Effect of natural organic matter on arsenic mobilization from mine tailings

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ABSTRACT

This research study was to elucidate the mechanisms of arsenic mobilization from mine tailings in the presence of natural organic matter (NOM). Humic acid (HA) was chosen as a model for NOM. The introduction of the HA at a low mass ratio (below 2 mg added HA/g mine tailings) inhibited arsenic mobilization under acidic conditions. Arsenic mobilization increased with increasing mass ratio. When pH was above 7, the addition of HA enhanced arsenic mobilization significantly. A mobilization isotherm was developed to predict arsenic mobilization from the mine tailings in the presence of HA. It was indicated that HA sorption to the mine tailings was essential for arsenic mobilization. HA might enhance arsenic mobility through formation of aqueous complexes, competition for adsorption and electrostatic interactions. Capillary electrophoresis analyses indicated that arsenic redox reactions might not have a significant effect on arsenic mobilization in this study. The mobilization of co-existing metals could enhance arsenic mobilization by helping incorporating it into soluble complexes in the presence of HA.

1. Introduction

Mine tailings enriched in arsenic and heavy metals have been considered as potential contamination sources [1]. It was estimated that about 10% of the total arsenic added to soils originates from mine tailings [2]. Arsenic exits essentially in the environment in four oxidation states (i.e., −III, 0, +III and +V) and forms various compounds. It has been established that the mobility and toxicity of arsenic are dependent on the chemical form and oxidation state in which it exists [1]. Inorganic arsenic species generally are more toxic and mobile than organoarsenic species, while arsenite [As(III)] is considered to be more toxic and mobile than arsenate [As(V)].

Prevalent in subsurface, natural organic matter (NOM) has demonstrated potential in influencing arsenic sorption behavior by interacting with mineral surfaces and/or with arsenic itself, and thus may play a substantial role in the release of arsenic from soils and sediments into groundwater [3–6]. Grafe et al. [5] demonstrated the competition between organic substances and arsenic for sorption to a crystalline iron oxide. Redman et al. [6] suggested NOM might greatly influence the redox condition as well as the complexation speciation of arsenic in freshwater environments. However,

more extensive investigations on various geological materials are required to achieve a thorough understanding. Further research is needed to evaluate the complex role of NOM on arsenic redox cycling. Moreover, the role of metal cations in the interaction between arsenic and NOM has not been elucidated well.

HA was chosen in this study as a model for NOM to evaluate its effects on arsenic mobilization from a Canadian mine tailings. The objectives of the kinetic batch tests were to examine the effects of pH, mass ratio of added HA to mine tailings and reaction time. The correlation between the mobilization of arsenic and co-existing metals in the mine tailings was monitored. The results and their implications on the release of arsenic from soils and sediments into groundwater and the remediation of arsenic contaminated sites are discussed.

2. Experimental materials and methods

2.1. Reagents

Arsenic trioxide, sodium metaarsenate and dimethylarsinic acid (DMAA) were purchased from Sigma, USA. Monomethylarsinic acid (MMAA) was purchased from Welck, USA. The reagents are of analytical grade. Acetic acid, sodium acetate (NaOAc), ammonium acetate (NH$_4$OAc), magnesium chloride (MgCl$_2$), hydroxylamine hydrochloride (NH$_2$OH·HCl), sodium phosphate dibasic anhydrous (Na$_2$HPO$_4$), nitric acid (HNO$_3$), hydrochloric acid (HCl), sodium hydroxide (NaOH), hydrogen peroxide (H$_2$O$_2$), ethylene glycol monoethyl ether (EGME) and sodium dodecyl sulphate (SDS) were purchased from Fisher Scientific Co. (Canada).

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2.2. Analytical methods

To determine the total arsenic concentration in the mine tailings, the mine tailings were first digested by aqua regia method. The extract was then diluted before measuring arsenic concentrations. The total arsenic concentration in solutions was determined by a Hach method (Hach-28228-00, Anachemia Canada Inc.). The detection limit is 10 μg/l. Good agreement was achieved between the data from the Hach method and ICP-MS analyses. Metal (i.e., Fe, Cu, Pb and Zn) concentrations were measured with an Atomic Absorption Spectrophotometer (PERKIN ELMER, AAnalyst 100, PerkinElmer Inc., Canada).

2.3. Fluka HA

A commercial and standardized HA (Fluka, Saint-Quentin Fallavier, France) was chosen as a model for NOM. It was used without any further purification.

2.4. Mine tailings

Samples of oxidized Pb–Zn mine tailings were collected from the top of the tailing piles in Bathurst, Canada. It was air-dried and homogenized through mixing. Its extractable Fe content was around 23.8%. The measured total arsenic, copper (Cu), lead (Pb) and zinc (Zn) concentrations were 2,180, 1,100, 12,860 and 5,075 mg/kg, respectively.

Particle size distribution analysis (ASTM method D422) [7] indicated that it could be classified as a sandy soil. Specific gravity was determined to be 3.65 (20 °C, ASTM method D854) [8]. Specific surface area measured by ethylene glycol monoethyl ether adsorption [9] was 1.84 m^2/g. The organic matter content based on weight loss after calcination at 550 °C was 4.67%. The pH of the mine tailings determined by using 1:2.5 (w/v) mine tailings with 0.01 M CaCl$_2$ [10] was 3.6. The cation exchange capacity determined through replacement of exchangeable cations by potassium acetate [11] was 10.38 cmol/kg.

2.5. Zeta potential measurement

Zeta potential of the mine tailings was determined by a Zeta Meter System 3.0 (Zeta-Meter Inc., USA) with an Automatic Sample Transfer System. Approximately 0.2 g of dried mine tailings (passing through a 200 mesh sieve) were added in 250 ml solutions (containing 100 mM NaCl as an electrolyte to maintain the ionic strength constant). The suspension was stirred on a magnetic stirrer. The pH of the solution was adjusted by 1N HCl or 1N NaOH. Measurements were performed 24 h after preparation of the suspension at room temperature. The applied voltage varied in the range of 50–200 mV. An average of 10–50 measurements was taken to determine the measured zeta potential.

2.6. Mineralogical analyses

X-ray powder diffraction (XRD) was applied to identify the existence of crystallized arsenic mineral phases. A Philip PW1710 diffractometer using Cu K$_\alpha$ radiation (λ = 15,418 Å) was employed (McGill University, Montreal, Canada). XRD patterns were collected over 3–60° θ. A step scanning technique with a fixed time of 0.5 s per 0.02° θ was adopted for the measurements.

Scanning electron microscopy–energy dispersive X-ray spectrometer (SEM–EDS) analysis were used to determine arsenic-containing phases in the mine tailings. The sample was examined at McGill University on a JEOL-JSM-840A Scanning Electron Microscope (JEOL, Tokyo, Japan) equipped with an energy dispersive

spectrometer. Analyses were carried out at an accelerating voltage of 20 keV.

2.7. Selective sequential extraction (SSE)

A SSE procedure based on Yong et al. [12] was applied. For each procedure, 2.0 g dried mine tailings sample used. Between each successive extraction, separation was made by centrifugation at 3000 rpm for 15 min. The supernatant was collected and the residue was washed with distilled water. Each extract and the rinse water associated were pooled together. Each of the fractions was collected and the concentrations of arsenic were determined. The amounts of arsenic extracted from the mine tailings by each of the extractants were then calculated.

The sequential extraction procedure that was used is as follows:

F1. Water soluble: 8 ml of distilled water or washing solution added, shaking at room temperature for 30 min;
F2. Exchangeable: 8 ml of 1 M MgCl$_2$, pH 7, 1-h shaking at room temperature;
F3. Carbonate associated: 8 ml of 1 M NaOAc, pH adjusted to 5 with acetic acid, 5-h shaking at room temperature;
F4. Oxide and hydroxide associated: 8 ml of 0.04 M NH$_2$OH·HCl in 25% (v/v) acetic acid, pH 2.5, at 96 °C in a water bath for 6 h;
F5. Organic matter and sulphide associated: 3 ml of 0.02 M HNO$_3$ and 5 ml of 30% H$_2$O$_2$ (pH 2) at 85 °C for 2 h, followed by 3 ml of 30% H$_2$O$_2$ (pH 2) at 85 °C for 3 h, and then 5 ml of 3.2 M NH$_4$OAc in 20% (v/v) HNO$_3$ diluted to 20 ml at room temperature for 30 min; and
F6. Residual fraction: digestion at 90 °C with 25 ml of dilute aqua regia (50 ml HCl + 200 ml HNO$_3$ + 750 ml water) for 3 h.

2.8. Batch tests

Batch tests were run to elucidate the effects of HA on arsenic mobilization from the mine tailings. The HA was dissolved in distilled water first, with the concentrations varied from 25 to 1200 mg/l. 20 ml solution and 2 g mine tailings (10:1, v/w) were added together into 50 ml polypropylene centrifuge tubes with varying the mass ratio of HA to mine tailings from 0.25 to 12 mg/g through changing HA concentration, pH, and reaction time. The mixtures were shaken at 60 rpm for a desired time period. The mixture was then centrifuged to separate the supernatant and mine tailing residue.

All batch tests were conducted at room temperature. The pH values (i.e., 3, 5, 7, 9 and 11) were adjusted by 1N NaOH or 1N HCl solutions which altered the volume by less than 2%. The deviation from the originally adjusted pH values was corrected by re-adjustment after a 1 h equilibration. Distilled water alone with pH adjustment was used to compare with HA. Though pH adjustment introduced HCl or NaOH into the solution at a concentration level of 1×10^{-3} to 1×10^{-11} M, the term "distilled water" was used in the text for convenience. The supernatants and residues were analyzed to determine the concentrations of arsenic and heavy metals. To determine the effect of reaction time, sampling was performed after every 6 or 12 h of shaking of the mixture of mine tailings and HA until a constant arsenic concentration was reached in the supernatant.

Mass balances were verified by comparing the sum of arsenic in the supernatant and residual arsenic in mine tailings with the initial amount of arsenic in the mine tailings. The mass balances were good during the batch experiments, though a little variation was observed. It might be caused by the analytical and operation errors, which were unavoidable but expected during the experiments.
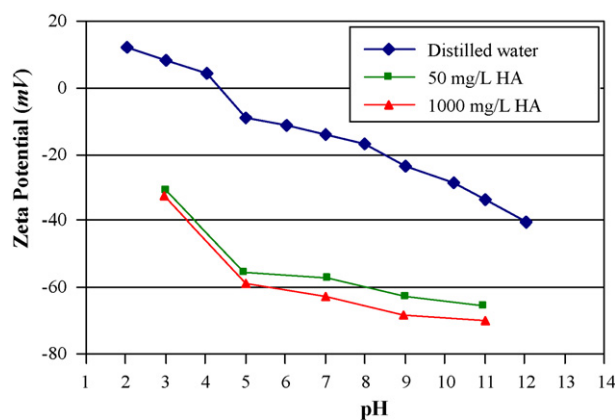
Fig. 1. Zeta potential measurement of the mine tailings.

Fig. 3. Effect of reaction time on arsenic mobilization.

2.9. Arsenic speciation by capillary electrophoresis (CE)

All CE separations were carried out on a Beckman P/ACE MDQ CE system (Beckman Coulter, Inc., California, USA) with direct UV detection. A fused-silica capillary tube ($70\,cm \times 75\,\mu m$ I.D., 61 cm effective length) was used. Stock solutions (1 g/l) were prepared by dissolving appropriate amounts of As(III), As(V), MMAA, and DMAA in distilled water. The buffer solution consisted of 15 mM Na_2HPO_4 adjusted to pH 6.5. 10 mM SDS was added as the electroosmotic flow (EOF) modifier.

The extracts from the batch tests were analyzed to examine the effect of HA on arsenic speciation. Before the separation procedure, the buffer solution and extracts were filtered through a 0.45-μm filter and degassed by vacuum. The samples were injected hydrostatically by a pressure of 3.45 kPa for 10 s. The capillary temperature was adjusted to 28 °C. A positive voltage of 25 kV on the injection side was applied for separation. The detection wavelength was 200 nm.

3. Results and discussion

3.1. Characterization of the tailings

The zeta potential of the mining tailings was evaluated as a function of pH. The negative zeta potential increased with an increase of pH, due to the ionization of acidic groups on the tailings surface (Fig. 1). The isoelectric point of the mine tailings was determined to be around 4.3. The introduction of HA decreased the zeta potential
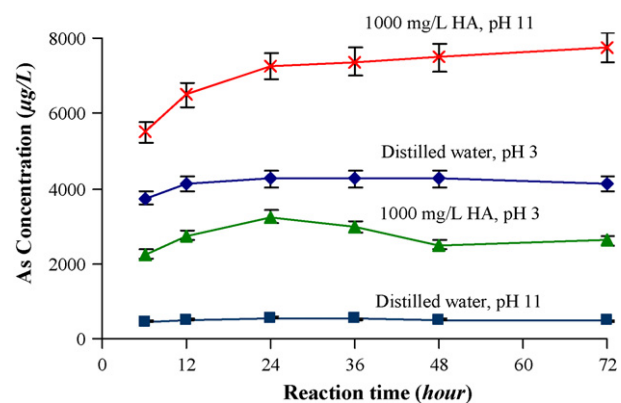
significantly. The zeta potential of the mine tailings became slightly more negative with an increase of the HA concentration from 50 to 1000 mg/l, probably due to the increased sorption of the HA on the mine tailings, which increased the density of negatively charged functional groups on the surfaces. The increased density of negative charges might enhance arsenic mobilization through repulsive electrostatic interactions [13,14].

The XRD analyses were performed to determine the presence of crystalline arsenic phases. However, none were found. This was not entirely unexpected probably due to the detection limits of this method (2–5 wt.%). SEM–EDS analyses detected possible arsenic-enriched particles in the mine tailings. The arsenic was detected mainly in association with Fe, Ca, Si, and S as well as O (Fig. 2).

3.2. Mobilization tests

3.2.1. Effect of reaction time

The effect of reaction time on arsenic mobilization from the mine tailings was examined with distilled water and HA. The pH value was adjusted to various values between 3 and 11. The equilibrium state was assumed to be reached when there was no significant effect of reaction time on the dissolved arsenic concentration. At pH 3, the equilibrium state of the distilled water–mine tailings system was reached after about 12 h, but for the HA–mine tailings system, a longer reaction time, more than 48 h, was required. At pH 11, the equilibration time was between 12 and 24 h (Fig. 3).

However, at pH 3, it was observed that the dissolved arsenic concentrations in the HA–mine tailing system increased with time
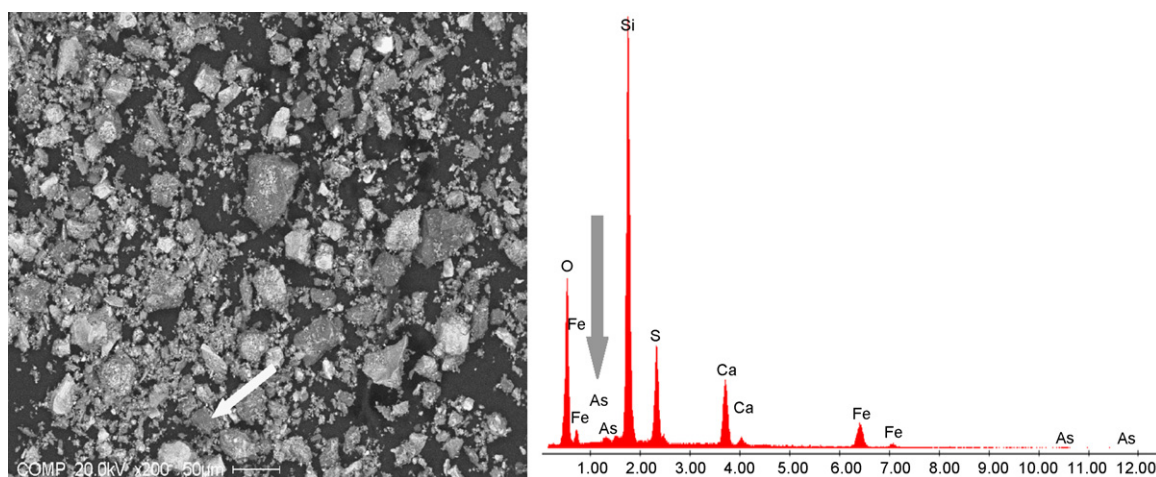

Fig. 2. SEM image and associated EDS spectrum of the mine tailings sample.

to 24 h, and then decreased and reached equilibrium after 48 h or longer. It indicated a portion of the dissolved arsenic anions might be re-adsorbed onto the HA adsorbed on the mine tailings or to the remaining mine tailings. Furthermore, the arsenic anions might adsorb onto HA first and then to the remaining surfaces of the mine tailings [15].

3.2.2. Arsenic mobilization by distilled water with adjusted pH

Batch tests with distilled water at different adjusted pH values (i.e., 3, 5, 7, 9, and 11) were used to examine the mobilization of arsenic from the mine tailings without additives. Arsenic was found to be most mobilized at pH 3 with distilled water (Fig. 4), probably due to the dissolution of the components of the mine tailings such as metal oxides, which released the associated arsenic. A high content of arsenic in the mine tailings and the high mobility of arsenic at low pH suggested that the mine tailings might impose a high risk to the surface- and groundwater quality under acidic conditions.

3.2.3. Arsenic mobilization by HA

The addition of HA under acidic to neutral conditions with a low mass ratio inhibited arsenic mobilization (Fig. 4). Compared to distilled water, even at pH 5 or 7, arsenic mobilization was inhibited by the addition of HA at a mass ratio of 0.25–1 mg/g, and it was enhanced when the mass ratio was above 2 mg/g. The addition of HA at pH 3 inhibited arsenic mobilization from the mine tailings significantly. Even when the mass ratio was 10 mg/g at pH 3, the concentration ratio (the ratio of arsenic mobilized by HA to that by distilled water at same adjusted pH) was 0.76. The decrease in arsenic mobilization by HA under acidic conditions might involve the sorption of HA to the mine tailings and the re-sorption of arsenic to the sorbed HA and to the remaining mine tailings. The results were consistent with the previous observation that HA could contribute more to the retention process of arsenic in acidic environments and to the formation of aqueous arsenic phases under alkaline conditions [16].

The mobilization of arsenic increased with the mass ratio of added HA to the mine tailings (Fig. 4). Especially, arsenic mobilization was significantly enhanced when the mass ratio was increased from 2 to 10 mg/g under alkaline conditions. However, increasing both the mass of mine tailings and added HA while keeping the same mass ratio (2 mg/g) increased the dissolved arsenic concentrations in the supernatants significantly, but had no significant effect on the portion of arsenic mobilized. This might indicate that arsenic mobilization by the HA was controlled mainly by the interaction between the HA and the mine tailings. HA sorption to the mine tailings was essential for the mobilization of arsenic. When the mass ratio was 10 mg/g at pH 11, arsenic was most mobilized, with a corresponding concentration ratio of 13.18.

3.2.4. pH-dependency

Arsenic mobilization in the presence of HA was evaluated at different values of pH. It was found to be highly pH-dependent (Fig. 3), due to the fact that the distribution of arsenic species and the development of surface charge on the solids are highly pH-dependent [4]. The formation of the OH_2^+, OH and O^- surface functional groups due to pH changes might have a significant effect on the adsorption of HA to the mine tailings and the interaction between arsenic and HA [17].

Low arsenic mobilization at pH 3 in the presence of HA (Fig. 3) might result from HA sorption to the mine tailings and the retention of arsenic to the sorbed HA through metal-bridging mechanisms. The mine tailings possessed a positive zeta potential at pH 3. HA might first be adsorbed to the mineral surfaces through hydrogen bonding and electrostatic interactions [5,13]. The dissolution of metal oxides in the mine tailings under acidic conditions provided more active adsorption sites for the HA. Arsenic might also be
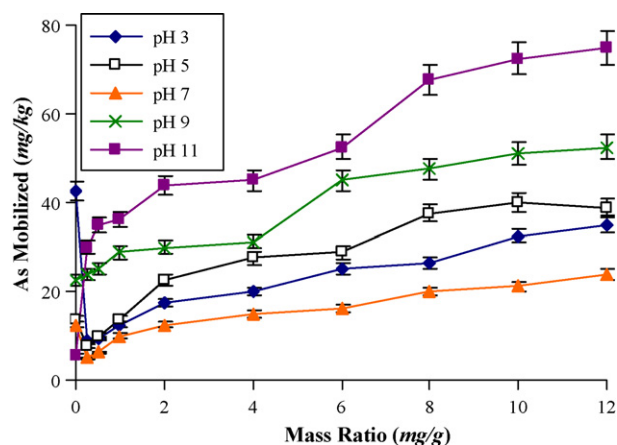

Fig. 4. Arsenic mobilization by HA as a function of mass ratio and pH.

released in this phase as a result of the dissolution of metal oxides, anion exchange and competition adsorption with the HA. Consequentially, the dissolved arsenic was re-adsorbed to the positively charged solid surface or to the organic matter by electrostatic interactions or forming inner-sphere complexes presumably through metal-bridging mechanisms [4,5,13].

When pH increased from 3 to 5, arsenic mobilization from the mine tailings was increased because the solubility of HA increased and the available metal cations were decreased due to pH increase. The mobilization of arsenic was decreased significantly at pH 7, probably due to the decrease of HA sorption to mine tailings [18]. High arsenic mobilization was observed when pH was greater than 7. Dissociation of HA and formation of soluble aqueous complexes contributed to the high arsenic mobilization. It was demonstrated that arsenic was mobilized the most by the HA at pH 11. Desorption of arsenic from Fe (hydro)oxides and the dissolution of organic matter in the mine tailings at high pH values might release associated arsenic, thus contributing to the high mobility of arsenic [19,20]. The adsorption of organic matter increased the density of negatively charged functional groups on the mineral surfaces, producing a greater repulsive interaction between the mine tailing surface or the organic matter surface and arsenic anions, thus leading to the increase of the mobilization of arsenic.

The formation of soluble arsenic–HA and/or arsenic–metal–HA complexes at high pH was another potential mechanism contributing to the high arsenic mobilization from the mine tailings. It has been proposed that HA is a supramolecular association, in which many relatively small and chemically diverse organic molecules form clusters linked by hydrogen bonds and hydrophobic inter-
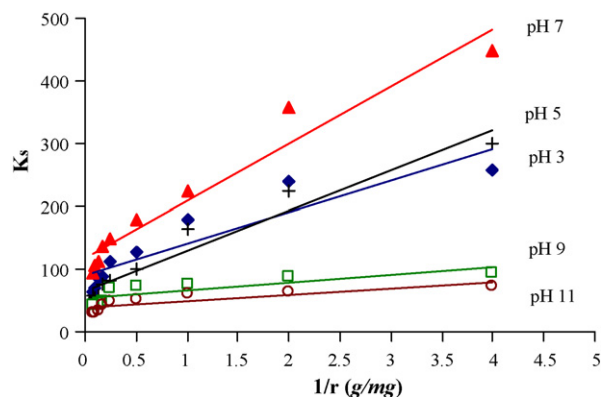

Fig. 5. Mobilization isotherms of arsenic from the mine tailings in the presence of HA at different pH values.

actions [21]. The supramolecular association dissociated into low molecular weight organic matter at high pH, which might form soluble complexes with arsenic. Moreover, Spark et al. [22] observed that the interaction between HA and metal cations resulted in the formation of soluble metal-humate species instead of the precipitation of metal hydroxides at pH above 8, which further prevented the re-precipitation of arsenic by adsorption to and/or co-precipitation with the hydroxides. It was also found that the solubility of the metal–HA complexes increased at high pH. Arsenic can be bound to the complexes through metal-bridging mechanisms or form aqueous complexes with HA directly [4,23], which might enhance arsenic mobilization from the mine tailings.

3.3. Arsenic mobilization modeling

The degree of arsenic mobilization can be described by a mobilization coefficient (K_s):

$$K_s = \frac{\text{residual mass of As in the tailings (mg/kg)}}{\text{mass of As in the aqueous phase (mg/kg)}} \quad (1)$$

The K_s, similar to the soil distribution coefficient in contaminant sorption studies [24], could be a useful predictor of the mobilization of arsenic, because it takes the residual arsenic concentrations in the mine tailings into consideration, which eliminates the effect of initial arsenic concentrations in the mine tailings.

By examining the experimental data from batch tests with HA, it was found that K_s fell into a linear relationship with the reciprocal of the mass ratio of added HA to mine tailings (r, mg/g) (Fig. 5). It can be expressed as

$$K_s = \frac{b}{r} + a \quad (2)$$

where $r > 0$, a is a dimensionless constant, and b is a sorption coefficient (mg/g). The coefficient b reflects the sorption extent of HA to the mine tailings.

This mobilization isotherm can be used to predict arsenic mobilization in the presence of HA. From the isotherm, it can be postulated that arsenic mobilization was mainly determined by the mass ratio of added HA to mine tailings and the sorption extent of HA to the mine tailings. It explains the observation that increasing the mass of both HA and mine tailings without changing the mass ratio did not significantly affect the portion of arsenic mobilized from the mine tailings.

3.4. Selective sequential extraction

Selective sequential extraction tests were performed to evaluate the fractionation of As among the soil fractions. It was indicated that arsenic in the mine tailings was of relatively low mobility, because water soluble and exchangeable arsenic levels accounted for less than 1% of the total arsenic, and the arsenic was concentrated (>90%) in the oxides, organic and residual fractions. Similar observations were reported in the mine tailings (abandoned Au–Ag and Au–Ag–Pb–Zn mines) of South Korea [25]. The low mobility of arsenic in the mine tailings could help reduce the bioavailability and then the toxicity of arsenic in the environment.

Arsenic was easily mobilized from the weakly bound and relatively more mobile fractions by the HA (Table 1). Almost all of the arsenic in the water soluble and exchangeable fractions was mobilized by HA washing. Arsenic in the fraction associated with carbonates was also mobilized by the HA due to the competition effect between arsenic and HA. It showed that HA was able to mobilize arsenic in the oxide associated fraction, probably through competition for adsorption sites and/or anion exchange between humate and arsenic. About 4.2% of the arsenic associated with the organic fraction was mobilized. Arsenic in the residual fraction was negligibly affected by HA. This could be expected, since arsenic in

Table 1
Percentage of arsenic mobilized from each fraction by washing with HA at a mass ratio of 10:1 at pH 11.

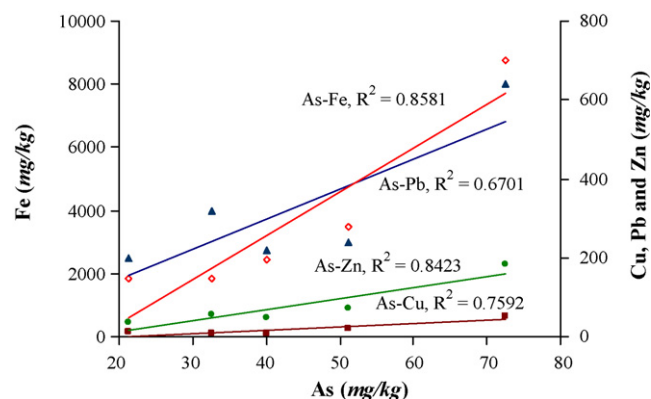| Fractions	Percentage
Water soluble	100.0%
Exchangeable	94.7%
Carbonate	21.4%
Oxide and hydroxide	1.6%
Organic matter and sulphide	4.2%
Residual	0.0%

Fig. 6. Correlation between arsenic and metal (Fe, Cu, Pb, and Zn) mobilization.

this fraction was of the most stable nature compared to that in other fractions.

3.5. Correlation between arsenic and metal mobilization

Correlations of the mobilization of arsenic with other metals were examined. The mobilization of arsenic was found to be closely related to the metals (i.e., Fe, Cu, Pb, and Zn) from the mine tailings in the batch test with a HA/mine tailings mass ratio of 10 (Fig. 6). The co-mobilization of arsenic and metals from the mine tailings indicated that the co-precipitation of arsenic and metals did not occur or was minimized. Aqueous arsenic and metals existed simultaneously in solutions. Therefore, the dissolved arsenic or metals must be incorporated into either soluble complexes. It further implicated that the mobilization of arsenic from the mine tailings was enhanced, to some extent, by the co-mobilization of the metals in the presence of HA.
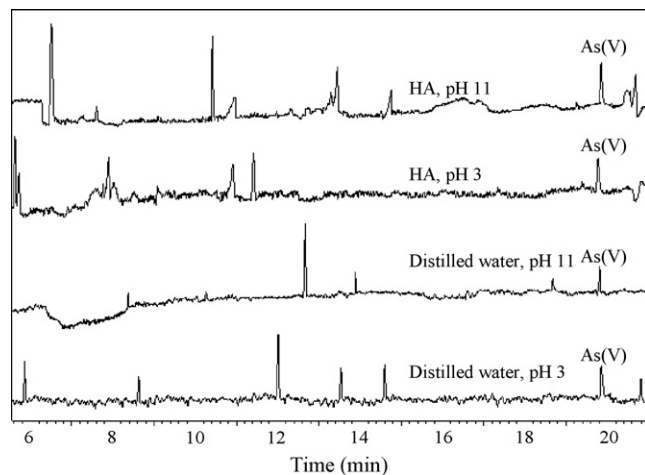

Fig. 7. Electropherograms of the mine tailings extracted by distilled water and HA at pH 3 and 11.

3.6. Arsenic speciation by CE analyses

CE analyses indicated that As(V) was the only water-soluble arsenic species from the mine tailings (Fig. 7), probably because the arsenic in the mine tailings has been oxidized completely and stabilized to As(V) due to the long-term on-site disposal. This was consistent with the previous observation that As(V) was the dominant oxidation state of arsenic in mine tailings [26].

Similarly, only As(V) was detected in the extracts by the HA, indicating that the HA did not incur the reduction of As(V) to As(III) or at least, the reduction reaction did produce a detectable level of As(III). Therefore, arsenic redox and methylation reactions might not play a significant role in arsenic mobilization from the mine tailings in the presence of HA in this study.

4. Conclusions and recommendations

The findings of this research study are important in advancing current understanding of the fate and transport cycle of arsenic in the environment and giving implications on the control of arsenic mobility. HA showed potential to influence arsenic mobile behavior by interacting with the mine tailings and with arsenic itself. Due to its ubiquity in the environment, HA may play an important role in the release of arsenic from soils and sediments into groundwater. The presence of HA may enhance arsenic release mainly through competition for available adsorption sites, formation of aqueous complexes under alkaline conditions and electrostatic interaction.

On the other hand, under acidic conditions, HA can help immobilize arsenic in soils and sediments by serving as a binding agent and forming insoluble complexes. Sorption of HA onto the solid surface may bind cations in solution and then re-adsorb arsenic onto the solid phases through metal-bridging mechanism. It may also reduce arsenic concentration in groundwater by transferring it into particulate phases. A direct result is the observation of decreasing arsenic mobilization from the mine tailings at pH 3 in this study. However, desorption and remobilization of the sorbed arsenic may occur when the site biological or physicochemical conditions such as pH and Eh change with time, thus releasing arsenic into groundwater.

This research study indicated that use of NOM in arsenic remediation may be developed as an environmentally benign and possible effective remedial option to reduce and avoid further contamination. HA could be used effectively to extract arsenic from soils, either *in situ* or *ex situ*, under alkaline conditions. It can also be used as a pretreatment for continuing treatment methods such as stabilization/solidification, bioremediation, or natural attenuation processes. Field demonstrations are required to evaluate the in-field performance and cost-effectiveness. Further efforts are required to develop applicable technologies for NOM recovery and recycle based on cost consideration.

Acknowledgments

References

[1] S. Wang, C.N. Mulligan, Occurrence of arsenic contamination in Canada: sources, behavior, and distribution, Sci. Total Environ. 366 (2006) 701–721.
[2] J.O. Nriagu, J.M. Pacyna, Quantitative assessment of worldwide contamination of air, water, and soil by trace metals, Nature 333 (1988) 134–139.
[3] S. Wang, C.N. Mulligan, Natural attenuation processes in remediating arsenic contaminated soils and groundwater, J. Hazard. Mater. 138 (2006) 459–470.
[4] S. Wang, C.N. Mulligan, Effect of natural organic matter on arsenic release from soil and sediments into groundwater, Environ. Geochem. Health 28 (2006) 197–214.
[5] M. Grafe, M.J. Eick, P.R. Grossl, Adsorption of arsenate(V) and arsenite(III) on goethite in the presence and absence of dissolved organic carbon, Soil Sci. Soc. Am. J. 65 (2001) 1680–1687.
[6] A.D. Redman, D. Macalady, D. Ahmann, Natural organic matter affects arsenic speciation and sorption onto hematite, Environ. Sci. Technol. 36 (2002) 2889–2896.
[7] ASTM (American Society of Testing Materials), Special procedure for testing soil and rocks for engineering purposes (D422-54), in: 1970 Annual Book of ASTM Standards, ASTM, Philadelphia, PA, 1970.
[8] ASTM (American Society of Testing Materials), Standard test method for specific gravity of soils, in: Annual Book of ASTM Standards, ASTM, Philadelphia, PA, 1999.
[9] D.L. Carter, M.M. Mortland, W.D. Kemper, Specific surface. In: A. Klute (Ed.), Methods of Soil Analyses: Part 1. Physical and Mineralogical Methods Agronomy Monograph, Soil Sci. Soc. Am., Madison, WI, 1986, pp. 413–423.
[10] R.K. Schofield, A.W. Taylor, The measurement of soil pH, Soil Sci. Soc. Am. Proc. 19 (1955) 164–167.
[11] S. Wang, Biosurfactant enhanced remediation of heavy metal contaminated soil, Master Thesis (M.A.Sc.), Concordia University, Montreal, Canada, 2003.
[12] R.N. Yong, A.M.O. Mohamed, B.P. Warkentin, Principles of Contaminant Transport in Soils, Elsevier, Amsterdam, 1992.
[13] B. Gu, J. Schmitt, Z. Chen, L. Liang, J.F. McCarthy, Adsorption and desorption of NOM on iron oxide: mechanisms and models, Environ. Sci. Technol. 28 (1994) 38–46.
[14] H. Jezequel, K.H. Chu, Removal of arsenate from aqueous solution by adsorption onto titanium dioxide nanoparticles, J. Environ. Sci. Health Part A 41 (2006) 1519–1528.
[15] A. Saada, D. Breeze, C. Crouzet, S. Cornu, P. Baranger, Adsorption of As(V) on kaolinite–HA complexes: role of HA nitrogen groups, Chemosphere 51 (2003) 757–763.
[16] P. Thanabalasingam, W.F. Pickering, Arsenic sorption by humic acids, Environ. Pollut. 12 (1986) 223–246.
[17] G. Sposito, The Surface Chemistry of Soils, Oxford University Press, UK, 1984.
[18] M. Grafe, M.J. Eick, P.R. Grossl, A.M. Saunders, Adsorption of arsenate and arsenite on ferrihydrite in the presence and absence of dissolved organic carbon, J. Environ. Qual. 31 (2002) 1115–1123.
[19] C.C. Fuller, J.A. Davies, G.A. Waychunas, Surface chemistry of ferrihydrite. Part 2. Kinetics of arsenate adsorption and coprecipitation, Geochim. Cosmochim. Acta 57 (1993) 2271–2282.
[20] D.G. Lumsdon, J.C.L. Meeussen, E. Paterson, L.M. Garden, P. Abderson, Use of solid phase characterization and chemical modeling for assessing the behavior of arsenic in contaminated soils, Appl. Geochem. 16 (2001) 571–581.
[21] B. Sutton, G. Sposito, Molecular structure in soil humic substances: the new view, Environ. Sci. Technol. 39 (2005) 9009–9015.
[22] K.M. Spark, J.D. Wells, B.B. Johnson, The interaction of a humic acid with heavy metals, Aust. J. Soil Res. 35 (1997) 89–101.
[23] J. Buschmann, A. Kappeler, U. Lindauer, D. Kistler, M. Berg, L. Sigg, Arsenite and arsenate binding to dissolved humic acid: influence of pH, type of humic acid, and aluminum, Environ. Sci. Technol. 40 (2006) 6015–6020.
[24] R.N. Yong, C.N. Mulligan, Natural Attenuation of Contaminants in Soils, CRC Press, Boca Raton, 2004.
[25] J. Kim, A.P. Davis, K.W. Kim, Stabilization of available arsenic in highly contaminated mine tailings using iron, Environ. Sci. Technol. 37 (2003) 189–195.
[26] D. Paktunc, A. Foster, G. Laflamme, Speciation and characterization of arsenic in Ketza river mine tailings using X-ray absorption spectroscopy, Environ. Sci. Technol. 37 (2003) 2067–2074.