Research Article
Effects of Thiosulfate on the Adsorption of Arsenate on Hematite With a View to Phytoextraction

Gianniantonio Petruzzelli, Francesca Pedron and Irene Rosellini
Institute of Ecosystem Study, National Council of Research, Pisa, Italy

Abstract: A study was carried out to evaluate how the adsorption process of arsenate on hematite is influenced by the presence of thiosulfate ion. The competition in sorption between the two anions was examined in relation to potential use of thiosulfate as an additive for phytoextraction in arsenic contaminated soils. Results obtained from sorption isotherms can be described according to the Langmuir equation which allows, by comparing adsorption maxima, a quantitative evaluation of the effect of increasing concentration of thiosulfate on arsenate adsorption. Due to the competition between the two anions for available sites on hematite, arsenic sorption decreased at increasing thiosulfate concentration. The negligible effect of ionic strength on the sorption process, strongly suggests that thiosulfate can substitute arsenate ions in the inner sphere complexes on the surface of hematite. The interpretation of the As adsorption process on hematite in terms of distribution coefficient (K_d) shows that thiosulfate ions competing for sorption on the same surface may significantly reduce the arsenate adsorption and enhance the release of arsenic in the liquid phase of soil. Results have a direct influence on the applicability of phytoextraction in arsenic contaminated soils since plants can uptake arsenic only from the liquid phase. The obtained results can explain the increase in As concentration in plants, reported in a recent paper in which the addition of thiosulfate was shown to promote As phytoavailability.

Keywords: Anion adsorption, arsenic bioavailability, distribution coefficient, ion oxides, Langmuir equation, phytoremediation

INTRODUCTION

Soil is an important sink for arsenic, which is considered a hazardous priority pollutants (Nickson *et al*., 1998; Berg *et al*., 2001; Centeno *et al*., 2002; Nriagu *et al*., 2009) and its uptake by living organisms in contaminated soils, poses a serious threat to human health and to food security.

One of the major environmental emergencies worldwide is due to the high concentrations of As in the aquifers of Bangladesh, which have adversely affected the health of the local populations (Smedley and Kinnburg, 2002). The remediation of arsenic contaminated sites is an essential priority for the protection of human health. The most common approach to clean-up As contaminated soil is excavation followed by landfilling, which is a highly disruptive procedure for the environment. Alternative technologies are thus required in order to protect the environment without destroying the soil, which must be considered as an essential and non-renewable resource. Phytoremedation has great potential as a remediation technology: it is less invasive and is cost effective compared to conventional technologies.

The efficiency of phytoremediation strictly depends on soil properties, which regulate the distribution of contaminants among the different soil phases, since plants uptake substances only if they are present in the soil liquid phase (soil solution). Thus an understanding of arsenic sorption on the solid phases of soil is essential for managing arsenic contaminated sites.

Numerous investigations have focused on the sorption of As on various soil components. However, little attention has been paid to the implications for phytoremediation derived from the competitive sorption between arsenic and anionic additives on soil surfaces which are added to promote arsenic uptake by plants.

Thiosulfate is an additive used in phytoextraction to enhance Hg uptake by plants. In a recent paper the addition of thiosulfate was also shown to promote As phytoavailability in a multi-contaminated soil (Petruzzelli *et al*., 2014), but the role of soil components in the interactions between arsenate and thiosulfate needs further clarifications. Arsenate is mainly retained by Fe oxides (Fukushi and Sverjensky, 2007), thus the competition between arsenate and thiosulfate for adsorption on Fe oxides surfaces may be of primary importance in determining the amount of As

Corresponding Author: Gianniantonio Petruzzelli, Institute of Ecosystem Study, National Council of Research, Via Moruzzi 1, 56123 Pisa, Italy

in soil solution, as well as its mobility and bioavailability.

While many studies have described the competition between arsenate and phosphate, detailed information on the competitive sorption of thiosulfate and arsenate on various soil minerals and soils is not currently available. The aim of this study was to investigate the competition in sorption on hematite in relation to the potential use of thiosulfate as an additive for phytoextraction in arsenic contaminated soils.

MATERIALS AND METHODS

The commercial hematite (Fe_2O_3, CAS 1309-37-1) used in this study was characterized by a specific surface area of 256 m^2/g and an average particle size of 0.003 μm.

Sorption experiments were carried out at constant values of pH (7.4) and solid/liquid ratio (0.1:10). An arsenate solution (10 mL) at different concentrations from 1 to 15 μg/mL was added to 0.1 g of hematite. The arsenate solution was prepared from a NIST standard solution of 1000 mg As (V) per liter in MilliQ water. Sorption competition was studied by carrying out As sorption in solutions containing ammonium thiosulfate at 0.01M, 0.1M and 0.27M concentrations. Suspensions were shaken for 12 h at 20±0.5°C. Preliminary sorption experiments, showed no significant variation in As concentration for periods longer than 4 h. This time was considered adequate to obtain an arsenic distribution near the equilibrium.

After equilibration, the suspensions were centrifuged at 7000 xg to separate the solution phase from the suspensions and As concentrations in the supernatants were determined. The amount of arsenic adsorbed per mass of dry Fe-oxide was calculated by the difference between the quantity added and that recovered in the equilibrium solution, according to the equation:

$$\frac{x}{m} = \frac{V\,(C_i - C_e)}{m}$$

where,
x/m = The amount of As adsorbed (x) per unit mass of hematite (m)
C_i = The initial As concentration
C_e = The As concentration at equilibrium
V = The volume of As solution added

Further experiments to evaluate the effect of ionic strength on the adsorption process, were carried out by adding NH_4Cl at concentrations of 0.05M and 0.01M to the As solution with and without 0.27M thiosulfate addition. No modification of pH was necessary.

Arsenic analysis: As concentration was determined using ICP-OES (Varian AX Liberty) with a method for the generation of hydrides (Sparks, 1998).

Quality assurance and quality control were performed by testing a standard solution every 10 samples. A certified reference material (SQC001) was used to control the quality of the analytical system. The detection limit for As was 0.05 mg/L. The recovery of spiked samples ranged from 94 to 101% with an RSD of 1.91 of the mean.

RESULTS AND DISCUSSION

Adsorption experiments: The adsorption of arsenate on hematite, with and without thiosulfate addition were investigated by determining adsorption isotherms. Inspection of the obtained isotherms (Fig. 1) showed that they were "L type" according to the Giles classification (Giles and Smith, 1974).

The amount of As sorbed seemed to reach saturation, which indicates that arsenate ions filled all available sites on hematite in the experimental conditions adopted. The addition of thiosulfate to the arsenate solution produced a significant reduction in the amount of sorbed arsenate with every concentration used. The shapes of the isotherms were similar (L type), but the maximum of sorption greatly decreased. These findings indicate that lesser adsorbing sites were available for arsenate, because thiosulfate ions preferentially adsorbed on the solid phase as a consequence of a competition between the two ions.

Since the isotherm is L type, the adsorption can be described according to the Langmuir equation:

$$Q = \frac{Q_{max}KC_e}{1 + KC_e}$$

where,
Q = The amount of arsenate (μg/g) adsorbed per unit of weight hematite
C_e (μg/mL) = The equilibrium concentration
Q_{max} and K = Adjustable parameters linked to the maximum and to the energy of adsorption

Data from the Langmuir equation are reported in Table 1.

The Langmuir isotherm describes the experimental data well, suggesting that the sorption sites are filled in a form of a monolayer and all surface sites had nearly the same sorption energies. Similar results were found for As sorption on hematite, goethite and magnetite (Mamindy-Pajany *et al.*, 2009). This behaviour of As can be ascribed to the formation of a direct chemical linkage to the surface of hematite due to a specific sorption mechanism, with the formation of surface inner sphere complexes (Dixit and Hering, 2003). Based on the values of Q_{max} increasing thiosulfate concentrations decreased the arsenic sorption, due to the great competition between the two anions for available sites. The highest value of the constant K for As alone adsorption isotherm indicates a greater availability of sites for adsorbing arsenate ion, which are reduced as the competing thiosulfate ion is
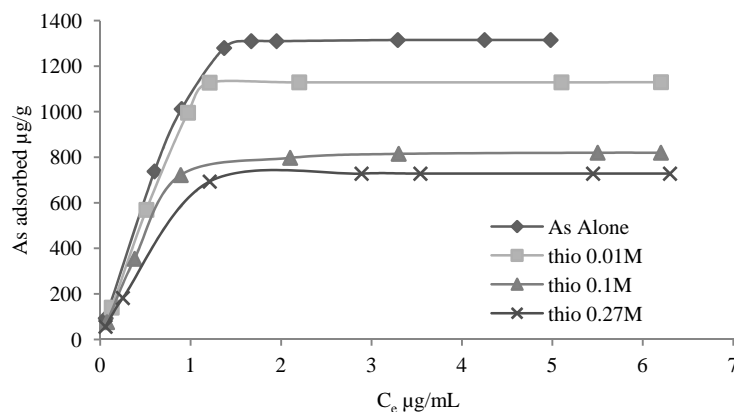
Fig. 1: As adsorption isotherms at increasing thiosulphate concentrations

Table 1: Parameters of the Langmuir equation obtained for As adsorption on hematite at pH 7.4 with and without thiosulfate addition

Solution	K mL/µg	Q_{max} µg/g	R^2
As alone	0.358	1398	0.990
As+Thio 0.01M	0.144	1070	0.997
As+Thio 0.1M	0.084	824	0.993
As+Thio 0.27M	0.075	736	0.996

Table 2: Parameters of the Langmuir equation obtained for As adsorption on hematite at pH 7.4 in presence of increasing sulfate concentrations

Solution	K mL/µg	Q_{max} µg/g	R^2
As alone	0.358	1392	0.990
As+sulfate 0.01M	0.151	1025	0.989
As+sulfate 0.1M	0.087	810	0.994
As+sulfate 0.27M	0.070	751	0.995

adsorbed. The isotherm pattern would seem to show that arsenate adsorption is reduced by thiosulfate addition at any concentration.

The reduction percentage of the maximum arsenate adsorption produced by the thiosulfate competition calculated as:

$$Red~\% = 100~\frac{(Q_{maxAs} - Q_{max~As+Thio})}{Q_{max}}$$

Increased according to the thiosulfate concentration from 16% (Thio 0.01M), to 36% (Thio 0.1M), up to 46% (Thio 0.27M). This behavior is quite similar to the phosphate/arsenate competition found in several clay minerals and soils (Violante and Pigna, 2002).

Although caution is needed when comparing adsorption the great influence of thiosulfate on As adsorption strongly suggests that thiosulfate can substitute arsenate ions in the inner sphere complexes. As stated by Benjamin and Leckle (1982), in their seminal work on adsorption, thiosulfate ion can be considered as a sulfate ion and a sulfide ion linked by a double bond. Based on the similarity between sulfate adsorption and thiosulfate adsorption, when $S_2O_3^{2-}$ anion adsorbs to an oxide, the most likely orientation is

with the oxygen atoms bonding to surface metal ions. Thus, thiosulfate replaces arsenate on hematite by the sulfate part of the molecule, with oxygen atoms bonding to the surface Fe ions. This is also supported by NMR studies on thiosulphate-metal complexes, in which thiosulfate is coordinate with Fe (III) by two oxygen atoms (Trachevskii *et al.*, 2008).

Thus, the quite strong competitive effect of thiosulphate could be reasonably ascribed to a inner sphere complexation process, with the possible formation of monodentate non protonated surface complexes similar to those suggested at alkaline pH for phosphate complexation on goethite (Persson *et al.*, 1996) and hematite (Elzinga and Sparks, 2007). Figure 2 shows the inner sphere complexes that could be formed with both arsenate and thiosulphate with soil Fe oxides-hydroxide surfaces.

To confirm this hypothesis, the adsorption of As on hematite was repeated in presence of sulfate, instead of thiosulfate, with the same concentrations, 0.01M, 0.1 M and 0.27 M.

The As adsorption data can also be described in this case by a "L" type isotherm and the Langmuir parameters are very similar to that obtained for As adsorption with thiosulphate (Table 2). The very close values of binding constants strongly suggests that the interaction between hematite and sulfate and thiosulfate ions is of the same kind. Results are in accordance with findings on adsorption of the two anions, sulfate and thiosulphate, on chromium oxide/hydroxide (Degenhardt and McQuillan, 1999).

Infrared and X-ray spectroscopic studies have shown that sulfate can form both inner-sphere and outer-sphere surface species on Fe oxy/hydroxides, in relation to pH, ionic strength and surface coverage (Wijnja and Schulthess, 2000; Fukushi and Sverjensky, 2007). Following adsorption through the sulfate moiety of the thiosulfate molecule, due to the similarity with the behavior of the sulfate ion, our results suggest that the same type of complexes can be formed by
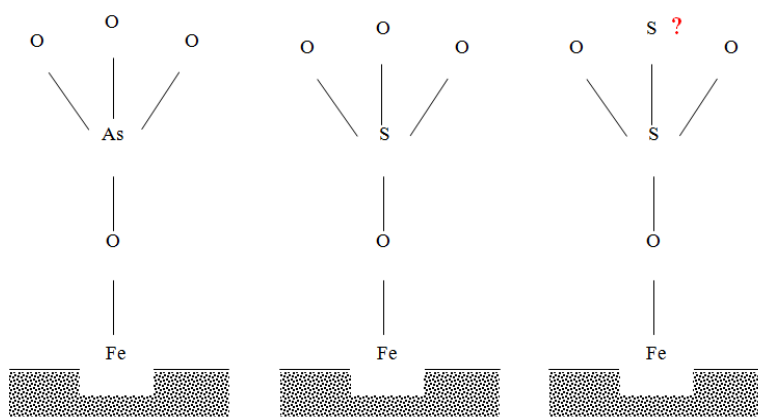
Fig. 2: Possible inner sphere complexes that could be formed with both arsenate and thiosulphate on hematite surfaces
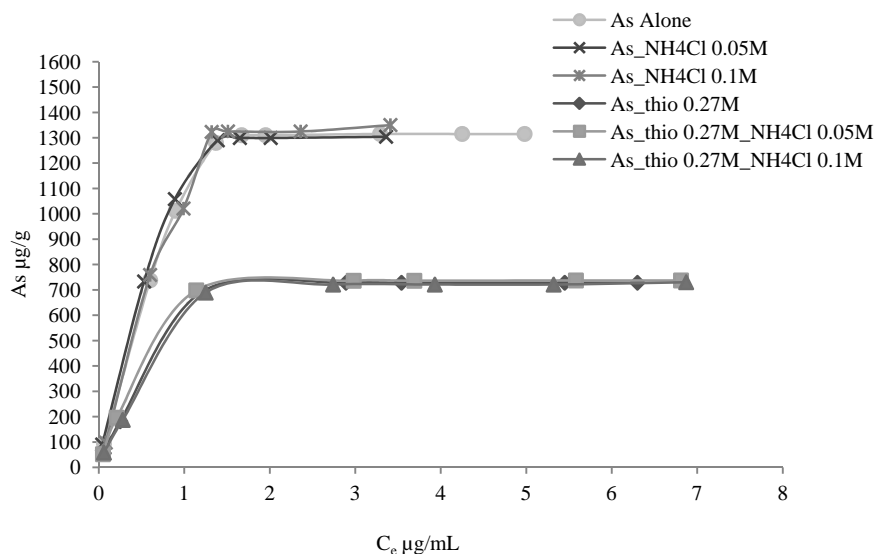

Fig. 3: As adsorption isotherms at increasing ionic strength with and without thiosulphate addition

thiosulfate, which thus replaces the arsenate on the surfaces of the iron oxides. The adsorption is likely to proceed through a ligand exchange mechanism and in this case all surface complexes formed can be inner-sphere complexes.

To further investigate the sorption competition between the two anions experiments were carried out with increasing ionic strength. The effect of ionic strength is considered as a measure of the relative contribution of Coulombic forces to the variation in free energy of the sorption process.

The adsorption isotherms of arsenate in presence of NH_4Cl at increasing concentrations are reported in Fig. 3.

The isotherm pattern clearly shows that there was no reduction in adsorption (upper curves), thus there was a negligible effect of ionic strength on the sorption of arsenate onto hematite. Although the occurrence of outer sphere complexes in the adsorption of As on

hematite has recently been reported (Catalano *et al.*, 2007a, b, 2008; Fukushi and Sverjensky, 2007), in our experimental conditions only inner sphere complexes seemed to occur, due to the absence of reduction in adsorption which should be expected when purely electrostatic linkages outer-sphere complexes are formed.

The same adsorption experiments with increasing ionic strength were carried out in the presence of thiosulfate (lower curves). The adsorption isotherms are identical to those shown in Fig. 1. The sharp decrease in arsenate adsorption can be ascribed to an increased competition in anion sorption with thiosulfate, with a negligible effect due to the increase in ionic strength.

The results obtained clearly show that the adsorbing behavior of thiosulfate and the competition with arsenate are comparable to that of strongly sorbing anions such as phosphate (Dzombak and Morel, 1990; Kanematsu *et al.*, 2013).

Table 3: Mean concentrations and standard deviations of As in plants of *Brassica juncea* and *Lupinus albus* growing in the contaminated soil. Data are expressed as mg/kg on a dry weight basis. CT are the control pots. Thio are thiosulfate treated pots (Rearranged from Petruzzelli *et al.*, 2014)

Plant	CT *B.juncea*	Thio *B.juncea*	CT *L.albus*	Thio *L.albus*
Shoots	n.d.	14.3±4.4	0.82±0.09	4.3±1.4
Roots	n.d.	54.3±4.4	1.6±0.60	14.2±3.2

Thiosulfate-arsenate adsorption competition in relation to phytoextraction: The nature of arsenic's behavior in the root zone depends largely on the interactions of As with soil components. The retention of As by the soil matrix influences its transport and bioavailability. Arsenate is mainly retained by Fe oxides, thus the competition between arsenate and thiosulfate for adsorption on Fe oxide surfaces may be of primary importance in determining the amount of As in soil solution and its bioavailability for plant uptake (Hartley and Edwards, 2004; Hartley and Lepp, 2008).

Thiosulfate ions competing for sorption on the same surface may significantly reduce the arsenate adsorption and enhance the mobility of arsenic in soil, similarly to the influence of phosphate on arsenate leaching (Peryea, 1991).

The addition of thiosulfate to soil is used in phytoextraction to enhance Hg uptake by plants (Moreno *et al.*, 2004, 2005; Pedron *et al.*, 2011, 2013). In a recent paper (Petruzzelli *et al.*, 2014) we showed that the addition of thiosulfate also promotes As phytoavailability in a multi-contaminated soil, thus increasing the As concentration both in the aerial and root portions of *Brassica juncea* and *Lupinus albus* (Table 3). In this phytoextraction experiment the same thiosulfate concentration as the adsorption experiments (0.27M) was used.

The results clearly showed an increase in As uptake after treatment with thiosulphate.

Bioavailability is the most important parameter which influences the plant uptake of arsenic, since only a fraction of total concentration is available for phytoextraction: the one in the soil solution. The As concentration in plants is a function of the root exposure to the bioavailable amount (E), which can be defined according to the following equation (Robinson *et al.*, 2006):

$$E = \int_0^z \int_0^t R_{(t,z)} C(M_{(t,z)}) d_t d_z$$

where,
z = The depth of soil explored by the roots
t = The exposure time
C = The bioavailable As concentration
M = The total As in soil
R = The root fraction that is in contact with the bioavailable amount C

The equation reveals that the distribution coefficient of arsenic K_d, defined as the ratio between As concentration in the solid and liquid phases, largely regulates the amount available for plant uptake. The increase in As concentration in plants (Table 3), is due to the competitive adsorption between thiosulfate and arsenate, which led to increasing concentrations of As into the soil solution. This statement is supported by the interpretation of the As adsorption process on hematite in terms of the distribution coefficient K_d (Fig. 4).

In the presence of thiosulfate the distribution coefficient of As tends to decrease. This behavior may be ascribable to a decrease in available adsorbing sites deriving from the competition between the two anions. The effect is particularly relevant with low additions of As when the molar concentration ratio of the two anions is low, while at higher As concentrations the pattern of K_d is less influenced by the presence of thiosulfate. The increase of As concentration in solution has a direct influence on the phytoextraction of the element, promoting the plant's uptake.

Iron oxides are among the most important components responsible for the reduction of arsenic
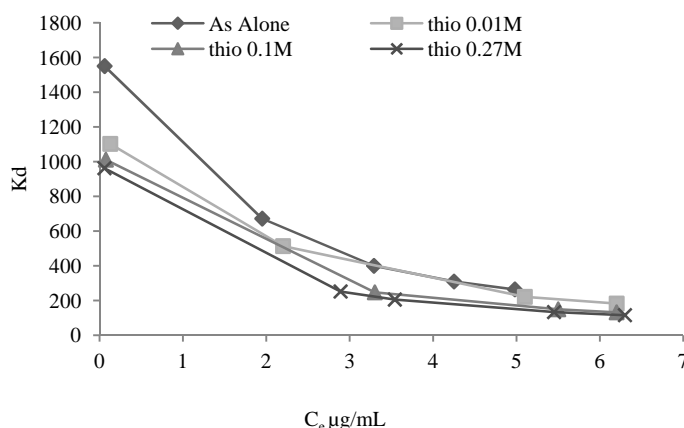
Fig. 4: Distribution coefficient K_d of As adsorption process at increasing thiosulfate concentration

mobility in soil (Dixit and Hering, 2003; Lenoble *et al.*, 2002). Many studies have reported that sorption behavior by single soil components and whole soil are generally similar (Violante and Pigna, 2002; Liu *et al.*, 1999), the behaviors of synthetic hematite and natural soil oxides are similar with similar sorption capacities and mechanisms (Gimenez *et al.*, 2007).

From the macroscopic adsorption data a complete understanding of the sorption mechanism is particularly difficult and it is not possible to conclusively identify all the kinds of complexes involved in the adsorption. In particular it should be defined which is the role of the S-S bonds (Fig. 2) in the adsorption processes need defining however this issue, which is of particular interest in the field of contaminated soils, can only be clarified by more detailed studies. Thus additional work is necessary, for instance using of spectroscopy techniques such as IR, extended X-ray absorption fine structure EXAFS, or resonance anomalous X-ray reflectivity RAXR.

In addition the data obtained from adsorption on hematite stimulate further research to better define the arsenate/thiosulfate competition for other soil surfaces. The results integrate opportunely those arising from phytoextraction tests of arsenic in the presence of thiosulfate (Petruzzelli *et al.*, 2014). They also confirm the possibility of using thiosulfate addition as a strategy in the clean-up by phytoextraction of multi-element contaminated soils.

REFERENCES

Benjamin, M.M. and M. Leckle, 1982. Effects of complexation by C1, SO4 and S203 on adsorption behavior of Cd on oxide surfaces. Environ. Sci. Technol., 76: 162-170.

Berg, M., H.C. Tran, T.C. Nguyen, H.V. Pham, R. Schertenleib and W. Giger, 2001. Arsenic contamination of groundwater and drinking water in Vietnam: A human health treat. Environ. Sci. Technol., 35: 2621-2626.

Catalano, J.G., Z. Zhang, C. Park, P. Fenter and M.J. Bedzyk, 2007a. Bridging arsenate surface complexes on the hematite (0 1 2) surface. Geochim. Cosmochim. Ac., 71: 1883-1897.

Catalano, J.G., P. Fenter and C. Park, 2007b. Interfacial water structure on the (0 1 2) surface of hematite: Ordering and reactivity in comparison with corundum. Geochim. Cosmochim. Ac., 71: 5313-5324.

Catalano, J.G., C. Park, P. Fenter and Z. Zhang, 2008. Simultaneous inner and outer-sphere arsenate adsorption on corundum and hematite. Geochim. Cosmochim. Ac., 72(8): 1986-2004.

Centeno, J.A., F.G. Mullick, L. Martinez, N.P. Page, H. Gibb and D. Longfellow, 2002. Pathology related to chronic arsenic exposure. Environ. Health Persp., 110: 883-886.

Degenhardt, J. and A.J. McQuillan, 1999. In situ ATR-FTIR spectroscopic study of adsorption of perchlorate, sulfate and thiosulfate ions onto chromium (III) oxide hydroxide thin films. Langmuir, 15: 4595-4602.

Dixit, S. and J. Hering, 2003. Comparison of arsenic (V) and arsenic (III) sorption onto iron oxide minerals: Implications for arsenic mobility. Environ. Sci. Technol., 37: 4182-4189.

Dzombak, D.A. and F.M.M. Morel, 1990. Surface Complexation Modeling: Hydrous Ferric Oxide. Wiley-Interscience, New York, pp: 393.

Elzinga, E.J. and D.L. Sparks, 2007. Phosphate adsorption onto hematite: An in situ ATR-FTIR investigation of effects of pH and loading level on the mode of phosphate surface complexation. J. Colloid Interf. Sci., 308: 53-70.

Fukushi, K. and D.A. Sverjensky, 2007. A surface complexation model for sulfate and selenate on iron oxides consistent with spectroscopic and theoretical molecular evidence. Geochim. Cosmochim. Ac., 71: 1-24.

Giles, C.H. and D. Smith, 1974. A general treatment and classification of the solute adsorption isotherm. J. Colloid Interf. Sci., 47: 755-765.

Gimenez, J., M. Martınez, J. de Pablo, M. Rovira and L. Duro, 2007. Arsenic sorption onto natural hematite, magnetite and goethite. J. Hazard. Mater., 141: 575-580.

Hartley, W. and R. Edwards, 2004. Arsenic and heavy metal mobility in iron oxide-amended contaminated soils as avaluated by short- and long-term leaching tests. Environ. Pollut., 131(3): 495-504.

Hartley, W. and N.W. Lepp, 2008. Remediation of arsenic contaminated soils by iron-oxide application, evaluated in terms of plant productivity, arsenic and phytotoxic metal uptake. Sci. Total Environ., 390: 35-44.

Kanematsu, M., T.M. Young, K. Fukushi, P.G. Green and J.L. Darby, 2013. Arsenic (III, V) adsorption on a goethite-based adsorbent in the presence of major co-existing ions: Modeling competitive adsorption consistent with spectroscopic and molecular evidence. Geochim. Cosmochim. Ac., 106: 404-428.

Lenoble, V., O. Bouras, V. Deluchat, B. Serpaud and J.C. Bollinger, 2002. Arsenic adsorption onto pillared clays and iron oxides. J. Colloid Interf. Sci., 255: 52-58.

Liu, F., J. He, C. Colombo and A. Violante, 1999. Competitive adsorption of sulfate and oxalate on goethite in the absence or presence of phosphate. Soil Sci., 164: 180-189.

Mamindy-Pajany, Y., C. Hurel, N. Marmier and M. Romeo, 2009. Arsenic adsorption onto hematite and goethite. CR. Chim., 12(8): 87-881.

Moreno, F.N., C.W.N. Anderson, R.B. Stewart and B.H. Robinson, 2004. Phytoremediation of mercury-contaminated mine tailings by induced plant-mercury accumulation. Environ. Pract., 6: 165-175.

Moreno, F.N., C.W.N. Anderson, R.B. Stewart, B.H. Robinson, M. Ghomshei and J.A. Meech, 2005. Induced plant uptake and transport of mercury in the presence of sulphur-containing ligands and humic acid. New Phytol., 166: 445-454.

Nickson, R.T., J. McArthur, W. Burgess, K.M. Ahmed, P. Ravenscorft and M. Rahman, 1998. Arsenic poisoning of Bangladesh groundwater. Nature, 395.

Nriagu, J.O., P. Bhattacharya, A.B. Mukherjee, J. Bundschuh, R. Zevenhoven and R.H. Loeppert, 2009. Arsenic in soil and groundwater: An overview. Trace Metals Other Contaminants Environ., 9: 3-60.

Pedron, F., G. Petruzzelli, M. Barbafieri, E. Tassi, P. Ambrosini and L. Patata, 2011. Mercury mobilization in a contaminated industrial soil for phytoremediation. Commun. Soil Sci. Plan., 42: 2767-2777.

Pedron, F., G. Petruzzelli, M. Barbafieri and E. Tassi, 2013. Remediation of a mercury-contaminated industrial soil using bioavailable contaminant stripping. Pedosphere, 23: 104-111.

Persson, P., N. Nilsson and S. Sjoberg, 1996. Structure and bonding of orthophosphate ions at the iron oxide-aqueous interface. J. Colloid Interf. Sci., 177: 263-275.

Peryea, F.J., 1991. Phosphate-induced release of arsenic from soils contaminated with lead arsenate. Soil Sci. Soc. Am. J., 50: 1176-1182.

Petruzzelli, G., F. Pedron, E. Tassi, E. Franchi, R. Bagatin, G. Agazzi, M. Barbafieri and I. Rosellini, 2014. The effect of thiosulphate on arsenic bioavailability in a multi contaminated soil: A novel contribution to phytoextraction. J. Environ. Earth Sci., 6(1): 786-791.

Robinson, B.H., R. Schulin, B. Nowack, S. Roulier, M. Menon, B. Clothier, S. Green and T. Mills, 2006. Phytoremediation for the management of metal flux in contaminated sites. For. Snow Landsc. Res., 80: 221-234.

Smedley, P.L. and D.G. Kinninburgh, 2002. A review of the source, behaviour and distribution of arsenic in natural waters. Appl. Geochem., 17: 517-568.

Sparks, D.L., 1998. Methods of Soil Analysis. Part 3 Chemical Methods, Soil Science Society of America Book Series. Soil Science Society of America, Madison, WI.

Trachevskii, V.V., S.V. Zimina and E.P. Rodina, 2008. Thiosulfate metal complexes. Russ. J. Coord. Chem., 34(9): 664-669.

Violante, A. and M. Pigna, 2002. Competitive sorption of Arsenate and phosphate on different clay minerals and soils. Soil Sci. Soc. Am. J., 66: 1788-1796.

Wijnja, H. and C.P. Schulthess, 2000. Vibrational spectroscopy study of selenate and sulfate adsorption mechanisms on Fe and Al (hydr) oxide surfaces. J. Colloid Interf. Sci., 229(1): 286-297.