.Deviation	Mean	Stand.Deviation	Mean	Stand.Deviation
As(III)	100:0	50	<DL	<DL	<DL	<DL	<DL	<DL
	80:20	50	<DL	<DL	<DL	<DL	<DL	<DL
	60:40	50	<DL	<DL	<DL	<DL	<DL	<DL
	100:0	500	<DL	<DL	<DL	<DL	<DL	<DL
	80:20	500	<DL	<DL	<DL	<DL	<DL	<DL
	60:40	500	<DL	<DL	<DL	<DL	<DL	<DL
As(V)	100:0	50	<DL	<DL	<DL	<DL	<DL	<DL
	80:20	50	<DL	<DL	<DL	<DL	<DL	<DL
	60:40	50	<DL	<DL	<DL	<DL	<DL	<DL
	100:0	500	<DL	<DL	<DL	<DL	<DL	<DL
	80:20	500	<DL	<DL	<DL	<DL	<DL	<DL
	60:40	500	<DL	<DL	<DL	<DL	<DL	<DL

DL : As:2.71 mg kg^{-1}; Fe: 0.012 mg kg^{-1}; Al:0.05 mg kg^{-1}

Table A10: Easily soluble phase in Fe (III) treatments

			Extraction with water (mg kg^{-1})					
			As		Fe		Al	
	Fe(III):Al	[As]	Mean	Stand.Deviation	Mean	Stand.Deviation	Mean	Stand.Deviation
As(III)	100:0	50	<DL	<DL	<DL	<DL	<DL	<DL
	80:20:00	50	<DL	<DL	<DL	<DL	<DL	<DL
	60:40:00	50	<DL	<DL	<DL	<DL	<DL	<DL
	100:0	500	<DL	<DL	<DL	<DL	<DL	<DL
	80:20	500	<DL	<DL	<DL	<DL	<DL	<DL
	60:40	500	<DL	<DL	<DL	<DL	<DL	<DL
As(V)	100:0	50	<DL	<DL	<DL	<DL	<DL	<DL
	80:20:00	50	<DL	<DL	<DL	<DL	<DL	<DL
	60:40:00	50	<DL	<DL	<DL	<DL	<DL	<DL
	100:0	500	<DL	<DL	<DL	<DL	<DL	<DL
	80:20	500	<DL	<DL	<DL	<DL	<DL	<DL
	60:40	500	<DL	<DL	<DL	<DL	<DL	<DL

DL: As:2.71 mg kg^{-1}; Fe: 0.012 mg kg^{-1}; Al:0.05 mg kg^{-1}

Table A10: First Step BCR

Extraction with Acetic Acid (mg kg^{-1}) – Acid Soluble Phase										
	Fe(II):Al	[As]	As	Fe	Al	Fe(III):Al	[As]	As	Fe	Al
As(III)	100:0	50	6.31(0.31)	301.25(4.95)	4.99(2.50)	100:0	50	4.50(0.26)	531.55(55.27)	6.40(1.90)
	80:20	50	9.30(2.70)	569.11(10.64)	1384.80(30.92)	80:20:00	50	4.93(0.67)	279.40(26.65)	1321.00(28.29)
	60:40	50	9.46(2.48)	246.75(77.19)	2541.67(326.18)	60:40:00	50	11.19(1.30)	530.96(164.07)	2320.72(219.38)
	100:0	500	422.04(83.87)	22.95(0,83)	4.73(1.14)	100:0	500	61.74(9.38)	400.16(53.85)	3.99(1.28)
	80:20	500	126.77(9.43)	78.96(8.82)	1644.79(89.47)	80:20	500	170.58(7.71)	329.63(89.92)	1531.29(71.01)
	60:40	500	154.26(18.41)	206.14(62.37)	2022.99(59.59)	60:40	500	423.40(56.01)	380.71(73.71)	1614.65(292.97)
As(V)	100:0	50	2.37(0.21)	129.78(23.30)	6.18(1.62)	100:0	50	3.11(1.02)	334.64(16.21)	4.95(0.44)
	80:20	50	19.51(3.27)	2833.09(274.00)	1539.90(414.16)	80:20:00	50	3.27(0.23)	384.92(14.86)	1752.54(85.43)
	60:40	50	21.16(8.01)	1840.27(365.83)	2637.57(289.37)	60:40:00	50	3.98(0.60)	494.22(73.00)	2100.12(96.29)
	100:0	500	2.89(0.21)	10.12(3.28)	0	100:0	500	19.08(7.53)	279.97(113.29)	2.47(0.44)
	80:20	500	15.74(0.54)	180.53(4.53)	1628.82(246.25)	80:20	500	25.64(7.25)	323.08(95.24)	2285.49(284.64)
	60:40	500	22.71(2.73)	215.27(23.36)	2510.84(271.10)	60:40	500	29.12(1.47)	324.40(58.65)	2571.32(163.09)

DL : As:0.019 mg kg^{-1}; Fe: 0.17 mg kg^{-1}; Al:0.73 mg kg^{-1}. Standard deviation in brackets

Tabela A11: Second Step BCR

	Extraction with hydroxylammonium chloride (mg kg^{-1})- Reducible Phase									
	Fe (II):Al	[As]	As	Fe	Al	Fe (III):Al	[As]	As	Fe	Al
As(III)	100:0	50	7.10(0.31)	8929.02(930.62)	0	100:0	50	0.74(0.75)	25.260.40(726.06)	0
	80:20:00	50	0	4791.18(1493.25)	1631.23(92.97)	80:20:00	50	0.00	14.493.06(1.350,66)	1173.20(12.28)
	60:40:00	50	0	5712.27(175.67)	1729.96(34.46)	60:40:00	50	1.25(0.19)	10763.45(1989.12)	1174.18(110.25)
	100:0	500	232.01(44.51)	10122.13(1026.97)	0	100:0	500	15.85(3.73)	28136.92(2725.83)	0
	80:20	500	5.21(2.20)	10131.20(809.98)	1338.69(132.70)	80:20	500	11.10(3.61)	13796.42(2079.11)	1119.20(28.15)
	60:40	500	9.36 (0.99)	11491.57(272.74)	1383.03(98.56)	60:40	500	7.66(2.85)	14460.40(1903.39)	1180.47(82.53)
As(V)	100:0	50	10.38(2.08)	9454.78(426.89)	0	100:0	50	1.60(1.58)	23003.25(1044.31)	0
	80:20:00	50	0	4685.98(6.89)	1108.28(8.00)	80:20:00	50	0.00	14427.62(363.10)	1402.01(19.05)
	60:40:00	50	0	5801.09(171.00)	1844.87(91.49)	60:40:00	50	0	12510.02(226.15)	1336.97(196.27)
	100:0	500	5.87(0.49)	11468.79(335.56)	0	100:0	500	7.52(2.58)	22676.27(8.481.85)	0
	80:20	500	3.48(0.30)	9405.90(193.72)	1570.08(116.77)	80:20	500	3.52(1.44)	15754.15(509.63)	1376.61(31.93)
	60:40	500	10.50(1.50)	7013.08(1948.04)	1553.71(113.84)	60:40	500	1.80(0.18)	11588.31(651.08)	1591.60(76.23)

DL: As:0.019 mg kg^{-1}; Fe:0.21 mg kg^{-1}; Al: 1.06 mg kg^{-1} . Standard deviation in brackets

Table A12: Third Step BCR

	Extraction with hydrogen peroxide (mg kg^{-1})- Oxidizable Phase									
	Fe(II):Al	[As]	As	Fe	Al	Fe(III):Al	[As]	As	Fe	Al
As(III)	100:0	50	<DL	2156.36(326.59)	0	100:0	50	2.44(1.65)	22.217.58(2.403.20)	10.12(2.20)
	80:20:00	50	<DL	1345.00(189.50)	0	80:20:00	50	19.00(9.97)	20.318.12(2.298.26)	1142912(1494.33)
	60:40:00	50	1.05(0.13)	4706.06(1181.84)	7423.07(272.80)	60:40:00	50	13.78(7.45)	10.747,20(3.931,98)	10427.35(1579.55)
	100:0	500	20.53(1.69)	250.61(112.12)	0	100:0	500	6.91(2.91)	16874.42(999.71)	14.43(1.57)
	80:20	500	18.68(7.20)	3537.34(132.93)	2453.95(781.01)	80:20	500	7.81(2.19)	15286.86(1367.76)	8060.85(162.23)
	60:40	500	26.16(9.59)	4272.25(314.43)	5559.44(464.53)	60:40	500	16.72(1.34)	14234.02(9116.45)	11835.34(962.42)
As(V)	100:0	50	1.36(0.54)	3701.39(63.92)	0	100:0	50	3.53(3.14)	17080.27(2254.51)	10.76(2.66)
	80:20:00	50	<DL	2984.18(404.29)	1728.06(82.08)	80:20:00	50	4.67(1.07)	18992.23(800.54)	10280.04(282.82)
	60:40:00	50	1.29(0.48)	4673.85(484.33)	5959.64 (480.96)	60:40:00	50	7.23(4.00)	18866.25(815.83)	8261.82(144.64)
	100:0	500	4.46(0.49)	303.94(14.26)	0	100:0	500	4.14(0.34)	14266.91(456.47)	0
	80:20	500	3.56(0.43)	2837.15(1047.59)	2361.98(1089.98)	80:20	500	25.10(19.89)	15376,81(402.57)	9281.52(744.66)
	60:40	500	22.17(4.18)	4376.49(1730.54)	5312.94(615.54)	60:40	500	17.61(7.32)	8184.84(1450.93)	3580.04(1004.34)

DL : As: 0.79 mg kg^{-1}; Fe: 0.04 mg kg^{-1}; Al:0.39 mg kg^{-1}. Standard deviation in brackets.

Table A13: Extraction with potassium phosphate

	Extraction with potassium phosphate (mg kg^{-1}) – Adsorbed Phase									
	Fe (II):Al	As (III)	As	Fe	Al	Fe (III):Al	As (III)	As	Fe	Al
As(III)	100:0	50	21.67(8.15)	0	0	100:0	50	70.54(1.32)	27.07(1.79)	0
	80:20:00	50	42.45(18.03)	12.53(6.57)	55.17(2.20)	80:20:00	50	58.72(12.77)	175.42(53.41)	60.12(10.79)
	60:40:00	50	132.85(6.83)	107.64(45.53)	326.31(38.24)	60:40:00	50	40.60(4.45)	151.69(18.66)	158.76(11.75)
	100:0	500	3133.10(244.95)	41.33 (17.39)	0	100:0	500	645.22(58.76)	158.88(17.06)	0
	80:20	500	2863.06(764.40)	85.87(15.14)	120.74(19.42)	80:20	500	856.73(67.73)	159.12(25.77)	126.08(9.16)
	60:40	500	3073.20(303.20)	108.05(46.05)	186.81(37.81)	60:40	500	1216.33(258.55)	218.87(32.46)	219.46(56.30)
As(V)	100:0	50	36.03(4.86)	0	0	100:0	50	306.28(19.68)	62.38(16.84)	0
	80:20:00	50	94.50(4.48)	70,10(36.27)	119.57(2.23)	80:20:00	50	293.53(56.64)	182.44(84.47)	60.76(34.32)
	60:40:00	50	140.95(6.73)	24.00(2.71)	144.63(9.07)	60:40:00	50	259.71(15.35)	91.62(15.43)	132.23(7.50)
	100:0	500	2475.09(31.15)	19.44(14.97)	0	100:0	500	4830.83(363.40)	117.45(3.97)	0
	80:20	500	2441.59 (58.07)	96.13(2.73)	132.64(2.78)	80:20	500	4013.87(229.51)	307.29(35.09)	228.29(33.29)
	60:40	500	4115.51(264.17)	110.32(7.57)	198.94(10.42)	60:40	500	3829.26(249.26)	159.22 (47.74)	239.23(83.56)

DL : As: 2.70 mg kg^{-1}; Fe: 2.60 mg kg^{-1}; Al: 1.71 mg kg^{-1}. Standard deviation in brackets

Table A14: Extraction with Ammonium Fluoride

	Extraction with Ammonium Fluoride (mg kg^{-1})-Phase associated to Al									
	Fe (II):Al	[As]	As	Fe	Al	Fe (III):Al	[As]	As	Fe	Al
As(III)	100:0	50	0	0	0	100:0	50	0	0	0
	80:20:00	50	<DL	0	0	80:20:00	50	0.00	0	879.53(158.32)
	60:40:00	50	<DL	0	1726.53 (537.80)	60:40:00	50	5.42(0.83)	0	308.98(52.29)
	100:0	500	212.97(16.99)	0	0	100:0	500	15.96(8.17)	0	0
	80:20	500	269.15(46.06)	0	354.52(125.98)	80:20	500	12.16(1.39)	0	642.65(134.57)
	60:40	500	102.84(7.95)	0	1178.81(262.54)	60:40	500	31.61(6.40)	0	130509(312.11)
As(V)	100:0	50	7.22(0.56)	0	0	100:0	50	0	0	0
	80:20:00	50	0	0	351.99(38.36)	80:20:00	50	0.00	0	1119.34(236.41)
	60:40:00	50	11.50(3.62)	0	3903.16(1498.30)	60:40:00	50	0	0	2917.96(911.24)
	100:0	500	47.47(3.93)	0	0	100:0	500	18.04(6.62)	0	0
	80:20	500	34.30(2.910)	0	440.30(220.21)	80:20	500	43.63(1.34)	0	856.35(152.06)
	60:40	500	96.91(25.00)	0	2654.73(1080.06)	60:40	500	115.28(24.53)	0	3950.12(340.40)

DL: As: 3.39 mg kg^{-1}; Fe: 187.00 mg kg^{-1}; Al: 197.46 mg kg^{-1}. Standard deviation in brackets

Table A15: Digestion with HCl : HNO3 (3:1)

	Digestion with HCl :HNO_3 (3:1) (mg kg^{-1})									
	Fe (II):Al	[As]	As	Fe	Al	Fe (III):Al	[As]	As	Fe	Al
As(III)	100:0	50	5144.98(89.28)	628758.57(3917.07)	0	100:0	50	5572.47(1172.05)	569064.16(67259.62)	0
	80:20:00	50	4908.80(371.35)	379258.35(79146.41)	47783.26(4627.57)	80:20:00	50	4571.01(869.54)	356064.78(15710.35)	41626.16(5800.66)
	60:40:00	50	4465.53(113.06)	326990.20(12740.09)	109515.85(1381.78)	60:40:00	50	4089.99(79.55)	290120.37(12690.19)	95030.05(5432.87)
	100:0	500	32702.78(5870.29)	482645.87(68351.18)	0	100:0	500	34330.10(863.95)	498969.41(12785.22)	0
	80:20	500	36138.59(3396.21)	312567.92(92926.98)	45857.34(2750.04)	80:20	500	30757.55(1135.36)	351509.32(15601.36)	39764.95(512.99)
	60:40	500	26822.11(3145.72)	252146.24(7235.05)	83344.08(3478.31)	60:40	500	32106.06(3234.37)	262531.56(8251.57)	95990.85(7899.18)
As(V)	100:0	50	6022.62(186.36)	649849.14(13383.64)	0	100:0	50	5073,26(404.93)	487841.73(638.29)	0
	80:20:00	50	4693.45(132.17)	422355.26(9489.59)	43451.88(8605.38)	80:20:00	50	4583.06(691.75)	361308.21(14352.18)	41997.80(1767.93)
	60:40:00	50	5356.77(210.01)	321659.30(11139.20)	99980.58(932.43)	60:40:00	50	4351.44(693.57)	291854.16(10035.64)	95525.07(4305.83)
	100:0	500	35997.33(2425.00)	483276.11(29851.11)	0	100:0	500	30964.87(177.62)	436170.66(27954.33)	0
	80:20	500	33489.74(592.08)	367453.03(10229.78)	43398.97(1530.33)	80:20	500	30893.45(322.60)	367162.96(6583.02)	43056.02(1635.85)
	60:40	500	30882.37(2474.49)	269810.44(20526.96)	90321.28(2622.90)	60:40	500	31069.59(1520.18)	275892.05(8278.62)	95941.30(13350.81)

DL: As: 822.91 mg kg^{-1} ; Fe:0.64 mg kg^{-1}; Al: 7.09 mg kg^{-1}. Standard deviation in bracket.