Full Length Research Article

ARSENIC COAGULATION/FLOCCULATION WITH IRON (III) HYDROXIDE: ADSORPTION MECHANISMS AND STABILITY CONSTANTS OF SURFACE COMPLEXES

*[1]Elyahyaoui, A., [2]Razzouki, B., [2]El Hajjaji, S. and [1]Bouhlassa, S.

[1]Department of Chemistry, Laboratory of Radiochemistry, Faculty of Science,
University Mohammed V, BP 1014, Rabat, Morocco
[2]Department of Chemistry, LS3ME, Faculty of Science, University Mohammed V, BP 1014, Rabat, Morocco

ARTICLE INFO

ABSTRACT

The adsorption of arsenic (V) on iron (III) hydroxide had investigated in function of sorbent amount, pH, and contact time. The surface complexation method is used to establish the interaction mechanisms. H_3O^+/OH^- stoichiometry is evaluated and varied between -2 and 2, in pH range of 3 to 12. This suggests that As (V) adsorbs in this conditions, via six predominant adsorption reactions. Stability constants of predominant species which are protonated and unprotonated, are obtained. The contribution of electrostatic effect to arsenic (V) uptake by Fe-hydroxide is evaluated. Obtained results show that adsorption is of electrostatic nature for $pH \leq 6$, and of chemical character at $pH \geq 7$. While the kinetics adsorption data suggest a complex changing of predominant adsorption reaction with time, involving the intrinsic (n= 0), and 1 or 2 H^+ or OH^- exchange reactions.

TOC
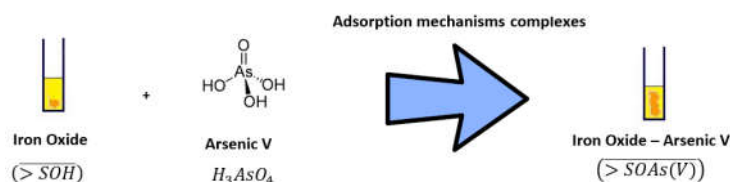
Adsorption mechanisms complexes

Iron Oxide ($> SOH$) + Arsenic V (H_3AsO_4) → Iron Oxide – Arsenic V ($> SOAs(V)$)

INTRODUCTION

Arsenic, which is a toxic element, is of a major concern in environmental chemistry. Between the two naturally occurring forms of arsenic, arsenite (As (III)) is more toxic than arsenate (As(V)) and has been reported more mobile in the environment (Grossl et al., 1997; Razzouki et al., 2015 and Razzouki et al., 2015). The presence of arsenic in aquatic environment is a result of rock weathering, human activities including mining, ore processing and fertilizers uses (Gao et al., 2001). It is more abundant in ground water than in surface water[5]. Under oxic conditions, arsenate is predominant and exists as $H_2AsO_4^{2-}$ species, while in anoxic conditions arsenic exists as uncharged species H_3AsO_3 or/and $H_2AsO_3^-$ anion (Vithanage et al., 2006; Raven et al., 1998; Goldberg et al., 2001).

The contamination of natural waters is governed by sorption process, especially, by adsorption on the surface of iron oxides and hydroxides (Grossl, 1997). Arsenic contaminated drinking water has been found in several countries (Vithanage et al., 2006; Bang et al., 2004; Carabante et al., 2013; Ghosh et al., 2006; Hlavay et al., 2005; Sharif et al., 2011; Vu et al., 2003). Hence, arsenic is of major concern to World Health Organization (WHO), United States Environment Protection Agency (USEPA), and other regulatory agencies. Thus, this element is severely controlled in soils and water, and the maximum contamination level (MCL) is lowered in drinking water from 50 to 10mg/L, in several countries (Jang et al., 2003). Consequently, the removal of arsenic from drinking water is extremely important and given much considerations (Cumbal et al., 2005; Dutta et al., 2006 and Teixeira et al., 2005). The most common method used for this purpose is coprecipitation with salts, followed by microfiltration. In order

*Corresponding author: Elyahyaoui, A.,
Department of Chemistry, Laboratory of Radiochemistry, Faculty of Science, University Mohammed V, BP 1014, Rabat, Morocco

to remove arsenic efficiently and economically and to better evaluate its environmental impact, the mechanisms of its release in aquatic environment must be well understood. Hence, more extensive information on the interaction of As in solution with various hydrous oxides is required. Due to their reactivates and large specific surface areas, iron (hydro) oxides are the most important adsorbents of microelements in natural environments (Luengo *et al*., 2006 and Waychunas *et al*., 1993). Adsorption at mineral surfaces is the primary processes controlling the mobility and bioavaibility of minor elements such arsenic, in soil and natural environments (Grossl *et al*., 1997; Luengo *et al*., 2006; Sverjensky *et al*., 2006). As a result, the nature of adsorbed As species on these oxides must be known over a wide range of pH. Adsorption of arsenic (V) on amorphous Irons oxides (III) is strongly pH-dependent and shows very different behaviours for As (III) and As(V). In general, apparent sorption maximum of arsenic (V) is observed at low pH in the range of 4 to about 7, whereas maximum arsenic (III) adsorption is occurring in the range of 7 to 8.5 (Goldberg *et al*., 2001; Arai *et al*., 2001; Harper *et al*., 2015). Often, arsenite is more strongly adsorbed than arsenate when solution, pH is greater than 8 (Bang *et al*., 2004). One can note however, that results quite variable are reported on optimal conditions removals of both As (V) and As (III), in these conditions (Raven *et al*., 1998 and Harper *et al*., 2015). These discrepancies are difficult to explain as discussed previously (Arai *et al*., 2001), due to the complexity of the adsorption phenomenon and to the various influencing parameters, must be due furthermore, to the experimental conditions in particular, those of pH control (Raven, 1998; Wang *et al*., 2008). The adsorption reactions of As(V) and surface speciation on iron oxides is investigated using macroscopic and microscopic techniques, such as extended X-ray absorption fine structure spectroscopy (EXAF), Fourier transform infrared (FTIR) (Harper *et al*., 2015 and Carabante *et al*., 2010), X-ray studying wave (XSW) (Catalano *et al*., 2007). It has been found that arsenic is sorbed to Fe(III) (Hydro) oxides predominantly by forming inner-sphere surface complexes via ligand exchange mechanism (Goldberg *et al*., 2001; Waychunas *et al*., 1993; Sverjensky *et al*., 2006; Wang *et al*., 2008; Carabante *et al*., 2010; Jain *et al*., 1999). The formation of outer-sphere complexes has been also observed for adsorption of arsenite on amorphous Fe oxides[7]. Quantum chemical calculations are performed for previously proposed surface complexes of arsenic (V) and arsenic (III). In general, the results are consistent with the tendency to form bidentate surface complexes at low pH, but however, the best results requires the correct protonation states (Catalano *et al*., 2007) and hydration of adsorbed arsenic Fe(hydr)oxide species (Kubicki *et al*., 2007). While most of these studies are successfully used to describe adsorption of arsenic at soil-mineral-water interfaces, the mechanisms are often postulated without considering protonation environment of As surface species, as discussed earlier (Arai *et al*., 2004). Also little information are reported on state protonation of the arsenic surface species (Sverjensky *et al*., 2006) and, especially, on the removal mechanism during coagulation/flocculation technique (Pallier *et al*., 2010). The surface speciation and state of protonation of arsenic(III, V) on iron (hydro)oxides was investigated by spectroscopic analysis (Arai, 2004; Carabante, 2010; Goldberg, 2001; Catalano, 2007; Fedorf, 1997; Masue, 2007 and Sherman, 2003), protonation surface titration (Gao *et al*., 2001; Jain, 1999; Zhang, 2008), combined with surface complexation adsorption experiments (Sverjensky, 2006; Pallier *et al*.,2010 and Fukushi *et al*., 2007b). Obtained results

show that arsenic (III, V) surface species are protonated at low pH and deprotonated at neutral to alkaline pH. Nevertheless, most of studies are often carried out at two fixed values in the ranges of 4-5 and 9-10.5, respectively that definitive experimental of state of protonation of As surfaces species is needed to achieve best fits of adsorption data over a wide range of pH (Goldberg, 2001; Sverjensky, 2006 and Arai, 2004).

MATERIALS AND METHODS

Coagulation experiments: All chemicals are of reagent grade are used without further purification. Arsenic adsorption experiments are carried out in batch systems to determine adsorption envelopes (amount of Arsenic adsorbed as a function of solution pH at fixed total concentration). Solutions of Arsenic (V) are freshly prepared using standard stock solutions of $1gL^{-1}$.Fe(III) is added as $Fe(Cl_3)_3.6H_2O$ to 50 ml of 10 mg/L Arsenic solution and equilibrated by chaking for time varying from 30 to 240 min. HNO_3 or KOH are used to adjust the starting acidity of aqueous solution. The samples are centrifuged and decantates are filtered through 0.45µm filter and analyzed for arsenic concentration using atomic absorption. The methods used for Arsenic determination are depicted in standard methods of water and wastewater analysis.

RESULTS AND DISCUSSION

Effect of pH and contact time on arsenic (V) adsorption
Effect of pH: The effect of pH on arsenic (V) adsorption, with amorphous iron (III) hydroxide is investigated in the pH range of 3 to 11.Contact time and sorbent amount are varying from 30 to 240 min, and 90 to 150mg L^{-1}, respectively. Obtained results (*Fig. 1, 2 and 3*) show that As(V) adsorption is typical of weak acid oxyanion with a maximum near their acid dissociation constant (pk_{ai}) (Shi, 2009; Kim, 2005). The pk_{ai} of arsenic (V) acid are $pk_{a1} = 2.24$, $pk_{a2} = 6.94$, and $pk_{a3} = 11.5$[1]. Similar adsorption edges are reported for magnetite, maghemite, amorphous iron(III) hydroxide, and goethite, showing optimal As(V) uptake about pH 7($\sim pk_{a2}$), which decreases rapidly with increasing pH (Goldberg, 2001; Arai *et al*., 2004; Shi *et al*., 2009; Goldberg, 1985 and Kim *et al*., 2005). The adsorption on iron (hydro) oxides is mainly by inner-sphere complexation at both acidic and alkaline media. Thus, arsenic (V) is adsorbed via ligand exchange reaction resulting in various surface complexes depending, furthermore, on surface coverage[31]. Taking into account the pH- diagram speciation, arsenic (V) is adsorbed as $H_2AsO_4^-$ at pH 2.3-7 and as $HAsO_4^{2-}$ at pH 7-11.5. The fast decrease in adsorption is observed for pH > 7 due to the dominant $HAsO_4^{2-}$ specie, combined with surface charge diminution of Fe(III) hydroxide which point of zero charge (PZC) is 7.5-9 (Goldberg *et al*., 2001; Chowdhury *et al*., 2010; Zachara *et al*., 1987). In pure alkaline conditions (pH ≥ 9), the effect of pH is no significant and a plateau is obtained, in all explored experimental conditions.

Effect of contact time; The effect of contact time (t) on arsenic (V) adsorption is studied in the range of 30 to 240 min, using sorbent amount (m) of 90, 100, and 150 mgL-1 (*Fig.1, and 3*). As shown, this effect is more significant in acidic to neutral pH. The optimal contact time (t_{max}) varies from 30 to 180 min and no simple correlation between (t_{max}) and m is

found. Although, the best As (V) recovery is achieved for 120 min, in all the cases.

Arsenic(V) adsorption reactions and stability constants: In general, adsorption process with hydrous metal (hydro) oxides is modeled thermodynamically as a complex reaction between surface sites ($\overline{> SOH}$) and hydrated adsorbate. The acid-base properties of the metal oxide surface sites is attributed to protonation/deprotonation reactions of surface functional $\overline{> SOH}$ expressed as:

$$\overline{> SOH} + H^+ = \overline{> SOH_2^+} K^+ \qquad (1)$$
$$\overline{> SOH} = \overline{> SO^-} + H^+ K^- \qquad (2)$$
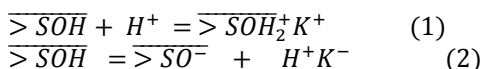
K^+ and K^- are the stability constants, and the one lined species refer to solid phase.

The adsorption reaction of arsenic (V) onto iron hydroxide is described with a method usually employed for solution complex description:

$$l(\overline{> SOH}) + H_3AsO_4 = \overline{(> SOH)_l(H_3AsO_4)H_{-n}} + nH^+,$$
$$l = 1 \text{ or } 2, K_{ln} (3)$$
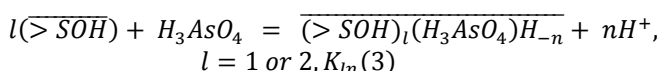
(Charges were omitted for the sake of simplicity)

The general symbol H_{-n} stands both for hydrogen atoms (n<0) and for OH groups (n>0). Taking into account the formation of $1 H_2O = H_{-1} + H_1$, the adsorption reaction can be formulated following general equilibrium:

$$l(\overline{> SOH}) + H_3AsO_4$$
$$= \overline{(> SO)_l(H_3AsO_{4-l})H_{-l-n}} + nH^+$$
$$+ lH_2O, l = 1 \text{ or } 2, K_{ln} \qquad (4)$$
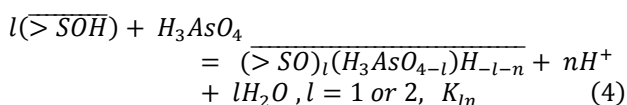
The surface complexation constant, K_{ln}, is given by:

$$K_{ln} = \frac{[\overline{(> SO)_l(H_3AsO_{4-l})H_{-l-n}}][H^+]^n}{[\overline{> SOH}]^l[H_3AsO_4]} \qquad (5)$$

Taking into account the expression of D given by:

$$D = \frac{[\overline{(> SO)_l(H_3AsO_{4-l})H_{-l-n}}]}{[H_3AsO_4]} \qquad (6)$$

We obtain:

$$logD = logK_{ln} + llogm + npH \qquad (7)$$

With $\overline{> SOH} = m$, is the concentration of sorbent used in g L^{-1}. The nature of surface complexes $\overline{(> SO)_l(H_3AsO_{4-l})H_{-l-n}}$, noted thereafter ($l$, n), can be obtained from As(V) distribution data according to:

$$\left(\frac{\delta logD}{\delta pH}\right)_m \qquad (8)$$

Fig. 1, 2 and 3 shows the plot of the curves of Log D versus pH ranges at different weight of Iron oxide (III).

The analysis of Fig.1, 2 and 3 shows that the plots of log D=f (pH) are linear in various pH ranges. The slopes of obtained straight lines whose correspond to mean values of n, are varying between -2 and 2. The predominant surface species are then (l, 0), (l, 1), (l, 2), (l, -1), and (l, -2).

Surface complexes and effect of pH and contact time on H_3O^+/OH^- exchange

Effect of pH: Basic research on the coprecipitation/adsorption process of arsenic and their optimization requires the knowledge of the interaction of this element with (hydro) oxides of metal. To achieve this purpose, the distribution data are best fitted ($R^2 \geq 99\%$) to a third order polynomial respectively in acidic to neutral pH, and in alkaline solution. The present work involves theoretical approach providing access to both surface complexes and their stability constants, using a macroscopic method in wide range of experimental conditions. The distribution data are described with one chemical equation. This could be of great interest for developing simple and approximate models of adsorption phenomenon. During arsenic(V) removal, the exchange of H^+ or OH^- increases gradually with pH to reach maximal values of about 1 or 2, and then decreases when the pH continues to rise. This exchange reaction is influenced by contact time and sorbent amount (surface coverage). Although the maximal l n l values are often obtained in the pH ranges of 6 to about 7, and 7 to 8.5, in all explored conditions.

Generally, the variation in removal efficiency of weak acid (HA) is due to protonation/deprotonation of both HA and functional surface groups (Jain *et al.*, 1999). When pH increases above 5.4 (pK$^+$) (Jain *et al.*, 1999; Kim, 2005; Zachara *et al.*, 1987), the positively surface (Fe-OH$_2^+$) favorable to H^+ exchange becomes not predominant, resulting then in a decrease of As (V) adsorption, in this case. The maximum adsorption occurs when the combination of high positive charge and concentration of favorable oxyanion is obtained (Wang *et al.*, 2013). A comparison of n = f(pH) plots with pH-diagram of As(V) distribution species shows that these curves have similar variations. Arsenic(V) is adsorbed as H_3AsO_4 for pH < 2.3, as $H_2AsO_4^-$ for $3.5 \leq pH \leq 6$ (90%), as $HAsO_4^{-2}$ for $8 \leq pH \leq 10.4$ (90%), as a mixture of these species between pH 6 and 8, and as AsO_4^{-3} for pH $\geq$ 10.4 (90%). Moreover, obtained results show that H_3O^+/OH^- exchange stoichiometry is not integer as suggested by the theoretical reactions. Similar results are reported for arsenate and similar other oxyanions on Fe (hydro) oxides (Jain, 1999 and Wang *et al.*, 2013). It is assumed that adsorption of oxyanions rises from different predominant reactions, and results in a combination of at least two predominant surface complexes.

The contribution of columbic effect to overall uptake of arsenic (V) with various metallic oxides is proposed to be significant, especially, in acidic conditions (Arai *et al.*, 2001; Carabante *et al.*, 2013; Dzombak *et al.*, 1985 Mähler *et al.*, 2013). Nevertheless, at pH around isoelectric point (IEP) or the point of zero charge (PZC)), the repulsion reaches a minimum (Antelo, 2005), and then the intrinsic process becomes the major adsorption mechanism. Accordingly the overall equilibrium is obtained by combining at least, the intrinsic reaction (n=0) with 1 or 2 H^+ moles (n=1; 2) or 1or 2 OH^- moles (n= -1; -2) exchange reaction per mole of H_3AsO_4. Taking into account these results there is a strong evidence that in basic pH, arsenate is adsorbed essentially by forming binuclear complexes as reported previously (Waychunas, 1993; Fedorf, 1997; Kim, 2005; Antelo *et al.*, 2005; Antelo *et al.*, 2012; Strugstad, *et al.*, 2013). Unfortunately, in acidic medium, we have no experimental evidence to decide about the formation of mono or binuclear As (V) complexes. Nevertheless, as shown from preliminary tests, anomalous

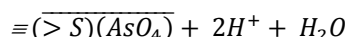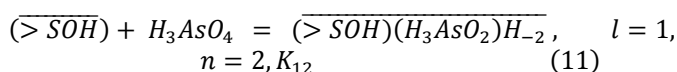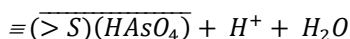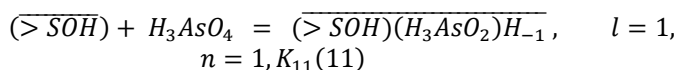**Table 1. Summarizes obtained results K_{col} associated with $K_{l\pm2}$ is**

Species	(l,n)	Adsorption Reaction	$\log K_{1n}$	$\log K_{col}$
		Acidic medium (pH<6)		
$(> \overline{SH_2AsO_4})$	(1,0)	$(> \overline{SOH}) + H_3AsO_4 \leftrightarrow (> \overline{S(H_2AsO_4)}) + H_2O$	4.50	
$(> \overline{SHAsO_4})$	(1,1)	$(> \overline{SOH}) + H_3AsO_4 \leftrightarrow (> \overline{S)(HAsO_4}) + H^+ + H_2O$	1.60	4.1
$(> \overline{SAsO_4})$	(1,2)	$(> \overline{SOH}) + H_3AsO_4 \leftrightarrow (> \overline{S)(AsO_4}) + 2H^+ + H_2O$	-7.04	17.28
		Neutral to alkaline medium ($7 \leq pH \leq 9$)		
$(> \overline{SO)_2(AsO_2})$	(2,-1)	$2(> \overline{SOH}) + HAsO_4^{2-} \leftrightarrow (> \overline{SO)_2(AsO_2}) + OH^- + H_2O$	12.64	-8.48
$(> \overline{SO)(HAsO_2})$	(2,-2)	$2(> \overline{SOH}) + HAsO_4^{2-} \leftrightarrow (> \overline{SO)_2(AsO_2}) + 2OH^-$	21.08	-16.88
		More Alkaline medium ($9 \leq pH \leq 11$)		
$(> \overline{SO)_2(HAsO_2})$	(2,0)	$2(> \overline{SOH}) + HAsO_4^{2-} \leftrightarrow (> \overline{SO)_2(AsO_2}) + 2H_2O$	3.53	

results in distribution of As (V) acid species with pH are obtained for binuclear surface complexes. Based on these considerations, the H^+ exchange is combined with a dehydration, andthe surface complexation of arsenic(V) with Fe (III) hydroxide can be summarized by the following general equilibrium:
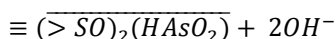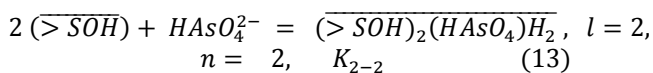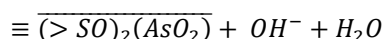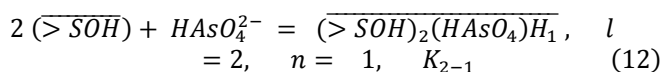
$$l(> \overline{SOH}) + H_3AsO_4 = \overline{(> SO)_l(H_3AsO_{4-l})H_{-n-2l}} + nH^+ + lH_2O \quad , K_{ln} \quad (9)$$
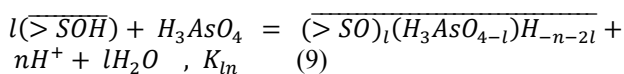
With l = 1, and 2 for pH $\leq$ 6 and pH $\geq$ 6 respectively, and $-2 \leq n \leq 2$.

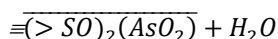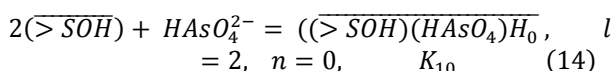Taking into account the experiment results, simplified predominant adsorption reaction could be written as:
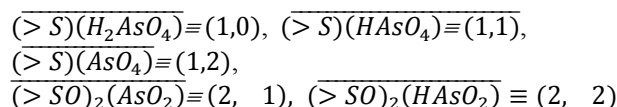For pH< 6, as:

$$(> \overline{SOH}) + H_3AsO_4 = \overline{(> SOH)(H_3AsO_4)H_0} \, l = 1, \quad n = 0, \, K_{10} \quad (10)$$

$$\equiv (> \overline{S)(H_2AsO_4}) + H_2O$$

$$(> \overline{SOH}) + H_3AsO_4 = \overline{(> SOH)(H_3AsO_2)H_{-1}}, \quad l = 1, \quad n = 1, K_{11} (11)$$

$$\equiv (> \overline{S)(HAsO_4}) + H^+ + H_2O$$

$$(> \overline{SOH}) + H_3AsO_4 = \overline{(> SOH)(H_3AsO_2)H_{-2}}, \quad l = 1, \quad n = 2, K_{12} \quad (11)$$

$$\equiv (> \overline{S)(AsO_4}) + 2H^+ + H_2O$$

For $7 \leq pH \leq 9$, and as:

$$2(> \overline{SOH}) + HAsO_4^{2-} = \overline{(> SOH)_2(HAsO_4)H_1}, \quad l = 2, \quad n = 1, \quad K_{2-1} \quad (12)$$

$$\equiv \overline{(> SO)_2(AsO_2})} + OH^- + H_2O$$

$$2(> \overline{SOH}) + HAsO_4^{2-} = \overline{(> SOH)_2(HAsO_4)H_2}, \quad l = 2, \quad n = 2, \quad K_{2-2} \quad (13)$$

$$\equiv (> \overline{SO)_2(HAsO_2}) + 2OH^-$$

Alkaline medium ($9 \leq pH \leq 11$):

$$2(> \overline{SOH}) + HAsO_4^{2-} = \overline{((> SOH)(HAsO_4)H_0}, \quad l = 2, \quad n = 0, \quad K_{10} \quad (14)$$

$$\equiv (> \overline{SO)_2(AsO_2}) + H_2O$$
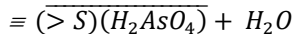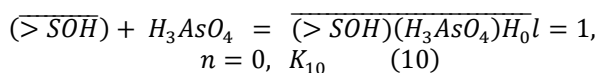
Consequently, As (V) adsorption occurs through six predominant reactions which result in

$$(> \overline{S)(H_2AsO_4}) \equiv (1,0), \quad (> \overline{S)(HAsO_4}) \equiv (1,1),$$
$$(> \overline{S)(AsO_4}) \equiv (1,2),$$
$$(> \overline{SO)_2(AsO_2}) \equiv (2, \quad 1), \quad (> \overline{SO)_2(HAsO_2}) \equiv (2, \quad 2)$$

and $(> \overline{SO)_2(AsO_2}) \equiv (2,0)$ species. The nature ofidentified complexes is consistent with previous results of As(V) surface speciation on Fe(III) (hydr) oxides[35, 51, 53], which indicate furthermore, that unprotonated mononuclear, $(> \overline{SO)(AsO_2})$ specie, predominates at lower surface coverage for pH > 8-9[4, 26, 35, 51], as shown in (Fig. 4, 5 and 6). In addition, it can be seen that the diprotonated $(> \overline{S)(H_2AsO_4}) \equiv (1, \quad 0)$ complex dominates at pH values less than about 5, in all cases. While $(> \overline{SO)_2(HAsO_2}) \equiv (2,-2)$ and $(> \overline{SO)_2(AsO_2}) \equiv (2,0)$ are the most dominant species for 90 and 150 mgL^{-1}, in the pH range of about 7-9. $(> \overline{S)(HAsO_4}) \equiv (1,1)$ complex is prevailing in particular, at m = 90 mgL^{-1} (high surface coverage) for pH ranging from 5.5 to 6.5. One can note that the interaction of arsenate ions with iron(III) hydroxide, is essentially of electrostatic nature in lower acidic medium (pH $\leq$ 6), and of chemical nature in near neutral to alkaline medium.

Conclusion

The adsorption of arsenic (V) on Fe(III) hydroxide is examined in order to develop a method for the study of surface complexation of this element. The distribution coefficient, D, is dependent on contact time, pH and surface coverage. The treatment of logD=f(pH) experiment data is used to evaluate H^+/OH^- exchange sotoechiometry in adsorption reaction and allows us to specify the predominant As(V) surface species. The surface complexes are found to be protonated and unprotonated. The stability constants are $\log K_{10} = 4.50$ for $(> \overline{S)(HAsO_4})$, $\log K_{11} = 1.60$ for $(> \overline{S)(HAsO_4})$, $\log K_{12} = -7.04$ for $(> \overline{S)(AsO_4})$, $\log K_{2-1} = 12.64$ for $> \overline{(SO)_2(AsO_2}})$, $\log K_{2-2} = 21.08$ for $> \overline{(SO)_2(AsO_2})$ and $\log K_{20} = 3.53$ for $(> \overline{SO)_2(AsO_2})$. The columbic effect is evaluated for the predominant species, and obtained results show that As(V) adsorption on iron(III) hydroxide is of electrostatic nature in acidic solutions, and chemical character in near neutral to alkaline solutions. Also the adsorption kinetics is examined and it is found that a complex changing of predominant adsorption reaction with time, involving the intrinsic (n= 0), 1, and 2 H^+ or OH^- exchange reactions.

REFERENCES

Antelo, J., Avena, M., Fiol, S., Lopez R., and. Arce, F. 2005. Effects of pH and ionic strength on the adsorption of

phosphate and arsenate at the goethite-water interface. *J. of Colloid and Interface Science*, 285 (2), 476-486.

Arai, Y., Sparks, D.L. 2001. ATR–FTIR Spectroscopic investigation on phosphate adsorption mechanisms at the ferrihydrite–water interface. *J. Colloid and Interface Science*, 241 (2), 317-326.

Arai, Y., Sparks, D.L., Davis, J.A. 2004. Effects of Dissolved Carbonate on Arsenate: adsorption and surface speciation at the hematite-water Interface. *Environ. Sci. Technol.*, 38 (3), 817-824.

BakiSenhaji, S., ElYahyaoui, A. Liquid-liquid Extraction of Zinc by3-methyl-quinoxaline-2-thione from Nitrate Medium.*Oriental Journal of Chemistry.*2015. Vol. 31, No. (3):Pg. 1601-1609.

Bang, S.,Meng, X. A review of arsenic interactions with iron and iron hydroxides. *Environ. Eng. Res.* 2004, 9 (4), 184-192.

Brechbühl, Y.P. Sorption of arsenic to hematite in the presence of carbonate and silicate: Combined ATR-FTIR and batch studies. *Ph.D. thesis.*2012, ETH Zurich Swiss.

Carabante, I.;Grahn, M.; Holmgren, A.; Kumpiene, J.; Hedlund, J. Adsorption of As(V) on iron oxide nanoparticle films studied by in situ ATR-FTIR spectroscopy. *Colloids and Surfaces A: Physicochemical and Engineering Aspects.*2013, 346 (1-3) 106-113.

Carabante, I.,Grahn, M., Holmgren, A.,Hedlund, J. In situ ATR–FTIR studies on the competitive adsorption of arsenate and phosphate on ferrihydrite. *Journal of Colloid and Interface Science*. 2010, 3[51] (2), 523–531.

Catalano, J.G., Zhang, Z., Park, C.,Fenter, P.,Bedzyk, M.J. Bridging arsenate surface complexes on the hematite (012) surface. *Geochim. Cosmochim. Acta.*2007, 71, 1883–1897.

Chowdhury, S.R.,Yanful, E.K. Arsenic removal from aqueous solutions by adsorption on magnetite nanoparticles. *Water and Environment Journal.*2010, 25 (3), 429–437.

Cumbal, L.,SenGupta A. K. Arsenic removal using polymer-supported hydrated Fe(III) oxide (HFO) nanoparticles: Role of donnan membrane effect. *Environmental Science & Technology.*2005, 39 (17), 6508-6515.

Dutta, P.K., Ray, A.K., Sharma, V.K.,Millero, F.J. Adsorption of arsenate and arsenite on titanium dioxide suspensions.*Journal of Colloid and Interface Science*. 2006, 278 (2), 270–275.

Dzombak, D.A., Morel Francois M.M.Adsorption of inorganic contaminants in ponded effluents from coal-fired power plants. *Energy laboratory Report No. MIT-EL.* 1985, 85-005 Massachusetts Institute of Technology, USA.

Fedorf,S., Eick, M.J.,Grossl, P., Sparks, D.Arsenate and chromate retention mechanisms on goethite. 1. Surface structure. *Environ.Sc. and Technol.* 1997, 31(2), 315-320.

Fitzpatrick, A.J. Adsorption of arsenate and phosphate on gibbsite from artificial seawater. Ph.D. thesis, Faculty of Graduate Studies and Research. McGill University, Montreal.1998, QC, Canada.

Fukushi,K.,Sverjensky, D.A. A predictive model (ETLM) for arsenate adsorption and surface speciation on oxides consistent with spectroscopic and theoretical molecular evidence. *GeochimicaetCosmochimicaActa*. 2007b, 71 (15), 3717–3745.

Gao, Y.,Mucci, A. Acid base reactions, phosphate and arsenate complexation, and their competitive adsorption at the surface of goethite in 0.7 M NaCl solution.*GeochimicaetCosmochimicaActa.*2001, 65 (14), 2361–2378.

Ghosh, U. C.,Bandyopadhyay, D., Manna, B., Mandal, M.Hydrous iron(III)-tin(IV) binary mixed oxide: Arsenic adsorption Behaviour from aqueous solution. *Water Qual. Res. J. Canada*. 2006, 41(2), 198–209.

Goldberg, S. Chemical modeling of anion competition on goethite using the constant capacitance model.*Soil Sci. Soc. Am.J.*1985, 49, 851-856.

Goldberg, V.,Johnstony, C.T.Mechanisms of arsenic adsorption on amorphous oxides evaluated using macroscopic measurements, vibrational spectroscopy, and surface complexation modeling.*Journal of Colloid and Interface Science*. 2001, 234 (1), 204–216.

Grossl, P.R., Eick, M., Sparks, D. L., Goldberg, S. Arsenate and chromate retention mechanisms on goethite. 2. Kinetic evaluation using a Pressure-Jump Relaxation Technique. *Environ. Sci. Technol.*1997, 31 (2), 321-326.

Hanna, N.Modelling precipitation and surface complexation reactions in systems with goethite, Cu (II) and oxyanions containing As (V) or P(V). Ph.D. thesis, Umea University. 2012,Sweden.

Harper, L. K., Bayse, C. A. Modeling the chelation of As(III) in lewisite by dithiols using densityfunctional theory and solvent-assisted proton exchange *Journal of Inorganic Biochemistry.* 2015, 153 60–67.

Hesami, F., Bina, B., Ebrahimi, A., Amin, M.M. Arsenic removal by coagulation using ferric chloride and chitosan from water. *International Journal of Environmental Health Engineering.* 2013, 2 (1), 17-22.

Hlavay, J.,Polyak, K. Determination of surface properties of iron hydroxide-coated alumina adsorbent prepared for removal of arsenic from drinking *water. J. Colloid Interface. Science*. 2005, 284 (1), 71–77.

Jain, A., Raven, K.P.,Loeppert, R.Arsenite and arsenate adsorption on ferrihydrite: surface charge reduction and net OH- Release stoichiometry. *Environmental Science & Technology.*1999, 33 (8), 1179–1184.

Jang, M., Shin, E.W, Park, J.K., Choi, S.Il. Mechanisms of arsenate adsorption by highly ordered Nano-structured silicate media impregnated with metal oxides. *Environ. Sci. Technol.* 2003, 37 (21), 5062-5070.

Jia, Y., Xu, L., Fang, Z, Demopoulos, G. P., 2006. Observation of surface precipitation of arsenate on ferrihydrite.Environ. Sci. Technol. 40 (10), 3248-3253.

Kim, J.W. The modeling of arsenic removal from contaminated water using coagulation and sorption. *Ph.D. thesis. Texas A&M University.*2005,USA.

Kubicki, J.D., Kwon, K.D.,Kubicki, K.W., Sparks, P.D.Surface complex structures modelled with quantum chemical calculations: carbonate, phosphate, sulphate, arsenate and arsenite. *European Journal of Soil Science.*2007, 58 (4), 932–944

Loring, J.S., Sandstrom, M.H., Noren, K., Persson, P. Rethinking Arsenate Coordination at the Surface of Goethite. *Chemistry-a European Journal*. 2009, 15 (20), 5063-5072.

Luengo, C., Brigante, M., Antelo, J., Avena, M. Kinetics of phosphate adsorption on goethite: comparing batch adsorption and ATR-IR measurements.*Journal of Colloid and Interface Science.*2006, 300 (2), 511–518.

Mähler, J. The Adsorption of Arsenic Oxyacids to Iron Oxyhydroxide Columns Including Studies of Weakly Hydrated Ions and Molecules in Aqueous Solution. *Doctoral thesis, Swedish University of Agricultural Sciences, Uppsala*, 2013. Sweden.

Masue, Y.,Loeppert, R., Kramer, T.A. Arsenate and arsenite adsorption and desorption behavior on coprecipitated aluminum: Iron hydroxides. *Environ. Sci. Technol.* 2007, 41 (3), 837-842.

Pallier, V.,Feuillade-Cathalifaud, G., Serpaud, B., Bollinger, J.C. Effect of organic matter on arsenic removal during coagulation/flocculation treatment. *Journal of Colloid and Interface Science*. 2010, 342 (1) 26-32.

Raven, K.P., Jain, A.,Loeppert, R.H.Arsenite and arsenate adsorption on ferrihydrite: Kinetics, equilibrium, and adsorption envelope. *Environ. Sci. Technol.*1998, 32 (3), 344-349.

Razzouki, B., EL Hajjaji, S., ElYahyaoui, A., Lamhamdi, A., Jaafar, A., Azzaoui, K., Boussaoud, A., Zarrouk, A. Kinetic investigation on arsenic (III) adsorption onto iron hydroxide (III). *Der Pharmacia Lettre*. 2015, 7 (9):53-59.

Razzouki, B., EL Hajjaji, S.,Azzaoui, K.,Errich, A.,Lamhamdi, A.,Berrabah, M.,Elansari, L.L. Physicochemical study of arsenic removal using iron hydroxide.J. Mater. Environ. Sci.2015, 6, 144-1450.

Roya, P.K., Choudhury, M.R., Alia, M.A.As (III) and As (V) adsorption on magnetite nanoparticles: Adsorption isotherms, Effect of pH and phosphate, and adsorption kinetics. *International Journal of Chemical and Environmental Eng*. 2013, 4 (1), 55-63.

Sharif, Md., Salah U., Davis, R.K., Steele, K.F., Kim, B., Hays, P.D.,Kresse, T.M.,Fazioc, J.A. Surface complexation modeling for predicting solid phase arsenic concentrations in the sediments of the Mississippi River Valley alluvial aquifer, Arkansas, USA. *Applied Geochemistry.*2011*, 26 (4), 496–504.

Sherman, D.M., Randall, S.R. Surface complexation of arsenic(V) to iron(III) (hydr)oxides: Structural mechanism from ab initio molecular geometries and EXAFS spectroscopy. *GeochimicaetCosmochimicaActa.*2003, 67 (22), 4223–4230.

Shi, R.,Jia,Y.,Wang,C. Competitive and cooperative adsorption of arsenate and citrate on goethite. *J. Environmental Sciences.*2009,21(1), 106–112.

Spiteri, C., Cappellen, P.V., Regnier, P. Surface complexation effects on phosphate adsorption to ferric iron oxyhydroxides along pH and salinity gradients in estuaries and coastal aquifers. *GeochimicaetCosmochimicaActa*. 2008, 72 (14), 3431-3445.

Strugstad, M.P. Individual and competitive adsorption of phosphate and arsenate onto manganese oxide in seawater. *A Ph.D. thesis, Faculty of Graduate Studies and Research, McGill University, Montréal, QC.*2013, Canada.

Sverjensky , D.A.,Fukushi, K.Anion adsorption on oxide surfaces: inclusion of the water dipole in modeling the electrostatics of ligand exchange.*Environ Sci Technol.* 2006, 40 (1), 263-71.

Teixeira, M.C., Ciminelli, Virginia, S.T. Development of a biosorbent for arsenite: structural modeling based on X-ray spectroscopy.*Environmental Science & Technology.*2005, 39 (3), 895-900.

Vithanage, M., Chandrajith, R., Bandara, A., Weerasooriya, R. Mechanistic modeling of arsenic retention on natural red earth in simulated environmental systems. *Journal of Colloid and Interface Science*. 2006, 294 (2), 265–272.

Vu, K.B., Kaminski, M.D.,Nuñez, L. Review of arsenic removal technologies for contaminated groundwaters. *Argonne National Laboratory, Illinois.*2003,USA.

Wang, S., Mulligan, C.N. Speciation and surface structure of inorganic arsenic in solid phases: A review. *Environmental International*. 2008, 34 (6), 867-879.

Wang, X., Liu, F., Tan, W., Li. W., Feng, X., Sparks, D.L.Characteristics of phosphate adsorption-desorption onto ferrihydrite: Comparison with well-crystalline Fe(Hydr)oxides.*Soil Science.*2013, 178 (1), 1-11.

Waychunas, G.A., Rea, B.A., Fuller, C.C., Davis, J.A. Surface chemistry of ferrihydrite. Part 1. EXAFS studies of the geometry of Co-precipitated and adsorbed arsenat. *GeochimicaetCosmochimicaActa.*1993, 57(10), 2251-2269.

Zachara, J.M.,Girvin, D.C., Schmidt, R L, and C.T., Resh, C.T. Chromate adsorption on amorphous iron oxyhydroxide in the presence of major groundwater ions. *Environ.Sci. Technol.* 1987, 21 (6), 589-594.

Zhang, J.S.,Stanforth, R.,Pehkonen, S.O. Irreversible adsorption of methyl arsenic, arsenate, and phosphate onto goethite in arsenic and phosphate binary systems. *Journal of Colloid and Interface Science*. 2008, 317 (1), 35–43.

****