Potential of Fe-Mn wastes produced by a water treatment plant for arsenic immobilization in contaminated soils

Karolina Lewińska [a],*, Anna Karczewska [b], Marcin Siepak [c], Bernard Gałka [b]

[a] Adam Mickiewicz University in Poznań, Institute of Physical Geography and Environmental Planning, ul. Bogumiła Krygowskiego 10, 61-680 Poznań, Poland
[b] Wrocław University of Environmental and Life Sciences, Institute of Soil Sciences and Environmental Protection, ul. Grunwaldzka 53, 50-350 Wrocław, Poland
[c] Adam Mickiewicz University in Poznań, Institute of Geology, ul. Bogumiła Krygowskiego 12, 61-606 Poznań, Poland

ABSTRACT

This work was aimed to examine the capability of Fe-Mn wastes produced by water treatment plant for arsenic sorption and immobilization in highly contaminated soils. In a batch experiment, As (III) and As (V) sorption on Fe-Mn wastes was examined at various initial concentrations of arsenic ($200–800 \, mg \, L^{-1}$), various pH conditions (pH in the range 4.5–9.5), and different contact time ($1 – 20 \, h$). Arsenic sorption depended on As species; and the amounts of As (III) adsorbed were by several fold higher compared to As (V). The maximum sorption capacity of As on Fe-Mn material was over $40 \, mg \, kg^{-1}$ at initial As (III) concentration $800 \, mg \, L^{-1}$ and shaking time 2 h (22 °C). Corresponding sorption capacity of As (V) in the same conditions was only $12.3 \, mg \, kg^{-1}$. The waste material was used in an incubation experiment with two highly contaminated soils collected from the area affected by former arsenic mining and processing. Total As concentrations in silt loam (soil I) and sandy loam (II) were 3619 and $1836 \, mg \, As \, kg^{-1}$, respectively. The Fe-Mn-rich wastes were applied to soils at the rates: 0.2, 1.0 and 5.0 g d.m. per 100 g (treatments: Fe1, Fe2, and Fe3, respectively), corresponding to 7.2, 36 and $180 \, Mg \, ha^{-1}$, respectively. Additionally, the effects of simultaneous sewage sludge application to soils were examined. Sewage sludge was applied at two rates, equivalent of 45 and $100 \, Mg \, d.m. \cdot ha^{-1}$ (SS1 and SS2). Soils were incubated for 5 months under changing water conditions (altering watering and drying), and thereafter As solubility in soils was determined in the extraction with $0.05 \, M \, (NH_4)_2SO_4$. Application of increasing doses of Fe-Mn wastes to both soils resulted in substantial decrease of As extractability. The presence of SS had apparently reverse impact on As solubility, and reduced the effect of immobilization particularly at lower rates of Fe-Mn wastes.

1. Introduction

In Poland, enhanced concentrations of arsenic in soils were reported from several sites, usually those situated in the surroundings of power plants or smelters, as arsenic is commonly present in various metal ores, including the ores of gold and copper (Matschullat, 2000). Extremely high concentrations of arsenic occur in soils of Zloty Stok, a town situated in the foothills of the Golden Mountains, a western part of the Sudety Mountains. For hundreds of years, gold and arsenic ores were mined and processed in this area. Mining activity, weathering of mine spoil material, smelting facilities and seepage from tailings impoundments were the main mechanisms to cause strong contamination of soils in large area, particularly in the valley of the Trujaca River

(Karczewska et al., 2013a). Nearly 50 years have passed since the factory was definitely closed in the mid-twentieth century, but contaminated areas have never been reclaimed.

Soils considerably polluted with arsenic occur in the world locally, for example in ore mining and processing sites (Mandal and Suzuki, 2002; Matschullat, 2000; Kabata-Pendias and Mukherjee, 2007; Karczewska et al., 2013a). Soil enrichment with As may cause serious environmental concern because of possible leaching of arsenic compounds into groundwater and surface waters. Therefore, highly contaminated soils should be remediated. Two different strategies of soil remediation may be applied to polluted soils: either immobilization of contaminants or decontamination. The latter approach may in some cases turn out unfeasible, and may cause temporarily detrimental effects to soil biota. Moreover, the technologies of soil decontamination are very expensive. On the contrary, the techniques of immobilization are widely used for remediation of polluted soils because of their low costs, low risk of side effects, and social acceptance. In addition, they have recently been accepted by legal regulations in many countries,

* Corresponding author.
E-mail address: karolina.lewinska@amu.edu.pl (K. Lewińska).

including Poland; and soil decontamination to the level of soil quality standards is no longer required (Karczewska, 2014).

Immobilization of toxic elements in soils usually involves modification of soil properties, mainly pH and sorption capacity. Soil liming is a commonly used treatment, applied as the first step for immobilization of pollutants, and then various additives, such as peat, ground lignite, zeolites, phosphates, iron and manganese compounds, etc., are introduced into soil in order to increase its sorption capacity. Finally, the surface of contaminated land should be covered with plants. Mineral and organic fertilizers are used to improve the effects of phytostabilization.

The methods of remediation considered for soils polluted with arsenic are not identical with those commonly used for soils polluted with heavy metals, as arsenic usually occurs in soil solution in anionic, and not in cationic, form. Unlike other metals, arsenic shows increasing solubility in alkaline conditions. Its solubility in soil depends on numerous factors, including pH (Sadiq, 1997; Karczewska et al., 2007), the amount and properties of organic matter (Harvey and Swartz, 2002), soil sorption capacity, the presence of phosphates (Mandal and Suzuki, 2002), and a redox potential related to water conditions (Bose and Sharma, 2002; Karczewska et al., 2007; Krysiak and Karczewska, 2011). Arsenic is strongly sorbed by Fe and Al oxides, and also by non-crystalline aluminosilicates and clay minerals (McBride, 1994; Sadiq, 1997). Moreover, soil amendment with organic matter - instead of reducing arsenic mobility, may promote its desorption from soils. Various bibliographic sources provide diverse data on that effect (Kalbitz and Wennrich, 1998; Harvey and Swartz, 2002; Karczewska et al., 2013b), therefore the changes of arsenic mobility in soils caused by application of various amendments should be thoroughly examined.

Recently, many studies have been carried out, in which various iron compounds or iron-rich wastes were tested as soil amendments, to immobilize arsenic present in soil or to precipitate arsenic from contaminated water. The technologies based on arsenic sorption on iron compounds seem to be of particular importance for arsenic removal from groundwater, and the results of studies reported from India, Chile, West Bengal or others countries, where arsenic concentration in drinking water exceed acceptable limits (Chakravarty et al., 2002; Mandal and Suzuki, 2002; Kabata-Pendias and Mukherjee, 2007), are quite encouraging. Several authors examined various types of wastes rich in iron and manganese for arsenic sorption (Choi et al., 2011; Wang and Tsang, 2013). The examples of such materials are waste cast iron, poorly-crystalline, phyllomanganate (Wu et al., 2015), ceria incorporated manganese oxide (NCMO) (Gupta et al., 2011), bagasse fly ash-iron coated char (BFA-IC) or sponge iron char (SIC) (Yadav et al., 2014).

One kind of the most commonly produced wastes, rich in iron, is the sludge from underground water treatment plants. High concentrations of Fe and Mn compounds, usually present in underground water, should be reduced in water treatment process because they cause technical problems in water supply facilities, as they get oxidized and precipitate rapidly inside water pipes. Furthermore, permissible concentrations of Fe and Mn in drinking water are limited (Minister of Health, 2007; WHO, 2014). Water treatment plants use a variety of technologies to remove Fe and Mn from water, and usually produce large amounts of wastes rich in Fe-Mn hydroxides and oxides. Such waste material may be considered for usage in remediation of soils contaminated with toxic elements, particularly those occurring in anionic forms, such as arsenic (Bose and Sharma, 2002; Matera et al., 2003; Warren et al., 2003).

This work was aimed to examine the capacity of waste material produced by a local water treatment plant to adsorb arsenic from a liquid phase and to immobilize arsenic in soils. The study of As adsorption from the liquid was based on the batch experiments with solutions containing dissolved salts of As (III) and As (V). Arsenic immobilization in soils was examined in soil incubation tests in which strongly polluted soils were amended with Fe-Mn waste or subjected to combined treatment with Fe-Mn waste and sewage sludge.

2. Materials and methods

2.1. Fe-Mn waste material

The Fe-Mn waste material was collected from Olesnica water treatment plant (Lower Silesia, Poland) with water production capacity of approx. 5400 m^3/day. The concentrations of Fe and Mn in raw water, collected from deepwater wells, considerably exceed permissible limits. Raw water has alkaline pH and is slightly mineralized. Groundwater treatment technology involves aeration followed by filtering process which creates a large quantity of sludge rich in Fe and Mn hydroxides. The waste material is disposed in the landfill. Basic properties of Fe-Mn wastes, important from the standpoint of potential arsenic sorption, were determined (Table 1). The content of total organic carbon in water waste material was determined by CNS-MAX (Vario) analyzer. "Pseudototal" concentrations of Fe and Mn and some heavy metals in waste material, were determined by atomic absorption spectrometry (SpectraAA 280FS and 280Z, Varian, Australia) after digestion with 60% perchloric acid (Chempur), in the open system with reflux. Mineralogical composition and structure of waste material was analysed using XRD (ARL X'tra, Thermo Electron) and Scanning Electron Microscope (Hitachi S-3700N).

2.2. Batch experiment

In a batch experiment, sorption of As (III) and As (V) on Fe-Mn rich waste material was examined at various initial concentrations of arsenic (200–800 mg L^{-1}), various pH conditions (pH in the range 4.5–9.5), and different contact time (1–20 h). A solution of 0.01 M sodium nitrate (NaNO$_3$) was used as a background electrolyte. Sodium arsenite (99.99%) (NaAsO$_3$) and sodium arsenate dibasic heptahydrate (> 98.00%) (Na$_2$HAsO$_4$·7H$_2$O) were used for solutions of As (III) and As (V), respectively. Standard acid and base solutions (0.1 M HCl and 1 M NaOH) were used for pH adjustment. All the reagents used in the experiment were of analytical grades.

The m:v ratio in the batch experiments was established as 1:100. The tests were carried out in 200-ml polyethylene bottles with 50 ml of As solution and 0.5 g of Fe-Mn material. The bottles were shaken overhead in the room temperature (22 °C ± 2 °C) with stable speed, ST = 280 ± 5 rpm, and then centrifuged and double filtered through paper filters (Munktell). Arsenic concentrations in solutions were measured by Inductive Coupled Plasma Mass Spectrometry (8800 QQQ model, Agilent Technologies, Japan).

2.2.1. Effect of pH

The initial As concentration in solutions was 200 mg L^{-1}. In order to adjust pH to various levels: 4.5; 5.5; 6.5; 7.5; 8.5 and 9.5, adequate amounts of 0.1 M HCl or 1 M NaOH were added under potentiometric pH control. The bottles were shaken (time: 2 h) at room temperature.

Table 1
Basic chemical properties of Fe-Mn wastes and sewage sludge used in the experiment.

Feature	Unit	Fe-Mn waste	Sewage sludge
Corg	%	±2.19[a]	33.5[b]
N$_{tot}$	%	±0.12	4.94
pH	–	±7.2	7.5
CEC	cmol kg^{-1}	8	43
Fe	mg kg^{-1}	±368,000	–
Mn	mg kg^{-1}	±7308	49.8
As	mg kg^{-1}	–	3.20
Pb	mg kg^{-1}	0.40	9.25
Zn	mg kg^{-1}	1.71	1055
Cu	mg kg^{-1}	8.05	65.0
Cd	mg kg^{-1}	2.60	–

[a] CNS (Vario MAX).
[b] CS MAT-5500.

After shaking, pH of the samples was measured. The samples were double filtered, and the concentrations of As in filtrates were determined.

2.2.2. Effects of different initial as concentration

The solutions containing various concentrations of As (III) and As (V) 200, 300, 400, 500, 600, 700 and 800 mg L^{-1} were used for this series of experiments. The tests were conducted at pH adjusted to 7.0 (± 0.5), with shaking time 2 h.

2.2.3. Sorption kinetics

The effects of shaking time on As adsorption were examined at initial As concentration of 200 mg L^{-1} and pH adjusted to 7.0 (± 0.5) was stable. The concentrations of As remaining in solutions were measured after different shaking time: 1, 2, 3, 4 and 20 h.

2.3. Incubation experiments

Incubation experiments were carried out with two highly contaminated soils collected from the valley of Trująca river (Karczewska et al., 2013a), amended with the Fe-Mn-rich wastes applied to soils at various rates. Additionally, the effects of simultaneous application of sewage sludge to soils were examined. For soil incubation, 100 ml plastic cups were filled with 100 g of air-dried soil and mixed with adequate amounts of Fe-Mn wastes: 0.2, 1.0 and 5.0 g d.m. per 100 g (treatments Fe 1, Fe 2 and Fe 3, respectively), corresponding with the rates of approx 0.72, 36 and 180 Mg d.m. ha^{-1}. Additional treatments involved sewage sludge application to waste-amended soils, in the amounts corresponding to 45 Mg d.m. ha^{-1} (SS 1) and 100 Mg d.m. ha^{-1} (SS 2). The amounts of SS added to each incubation cup filled with 100 g soil were: 6.51 and 14.4 g/cup, respectively. Control treatments (C), without amendments, were included in the experimental scheme. The experiment was carried out in changing water conditions, i.e. soils incubated in the cups were alternately flooded (filled with water to 100% of water capacity) and air-dried every two weeks, in order to mimic the conditions typical for soil sampling sites. The incubation process was carried out indoor, at room temperature, for 5 months. All treatments were examined in 3 replicates. Soluble forms of arsenic in soils after incubation were determined in extraction with 0.05 M (NH$_4$)$_2$SO$_4$ (1:25, shaking 4 h/20 °C, v:w = 1:25), as proposed in the first step of sequential extraction, according to Wenzel et al. (2001).

2.3.1. Soils.

Soil material used in the experiment was collected from two sites situated in the valley of Trujaca river, close to the town Zloty Stok. The site is located next to the Polish-Czech Republic border, at the foothills of Złote Mountains. In the past, Zloty Stok was the largest European centre of arsenic ore mining and processing. Soils in its surroundings were highly polluted by industrial emissions as well as via accidental release of tailings material from disposal sites (Karczewska et al., 2013a). Two samples of soil material were collected from the sites differing in the level of contamination. Soil material was air-dried and sieved to 2 mm prior to the experiment and analyses. Basic soil properties: grain size distribution, pH, and organic matter content were determined with commonly used methods (Tan, 2005). The content of total organic carbon in soils was determined by CS-MAT 5500 analyzer. Soil cation exchange capacity (CEC) was calculated as a sum of soil acidity and base cations BC, determined in extraction with ammonium acetate at pH 8.2. For analysis of total As and other heavy metals, soil material was digested in microwave (Milestone) with concentrate nitric acid (Merck) and the concentrations of As in digests were determined by ICP-MS (Agilent). The data characterizing soil properties are presented in Table 2.

2.3.2. Sewage sludge

Biochemically stabilized, composted sewage sludge used in incubation tests was collected from Sroda Slaska wastewater treatment plant

Table 2
Basic properties of soils used in the experiment.

Feature	Unit	Soil	
		I	II
Texture	–	Silt loam	Sandy loam
Clay content	%	6	3
Corg	%	3.12	2.95
pH (H$_2$O)	–	7.2	7.4
CEC	cmol·kg^{-1}	26.6	13.6
As	mg·kg^{-1}	3619	1836
Pb	mg·kg^{-1}	256	193
Zn	mg·kg^{-1}	142	128
Cu	mg·kg^{-1}	71	47

(Lower Silesia, Poland). Basic properties of sewage sludge were determined with the same methods as those used for soil analysis. The results are presented in Table 1.

2.4. Statistical analysis

For each treatment, the mean values, standard deviations (SD) and confidence ranges were calculated at the 0.05 probability level. Significance of differences between the means was checked on the basis of SD at the 0.05 probability level. Statistical analysis was performed by a software Excel XP 2007 (Microsoft).

3. Results and discussion

3.1. Properties of Fe-Mn waste material

The XRD analysis of Fe-Mn waste material showed, that material is built mainly of amorphous substances (Fig. 1) and due to its non-crystalline structure, any XRD reflexes were not detected. The SEM images of Fe-Mn waste samples are shown in Figs. 2 and 3. SEM analysis revealed that the surface of Fe-Mn waste grains is uneven and rough, which is well visible in the Fig. 3. Apparent lack of a crystalline structure, confirmed by SEM images, is consistent with XRD results. Similar SEM images of the same type of Fe-rich waste material was presented by Shih et al. (2015). The results of chemical analysis indicated high contribution of Fe compound in the wastes (Table 1). The material examined in this study contained on average 36.8% of Fe and 0.73% of Mn (the data refer to perchloric acid-digestible amounts). The concentrations of toxic heavy metals, including Cd and Pb, were low (Table 1), which should be considered as a beneficial feature of waste material intended to be used for soil remediation.

3.2. Batch experiments

Batch experiments were conducted to show sorption behavior of arsenic on Fe-Mn waste material as dependent on initial concentration of As in solution, pH and contact time (Figs. 3–5). The capacity of waste material to adsorb As(III) and As(V) was then compared. In the experiment with different initial concentrations of arsenic in solutions, carried out at pH adjusted to 7.0 (± 0.5), both As (III) and As (V) showed similar behavior, but the amounts of both As species removed from solution differed considerably (Fig. 3). The higher was initial As concentration, the lower efficiency of adsorption, expressed as percentage of As removed from solution. Maximum efficiency of As removal, i.e. 76%, was observed at the lowest concentration (200 mg L^{-1}) of As (III) (Fig. 3). Similar tendencies were described by Gupta et al. (2005) for As (III) in the batch experiment with iron oxide-coated sand. However, the concentrations of As in solutions were in our experiment by 3 orders of magnitude higher (200–800 mg L^{-1} vs. 100–800 μg L^{-1}), and consequently, the absolute amounts of As(III) adsorbed by the waste material were also by 3 orders higher than those reported by Gupta et al. (2005). The amounts of As (III) adsorbed by waste material at neutral pH were assessed in our
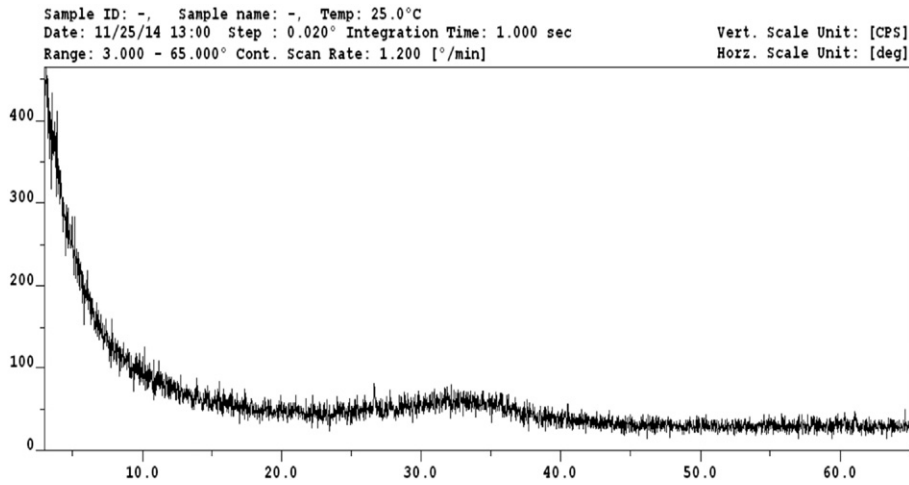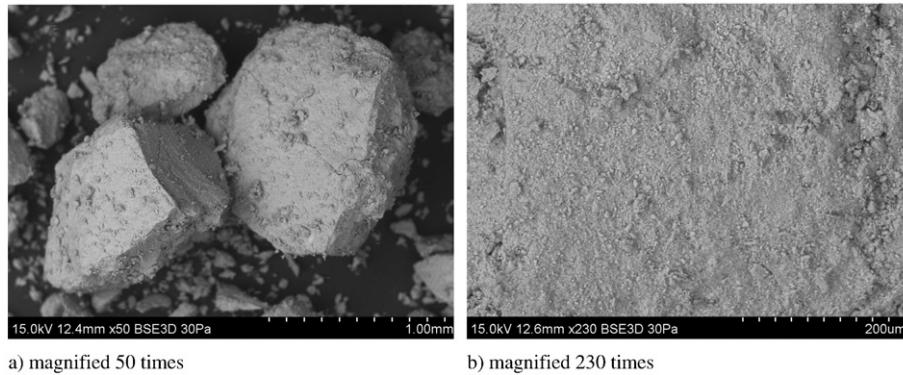
Fig. 1. XRD spectrum of Fe-Mn waste material.

a) magnified 50 times   b) magnified 230 times

Fig. 2. SEM images of Fe-Mn waste material used in the experiment. (a) ×50 (b) ×230 magnifications.

experiment in the range 15.2–41.3 mg g^{-1}, depending on initial As concentrations in solution (Fig. 3a). These values are comparable with, or even higher than As sorption capacity of goethite (Gräfe et al., 2002) or iron oxide-loaded porous slag material examined by Zhang and Itoh (2005).

As mentioned above, sorption efficiency of As (III) on Fe-Mn waste material was much higher than the efficiency of As(V) sorption in similar conditions (Figs. 3–5). The amounts of As (V) adsorbed by solid phase from 200 to 800 mg L^{-1} solutions were in the range 8.1–12.3 mg g^{-1}. In their experiment with waste cast iron, Choi et al. (2011) obtained similar results, i.e. the efficiency of As (V) sorption

was much lower compared to As(III) Yadav et al. (2014) who examined two kinds of waste material, rich and poor in iron oxides, reported different results, depending on the kind of material. The sponge iron industry wastes, rich in Fe, had much higher capacity of As(III) sorption, compared to As(V), which was similar to our results; whereas the ash from biofuel burning, poor in Fe, indicated higher capacity of As (V) sorption and was almost inefficient in As (III) removal from solution.

The series of batch experiments in which the kinetics of sorption was examined in the time of 1–20 h, indicated that As (III) and As (V) behaved similarly. Although the maximum As sorption was noted after the longest shaking time of 20 h, the fastest sorption was observed
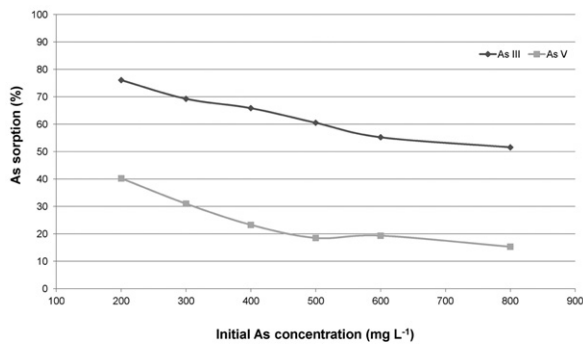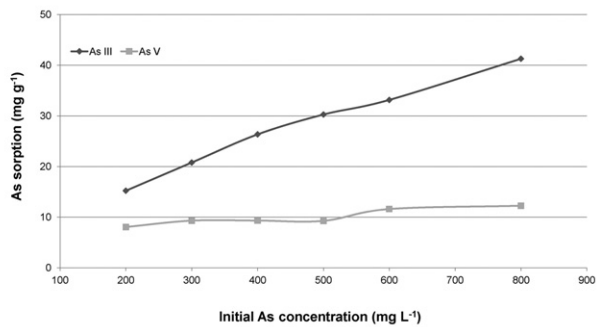
a) percent of initial concentrations   b) amounts of sorbed As, in mg g^{-1}

Fig. 3. As sorption from solutions differing in initial As concentrations. Time: 2 h, initial pH: 7.5. The graphs show the results of As adsorption from solution on waste material solid phase, expressed as a) percent of initial concentrations, b) amounts of sorbed As, in mg g^{-1}.
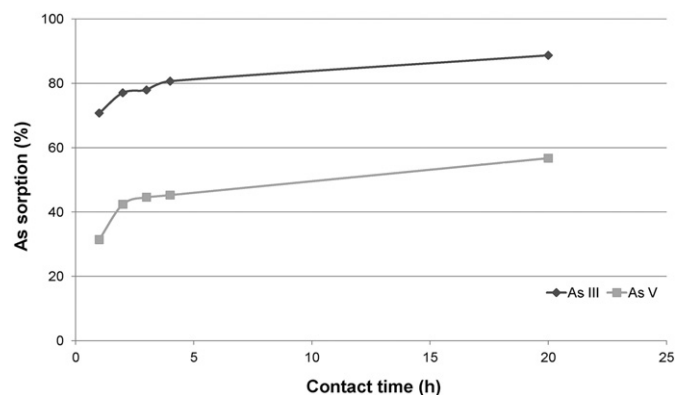
Fig. 4. Effects of time on As sorption. Initial As concentration in solution: 200 mg L^{-1}, pH = 7.5.

Fig. 6. Concentrations of easily soluble As in soil I amended with Fe-Mn wastes and different dosage of sewage sludge.

within the first 3 h of the experiment (Fig. 4). Similar results were also reported by Gupta et al. (2005), Yadav et al. (2014) and Wu et al. (2013), who confirmed that the fastest sorption of As on iron oxide-rich materials was observed within the first 3 h, and particularly within the first 100 min. of contact time.

The dependence of As(III) and As(V) sorption on Fe-Mn waste material on the pH of solution is presented in Fig. 5. The efficiency of As(III) sorption turned out to be almost independent on pH within a broad range of pH values 4.5–8.5, and increased slightly at pH above 8.5. The behavior of As(V) was quite different. The highest efficiency of As(V) removal from solution was observed in acidic conditions (pH 4.5–5.5) while at higher pH, in the range pH 5.5–7.5, a considerable decrease in the capacity of As (V) sorption was observed with increasing pH value. Several other authors reported similar effects of pH on arsenate sorption by Fe-rich materials from a liquid phase. Nagar et al. (2010) who examined As (V) sorption in drinking-water treatment and Basu and Ghosh (2013) in their experiments with nanostructured iron(III)–cerium(IV) mixed oxides, confirmed decreasing efficiency of As(V) adsorption with increasing pH.

To sum up, the results of batch experiments confirmed that the Fe-Mn rich waste material produced by water treatment plant has a very high capacity of arsenic sorption from liquid phase, that remains high enough in a broad range of pH between 4.5 and 9.5. The efficiency of As(III) sorption is by several fold higher compared to As(V), but this effect should be assessed as advantageous if considering that the toxicity of As(III) to biota is much higher than the toxicity of As(V) species (Mandal and Suzuki, 2002; Kabata-Pendias and Mukherjee, 2007). The processes of arsenic sorption on Fe-Mn rich waste material run considerably fast, and therefore this material should be considered as potential amendment arsenic immobilization in contaminated soils.
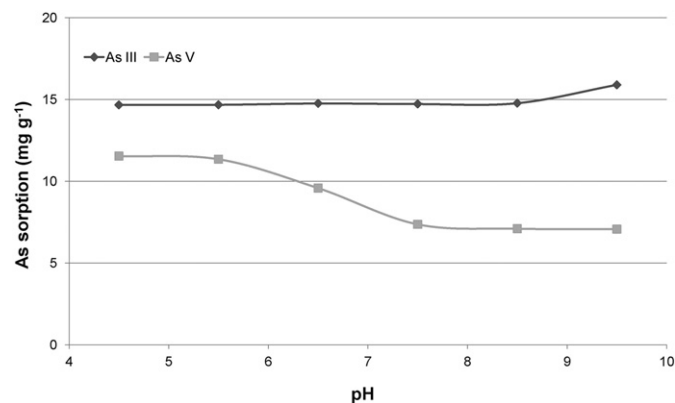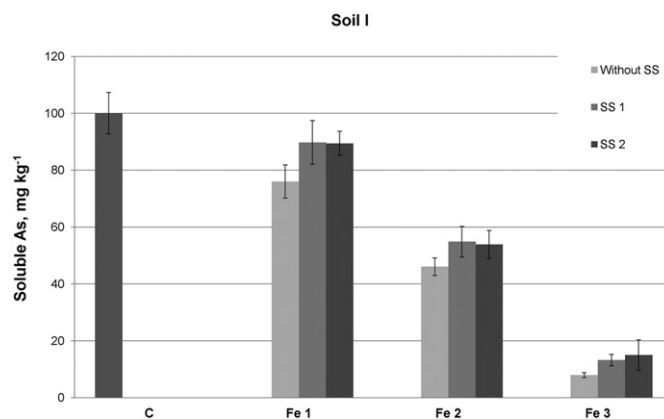
3.3. Incubation experiment

Two kinds of soil material used in the experiment differed substantially in their basic properties and arsenic concentrations (Table 2). Soil I had a heavier texture (silty loam) than soil II (sandy loam), consequently its CEC value was twice as high as that of soil I (26.6 vs. 13.6 cmol·kg^{-1}). Total arsenic concentrations in soils I and II were 3619 and 1836 mg As kg^{-1}, respectively. Such high concentrations exceed by two orders of magnitude the values of Polish soil quality standards, established at the level of 20 mg As kg^{-1} for the lands used for agriculture or forestry. The amounts of soluble arsenic in soils I and II, determined in extraction with 0.05 M $(NH_4)_2SO_4$, differed dramatically, and were: 98.0 and 0.5 mg As kg^{-1}, which corresponded to 1.6% and 0.03% of total arsenic concentrations in soils, respectively. Relatively high extractability of As in the soil I, in spite of its heavier texture, higher CEC and higher content of Corg, should be explained by much higher total As concentration in soil.

The amendment of soils with Fe-Mn wastes caused a considerable, statistically significant, decrease in arsenic solubility in both soils, compared to control (Figs. 6 and 7). Reduction of arsenic extractability in soils depended on the rate of waste material added, and was the highest at the highest dose of wastes, i.e. 5 g Fe-Mn material per 100 g (treatment Fe 3). The amount of easily extractable As in soil I decreased in that case by 96% compared to non-amended soil illustrated by control treatment (Fig. 6). Similar effects were described in our previous experiment with arsenic-polluted soils treated with iron nitrate Fe(NO$_3$)$_3$ (Karczewska et al., 2013b).

Fig. 5. Effects of pH on As sorption from the solutions at initial As concentration 200 mg L^{-1}. Sorption time: 2 h.
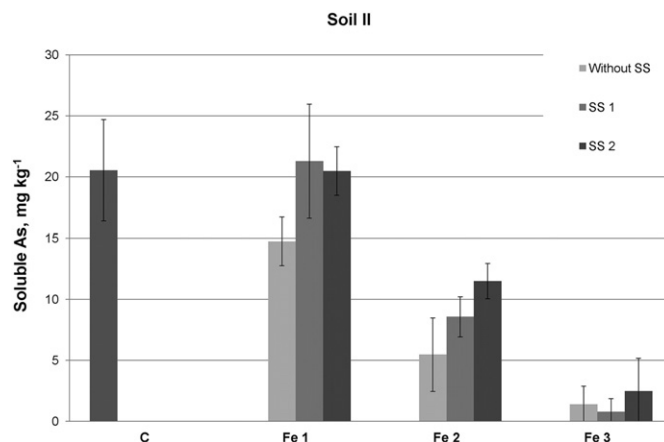

Fig. 7. Concentrations of easily soluble As in soil II amended with Fe-Mn wastes and different dosage of sewage sludge.

Simultaneous application of sewage sludge to the soils treated with Fe-Mn wastes material had apparently reverse impact on As solubility, and reduced the effect of immobilization, particularly at lower rates of Fe-Mn wastes Fe1 and Fe 2. Comparison of the effects observed in the case of soils I and II, indicated that adverse effect of sewage sludge on As solubility in Fe-Mn waste-amended soils was more strongly pronounced in soil II (Fig. 7), which was apparently related to its lighter texture and lower specific surface.

An overall effect of combined soil treatment with sewage sludge and iron rich wastes was unquestionable at higher waste rates. Soil amendment with combinations of sewage sludge and Fe-Mn wastes caused a significant decrease of arsenic solubility compared to non-amended soils. This effect was particularly well pronounced in the treatments with the highest dose of Fe-Mn wastes (Fe 3).

The outcomes of various studies that examined the influence of organic matter on arsenic solubility in soils are much more ambiguous; and the processes governing arsenic mobilization vs. immobilization by organic matter are not sufficiently understood. Humic substances considerably improve soil sorption properties, and therefore their application to soils should cause immobilization of arsenic present in easily soluble forms. On the other hand, however, arsenic compounds, such as arsenates or arsenites (As III and V), may compete with organic matter for the places in sorption complex, and consequently, the release of arsenic to soil solution may be observed as a result of this competition (Kalbitz and Wennrich, 1998). The risk of arsenic mobilization increases considerably when the organic matter introduced into soil contains low-molecular organic compounds, such as citrates or oxalates (Mohapatra et al., 2005). Such compounds usually occur in fresh, non-stabilized organic soil improvers, such as sewage sludge. This effect explains well the results of our study, i.e. increased arsenic solubility in sewage sludge and Fe-Mn treated soils, compared to the soils treated with Fe-Mn alone. It should be mentioned, however, that some experiments described in the literature brought about quite opposite results. For instance, Gräfe et al. (2002) reported reduced arsenic mobility in soils under the influence of citric and fulvic acids. Therefore, in perspective of soil remediation with organic materials, it seems necessary to carry out preliminary incubation tests in the laboratory that will be helpful in predicting the behavior of As in soils, as dependent on soil properties, As concentrations and other conditions.

4. Conclusions

The Fe-Mn waste material examined in this study showed high capacity of arsenic sorption properties, up to 41.3 mg g^{-1} and 12.3 mg g^{-1} in the case of As(III) and As(V), respectively. All the batch experiments confirmed higher sorption of As(III) compared to As(V).

The effects of pH on the efficiency of As(III) sorption on Fe-Mn waste material should be considered as negligible, while in the case of As (V), the increase of pH in the range 5.5–7.5 causes significant reduction of sorption capacity, which can affect further arsenic behavior in soils.

Application of Fe-Mn wastes to the soils strongly contaminated with arsenic turned out to be an effective treatment to cause arsenic immobilization. This effect was obtained even with the lowest dose of wastes applied to soils, and arsenic extractability in soils decreased with increasing dose of waste material.

Sewage sludge application to arsenic-polluted soils reduced the effect of As immobilization by Fe-Mn wastes, particularly at lower rates of wastes introduced to soils. This effect should be taken into consideration when planning soil remediation with organic materials.

Acknowledgments

References

Basu, T., Ghosh, U.C., 2013. Nano-structured iron(III)–cerium(IV) mixed oxide: synthesis, characterization and arsenic sorption kinetics in the presence of co-existing ions aiming to apply for high arsenic groundwater treatment. Appl. Surf. Sci. 283, 471–481.

Bose, P., Sharma, A., 2002. Role of iron in controlling speciation and mobilization of arsenic in subsurface environment. Water Res. 36 (19), 4916–4926.

Chakravarty, S., Dureja, V., Bhattacharya, G., Maity, S., Bhattacharjee, S., 2002. Removal of arsenic from groundwater using low cost ferruginous manganese ore. Water Res. 36 (3), 625–632.

Choi, N.C., Kim, S.B., Kim, S.O., Lee, J.W., Park, J.B., 2011. Removal of arsenate and arsenite from aqueous solution by waste cast iron. J. Environ. Sci. 24 (4), 589–595.

Gräfe, M., Eick, M.J., Grossl, P.R., Saunders, A.M., 2002. Adsorption of arsenate and arsenite of ferrihydrite in the presence and absence of dissolved organic carbon. Environ. Pollut. 31, 1115–1123.

Gupta, V.K., Saini, V.K., Jain, N., 2005. Adsorption of As (III) from aqueous solutions by iron oxide-coated sand. J. Colloid Interface Sci. 288, 55–60.

Gupta, K., Bhattacharya, S., Chattopadhyay, D., Mukhopadhyay, A., Biswas, H., Dutta, J., Ray, N.R., Ghosh, U.C., 2011. Ceria associated manganese oxide nanoparticles: synthesis, characterization and arsenic (V) sorption behavior. Chem. Eng. J. 172, 219–229.

Harvey, C.F., Swartz, C.H., 2002. Arsenic mobility and groundwater extraction in Bangladesh. Science 298, 1602–1606.

Kabata-Pendias, A., Mukherjee, A.B., 2007. Trace Elements From Soil to Human. Springer Verlag, Berlin–Heidelberg, Germany.

Kalbitz, K., Wennrich, R., 1998. Mobilization of heavy metals and arsenic in polluted wetland soils and its dependence in dissolved organic matter. Sci. Total Environ. 209, 27–39.

Karczewska, A., 2014. Historically contaminated sites and their remediation in the light of act on environmental protection amended in 2014 – selected cases from south-western Poland. Zeszyt Nauk UP Wroc., Rol. CXI. 607, pp. 51–62.

Karczewska, A., Bogda, A., Krysiak, A., 2007. Arsenic in soils in the areas of former arsenic mining and processing in Lower Silesia, SW Poland. In: Bhattacharya, P., Mukherjee, A.B., Loeppert, R.H. (Eds.), Arsenic in Soil and Groundwater Environments: Biogeochemical Interactions. Elsevier Book Series: Trace Metals and Other Contaminants in the Environment vol. 9, pp. 411–440 (Series Editor: Jerome O. Nriagu, Chapter 16).

Karczewska, A., Krysiak, A., Mokrzycka, D., Jezierski, P., Szopka, K., 2013a. Arsenic distribution in soils of a former As mining area and processing. Pol. J. Environ. Stud. 22 (1), 175–181.

Karczewska, A., Lewińska, K., Gałka, B., 2013b. Arsenic extractability and uptake by velvetgrass Holcus lanatus and ryegrass Lolium perenne in variously treated soils polluted by tailing spills. J. Hazard. Mater. 262, 1014–1021.

Krysiak, A., Karczewska, A., 2011. Effects of soil flooding on arsenic mobility in soils in the area of former gold and arsenic mining in Zloty Stok. Soil Sci. Annu. 62 (2), 240–248.

Mandal, B.K., Suzuki, K.T., 2002. Arsenic round the world: a review. Talanta 58 (1), 201–235.

Matera, V., Le Hécho, I., Laboudique, A., Thomas, P., Tellier, S., Astruc, M., 2003. A methodological approach for the identification of arsenic bearing phases in polluted soils. Environ. Pollut. 126, 51–64.

Matschullat, J., 2000. Arsenic in the geosphere – a review. Sci. Total Environ. 249, 297–312.

McBride, M.B., 1994. Environmental Chemistry of Soils. Oxford University Press.

Minister of Health, 2007. Regulation of 29.03.2007 on Drinking Water Quality (Dz. U. 2007, No 61, 417) (in Polish).

Mohapatra, D., Singh, P., Zhang, W., Pullammanappallil, P., 2005. The effect of citrate, oxalate, acetate, silicate and phosphate on stability of synthetic arsenic-loaded ferrihydrite and Al-ferrihydrite. J. Hazard. Mater. 124 (B), 95–100.

Nagar, R., Sarkar, D., Makris, K.C., Datta, R., 2010. Effect of solution chemistry on arsenic sorption by Fe- and Al-based drinking-water treatment residuals. Chemosphere 78, 1028–1035.

Sadiq, M., 1997. Arsenic chemistry in soils: an overview of thermodynamic predictions and field observations. Water Air Soil Pollut. 93, 117–136.

Shih, Y.-J., Huang, R.-L., Huang, Y.-H., 2015. Adsorptive removal of arsenic using a novel akhtenskite coated waste goethite. J. Clean. Prod. 87, 897–905.

Tan, K.H., 2005. Soil Sampling, Preparation, and Analysis. second ed. CRC Press, USA.

Wang, Y., Tsang, D.C.W., 2013. Effects of solution chemistry on arsenic (V) removal by low-cost adsorbents. J. Environ. Sci. 25 (11), 2291–2298.

Warren, G.P., Alloway, B.J., Lepp, N.W., Singh, B., Bochereau, F.J.M., Penny, C., 2003. Field trials to assess the uptake of arsenic by vegetables from contaminated soils and soil remediation with iron oxides. Sci. Total Environ. 311, 19–33.

Wenzel, W.W., Kirchbaumer, N., Prochaska, T., Stingeder, G., Lombi, E., Adriano, D.C., 2001. Arsenic fractionation in soils using improved sequential extraction procedure. Anal. Chim. Acta 436, 309–332.

World Health Organization, 2014. Drinking water quality. http://www.who.int/water_sanitation_health/dwq/en/.

Wu, K., Liu, R., Li, T., Liu, H., Peng, J., Qu, J., 2013. Removal of arsenic (III) from aqueous solution using a low-cost by-product in Fe-removal plants-Fe-based backwashing sludge. Chem. Eng. J. 226, 393–401.

Wu, Y., Li, W., Sparks, D.L., 2015. The effects of iron (II) on the kinetics of arsenic oxidation and sorption on manganese oxides. J. Colloid Interface Sci. 457, 319–328.

Yadav, L.S., Mishra, B.K., Kumar, A., Paul, K.K., 2014. Arsenic removal using bagasse fly ash-iron coated and sponge iron char. J. Environ. Chem. Eng. 2, 1467–1473.

Zhang, F.S., Itoh, H., 2005. Iron oxide-loaded slag for arsenic removal from aqueous system. Chemosphere 60 (3), 319–325.