Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2019.24126

157 (2019) 138–147
July

Immobilization of arsenic compounds by bog iron ores

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Received 30 May 2018; Accepted 16 March 2019

ABSTRACT

Bog iron ores are known for their sorption properties regarding heavy metals. However, they have not been commonly used as sorbents of arsenic compounds. The aim of this study was to investigate As(III) and As(V) immobilization by bog iron. The tests included varying initial As concentrations (0.01–20 mM), and initial pH values (2–12), and also sorption experiments to evaluate the competition between both As(III) and As(V) and heavy metal cations. The results showed that As removal by bog iron ores depends on the oxidation state of As—the removal of As(V) is lower than the removal of As(III). Immobilization of As was the most effective at medium initial concentrations of As (0.25–1 mM) in a slightly acidic or neutral pH environment. Competitive sorption experiments revealed that the occurrence of several ions in the solution significantly affects the sorption effectiveness. The bonding strength of As with a bog iron ore surface was estimated on the basis of three-step desorption experiments. Desorption of As resulted in the extraction of less than 50% of adsorbed As(III) and As(V). This study shows that bog iron ores constitute an appropriate adsorption material for arsenic especially at concentration range 0.25–5 mM, pH 5–10 for As(III) and 0.25–0.5 mM, pH 2–5 for As(V). However, there are no simple correlations between mineralogy and sorption capacity.

Keywords: As(III); As(V); Competitive sorption; pH; Desorption; Iron oxyhydroxides

1. Introduction

Industrialization and urbanization significantly affect the composition of water on Earth. Currently, heavy metal contamination of groundwater and surface water is a common and worldwide problem within industrial areas, especially in the vicinity of abandoned mines and plants. The largest water contamination with arsenic (As) caused by both industrial and geogenic processes is observed in Argentina, Chile, Mexico, Slovakia, Hungary, Romania, Poland, and Bangladesh [1]. Strict standards regarding contents of heavy metals in tap water must be maintained. However, the water of wells, streams, rivers, and ponds, which is used for watering home gardens and given to animals, is not controlled in any way. Thus, dangerous heavy metals may be indirectly consumed by people.

Arsenic and its compounds are highly toxic and have the ability to accumulate in the body (nails, bones, hair, and liver). Consumption of water or food containing arsenic can cause skin changes, high blood pressure, diabetes, coronary or vascular diseases, and can also affect reproductive and developmental processes. Arsenic is commonly considered to be an environmental mutagenic and carcinogenic factor [2,3]. The mobility and toxicology of As are related to its

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valence state which can be (+III) or (+V), depending mainly on pH and redox conditions [4].

Technologies used to remove of As from aqueous solutions presented in the literature include coagulation and flocculation, precipitation, adsorption and ion exchange, membrane filtration, advanced oxidation processes, and biological treatments [2]. Adsorption and ion exchange onto iron oxyhydroxides or oxyhydroxide-rich sorbents (e.g., goethite, ferrihydrite, magnetite, hematite) is one of the most effective methods for removing various arsenic species from contaminated water [5,6 and references therein]. The process of adsorption and ion exchange depends on many factors that include the solution chemistry, the pH and the composition of the solution; hence, the effectiveness of these methods varies significantly. Despite many studies, the factors affecting the adsorption processes, particularly those related to the properties of materials, are still far from being fully understood [5]. Currently, there are many well-known sorbents that are used for the removal of As compounds, that is, activated carbon, active alumina, oxides, hydroxides and hydrated iron oxides, active silica coated with iron oxide, peat or red mud; however, most of them are expensive or difficult to synthesize and exploit [6].

Bog iron ores are quaternary ferruginous deposits occurring several centimeters below the land surface in shallow and wet depressions. These ores show good sorption capabilities, particularly regarding the adsorption of many metals. The adsorption process is relatively fast and efficient in a wide range of metal concentrations and pH [7]. Various possible applications of bog iron ores in soil and water remediation have been proposed so far, involving adsorption, precipitation and solidification processes [3,7–11]. Previous laboratory studies revealed that granulated, thermal modified, and unmodified bog iron ores are promising sorbents of arsenic compounds though they have different mineralogical structures and specific surface areas [12,13]. Iron oxyhydroxides, hydroxides, and oxides (all referred further as IO), the main components of bog iron ores, can possess high arsenite and/or arsenate sorption efficiencies, depending on specific pH and Eh conditions. Adsorption of oxyanions on the surface of IO consists of two main mechanisms: non-specific adsorption and specific adsorption. In non-specific adsorption, weak bonds between the surface of the adsorbent and the adsorbed ions are formed. These bonds arise due to the presence of electrostatic interactions, and their occurrence is closely related to pH. Depending on the pH, the surface of IO is negative, positive, or remains inert [14–16]. Oxyanion immobilization on the surface of IO is the most effective in a low pH environment and clearly decreases with increasing pH [17]. In non-specific adsorption, outer-sphere surface complexes (involving hydrated ions) are formed. Specific adsorption is the dominating binding mechanism of As(V) and As(III) [18–20]. It is caused by the formation of permanent coordination bonds between the active sites on the surface of the sorbent and the ions present in the solution [14]. This process is usually accompanied by the release of the ligand previously associated with the adsorbent surface. The active sites on the surface of IO that enable ligand exchange are the hydroxyl groups coordinated with one iron atom. Structurally, IO consists of octahedra linked by corners, edges, or faces. The resulting different structural arrays affect the amount and type of sites available for adsorption [14]. Therefore various IO may exhibit different affinities toward As(V) and As(III).

The aim of the present study was to extend current knowledge of the sorption properties of bog iron ores, comparatively with As(III) and As(V) compounds. The proper understanding of the mechanisms responsible for the immobilization of contaminants on the surface of the bog iron ores is necessary to the controlled use of this material as a sorbent. Since the removal of As and heavy metals from water using sorbents is one of the most popular methods of water purification, new, inexpensive, easily accessible to exploitation, and effective sorbents are highly desirable. Bog iron ores have a great potential to become an effective sorbent for the removal of heavy metals from water, therefore, an extensive and comprehensive study of their sorption properties are crucial. In this study, sorption experiments were performed using a wide range of concentrations and pH to provide a valuable guide for effective removal of As(III) and As(V). Due to their composition, properties, and ubiquity in many near-surface environments, bog iron ores can be invaluable sorbents for the removal of heavy metals from waters.

2. Materials and methods

2.1. Materials and methods

Samples of bog iron ores used in this project were collected from four locations in Poland: Kolechowice (KOL), Debe Male (DM), Biadaszki (BD), and Strzyzew (ST). Despite having different structures, mineral composition, and physical and chemical properties, bog iron ores revealed good sorption affinities for trace elements which was described in our previous work [7]. The most important parameters that include the chemical, physical, and mineral composition of the samples are presented in Table 1.

The samples represent two main types of bog iron ores: fine "soft" ores (DM and ST) and lump "hard" ores (BD and KOL). Fine ores occur in the form of a fine dust with visible plant debris and pieces of wood in different degrees of decomposition. In contrast, lump ores are cemented limonite resembling porous slag. These two types of bog iron ore differ in texture and phase composition. Lump ores consist mainly of quartz and iron oxyhydroxides with a common admixture of manganese oxides. They usually do not contain substantial amounts of organic matter. The average amount of total organic carbon in lump ores is about 1.64%, while in fine ores is 8.11% [21]. Authigenic iron oxyhydroxides are the main components of fine ores, whereas quartz and other silicates are usually minor compounds. Fine ores generally contain large amounts of organic matter but are poor in manganese oxides [7,21].

Prior to the experiments, the samples were air-dried, sieved through 2 mm sieve and thoroughly crushed in the agate mortar. For all experiments only a <0.2 mm fraction was used.

Chemical and mineral composition of the bog iron ores [7] were determined with X-ray spectroscopy (Philips PW-2400 sequential XRF analyzer, Netherlands) and X-ray diffractometry (Philips APD PW3020 diffractometer,

Table 1
Chemical, physical, and mineralogical characteristics of the samples [7]

	Kolechowice (KOL)	Debe Male (DM)	Biadaszki (BD)	Strzyzew (ST)
	Chemical composition			
SiO_2	7.88	15.00	3.03	16.50
TiO_2	0.02	0.09	0.01	0.02
MnO_2	0.27	0.65	4.23	0.18
Al_2O_3	0.28	1.62	0.19	0.29
Fe_2O_3	47.93	39.16	70.96	37.21
FeO	0.49	0.17	0.48	0.33
CaO	2.63	2.91	2.36	1.22
MgO	0.08	0.20	0.25	0.05
K_2O	0.07	0.27	0.01	0.06
Na_2O	0.04	0.12	0.01	0.05
P_2O_5	3.11	5.59	5.19	2.76
LOI	35.60	32.97	13.77	39.90
	Physical–chemical properties and mineral composition			
CEC (meq/1,000 g)	57.2	38.3	11.2	42.4
BET (m^2/g)	125	99	174	153
Fe_{DCB} (wt.%)	31.93	27.41	51.38	29.26
Fe_{OX} (wt.%)	24.94	21.06	23.00	27.16
C_{org} (wt.%)	3.5	6.6	0.50	4.9
Mineral composition	Fh, Q, Gt, P	Fh, Q, Gt, P, Mn	Gt, Fh, Mn, Q, S, V, P	Fh, Q,

LOI: loss on ignition; CEC: cation exchange capacity; BET: surface area; Fe_{DCB}: total iron contained in oxides and hydroxides; C_{org}: organic carbon; Fh: ferrihydrite; Gt: goethite; Mn: Mn oxides; P: amorphous phosphates; Q: quartz; S: siderite; V: vivianite (main phase underlined).

Netherlands) methods. Cation exchange capacity was measured by the $BaCl_2$ method [22] and the surface area was analyzed using the BET model (nitrogen adsorption). The amount of iron bound in oxides (Fe_{DCB}) and in ferrihydrite (Fe_{OX}), and the organic carbon content were examined by the following methods: dithionite–citrate–bicarbonate method [23], acid ammonium oxalate method [14], and infrared spectroscopy method (LECO analyzer, USA).

2.2. Experiments of As(III) and As(V) sorption

In batch experiments, the effect of initial As concentrations was studied in the range 0.75–1,498 mg As(III) or As(V) per L (0.01–20 mM) at pH 7.5. Since the bog iron ores contain mobile phosphates, the possibility of release of them was estimated using NaCl. The samples of bog iron ores were washed with 1 M NaCl solution to calculate the amount of released phosphate (anion exchange of Cl for PO_4). The influence of pH was evaluated in the range of 2–11 using 5 mM (375 mg/L) As(III) or As(V) solution.

Competitive sorption of As(III) and As(V) was studied for the BD sample, at variable initial concentrations and variable molar ratios of As(III) to As(V). Solutions with a constant pH of 7.5 and total As(III) and As(V) concentrations ranging from 0.025 to 20 mM were used (Fig. 1).

The experiments involving competitive sorption of Pb(II), Zn(II), Cd(II), Cu(II) in relation to As(III) and As(V) ions were conducted at pH 4. As(III) and As(V) concentrations varied in the range 0.025–2.5 mM, while total metal concentrations were either 0.025 or 0.25 mM (0,00625 mM or 0.0625 mM each). The above-mentioned experimental conditions were chosen to avoid the precipitation of the solution components at higher pH values and/or higher ion concentrations. Experiments of competitive sorption of cations in relation to As(III) and As(V) ions were conducted only for BD sample.

In all experiments, the suspensions (20 g of sorbent per 1 L of solution) were shaken for 24 h at room temperature; then centrifuged for 10 min at 14,000 rpm. The solutions were then decanted. Arsenic concentration in all supernatants was determined by colorimetric method using a Hitachi U-1800 (United Kingdom) UV-Vis (ultraviolet-visible) spectrophotometer at wavelength $\lambda = 870$ nm [24]. In samples

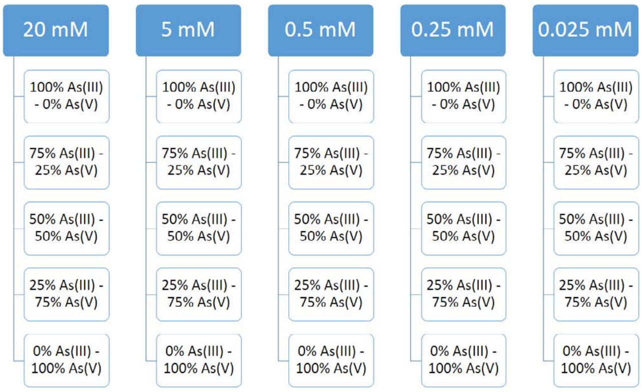

Fig. 1. Scheme of solution preparation for competitive sorption of As(III) and As(V).

containing arsenites, As(III) ions were oxidized to As(V) following the method described by Dhar et. al. [25] and then arsenic concentration was determined by the colorimetric method. Samples containing a mixture of both As (III and V) forms were analyzed in two steps. After As(V) measurement, As(III) was oxidized to As(V) and total As concentration was measured. As(III) was calculated as the difference between the total and As(V) concentrations. The contents of lead, zinc, cadmium, and copper were determined using atomic absorption spectroscopy (AAS) with a SavantAA GBC Scientific Equipment spectrometer (Australia). In all experiments, blank samples were used as a reference.

2.3. Sequential extraction experiment

The bonding strength of As with a bog iron ore surface was estimated on the basis of a three-step sequential extraction experiment. The experiment was conducted for the samples (KOL, DM, BD and ST) previously treated with 20 mM As(III) or As(V) at pH 7.5. Prior to the experiment, the As-loaded samples were dried at 60°C for 3 h. The first step involved washing with 1 M NaCl at pH 8 for 2 h; the second step involved washing with 1 M K_2HPO_4 at pH 5 for 2 h; and the third step involved washing with 1 M K_2HPO_4 at pH 5 for 24 h [26]. In the first step removal of ionically exchangeable As occur while ions removed in the second and third step are most likely strongly complexed by either IO or humic acids. After each step, samples were dried at 60°C for 3 h. As concentrations in the supernatants were analyzed using colorimetry (first step) or AAS (second and third step). In all the experiments, blank samples were used as a reference.

3. Results and discussion

3.1. As(III) and As(V) sorption as a function of initial concentration

The results clearly show that the removal of As(III) (Fig. 2a) and As(V) (Fig. 2b) depends on the type of bog iron ore. For KOL, DM, and ST samples, the immobilization of As(III) was about 33–35 mg of As(III) per g of the sorbent, while the sorption for the BD sample was about 25 mg/g. In all cases, the immobilization of As(V) was lower than As(III). The highest adsorption capacity of As(V) was observed for BD and ST samples (ca. 16–19 mg/g), while the adsorption capacity for KOL and DM samples was significantly lower (ca. 11–12 mg/g). All the results were recalculated considering blanks. The content of phosphates released to the solution was constant throughout the whole range of concentrations. The phosphate content was no more than 2% of the total amount of the ions (phosphate, arsenite, and arsenate) in the obtained solution (from 0.000037 to 0.69 mg/g, depending of the initial As (III or V) concentration).

The differences in sorption capacities, depending on the initial arsenic concentrations, can be associated with the surface coverage by ions and the active centers occupied by them. It is assumed that at first, active centers, in which ions are permanently attached to the surface, are occupied and no further changes occur. If more ions are available, then more sites are occupied [27].

The As (III, V) adsorption efficiency depends strongly on its valence. The higher sorption capacity of As(III) compared with As(V) is probably due to the oxidation of As(III) on the surface of IO, with simultaneous reduction of Fe(III)

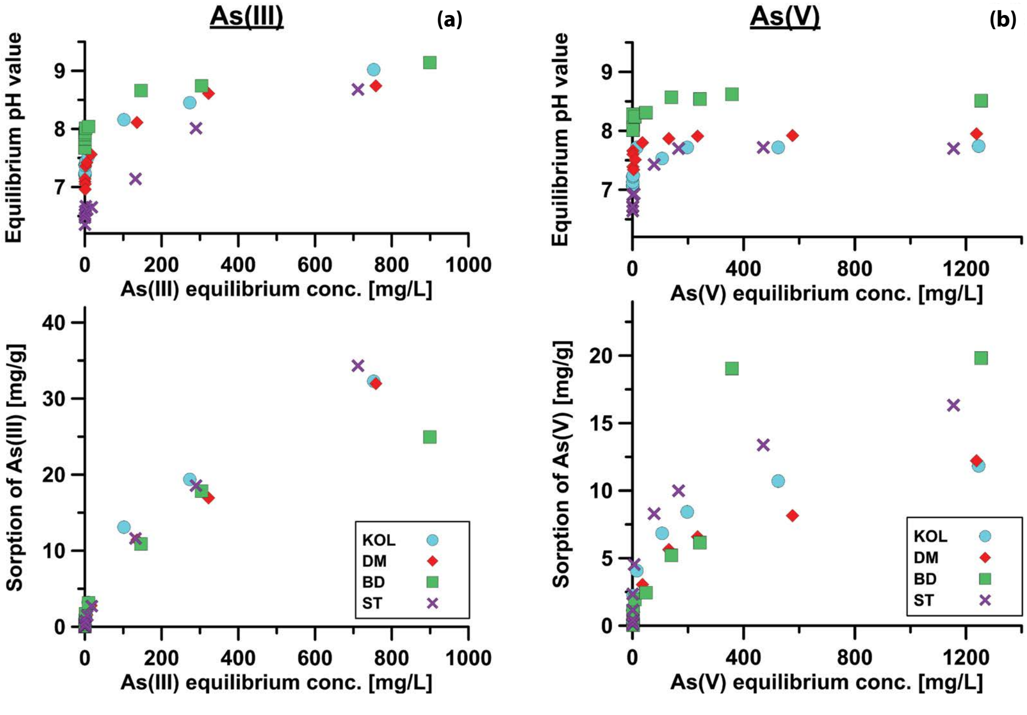

Fig. 2. (a) Sorption of As(III) as a function of concentration and (b) Sorption of As(V) as a function of concentration. (bottom plots – As(III) or As(V) sorption depending on the As(III) or As(V) equilibrium concentration; top plots – the equilibrium pH values of the solutions after sorption depending on the As(III) or As(V) equilibrium concentration).

to Fe(II). This process causes the emergence of new active centers where As ions can be adsorbed [27–29]. Moreover, some studies indicate, that depending on the conditions of adsorption and structure of the adsorbent, removal of As(V) occurs only by non-specific adsorption, without further structural changes [30–32].

This kind of adsorption is influenced by the formation of hydrogen bonds between surface hydroxyl groups and oxygen atoms in arsenate molecules, as well as the presence of a water film on the adsorbent surface affecting the dielectric constant of the IO surface [30]. Surface complexation with the iron hydroxyl groups via ligand exchange between the arsenate and the hydroxyl surface is probably the main adsorption mechanism [33]. The phosphate ions attached to the ore components could also be exchanged with either As(III) and As(V) in the solution. Due to the chemical similarity between As(V) and P(V), both ions compete in sorption processes [17,34,35]. In the case of As(III), a neutral pH enhances the ligand exchange between As(III) and phosphate [17,36]. This could explain why sorption of As(III) is more effective. However, to unambiguously confirm the occurrence of these processes, the detailed spectroscopic studies are required.

The differences between the sorption capacity of As(III) and As(V) could also be associated with the speciation of As, and the surface charge of adsorbent [13,17]. At neutral pH, As(V) exists as $HAsO_4^{2-}$ and $H_2AsO_4^-$, whereas the dominant As(III) form is $H_3AsO_3^0$ [1]. Thus, repulsion between As(V) and the negatively charged surface of IO is more important than for As(III) [13,17].

The mineral and chemical compositions of the samples are not clearly correlated with the sorption capacity of bog iron ores. This can be explained by the complex composition of the material. The variability of sorption capacities is related to the variability in the mineral composition of the ores since individual IO has different surface properties, and hence, different affinities toward arsenate [17]. Moreover, these properties could vary depending on the size and shape of particles and/or the presence of chemical impurities. Compared with ferrihydrite, goethite and hematite were less receptive to As (III, V) adsorption, which is primarily the consequence of the much lower surface area [17,18,37]. Thus, if ferrihydrite predominates in bog iron ore, the higher As (III, V) sorption capacity can be expected, compared with the samples where more crystalline goethite and/or lepidocrocite prevail. However, the sorption mechanisms are also influenced by the presence of other substances such as manganese oxides, aluminum oxides, and organic matter, which are also capable of binding metals [7,18,35,38]. The higher amount of natural organic matter and manganese oxides has a positive impact on immobilization of arsenic mainly through competition for available adsorption sites, forming aqueous complexes, and changing the redox chemistry of site surfaces and As species [38–41]. The samples differ significantly in chemical properties and mineral composition, which could be the main reason for their different sorption capacities.

The effect of pH on the sorption of As(III) and As(V) is shown in Fig. 3. The results revealed that pH significantly affects the effectiveness of As removal. For As(III) (Fig. 3a),

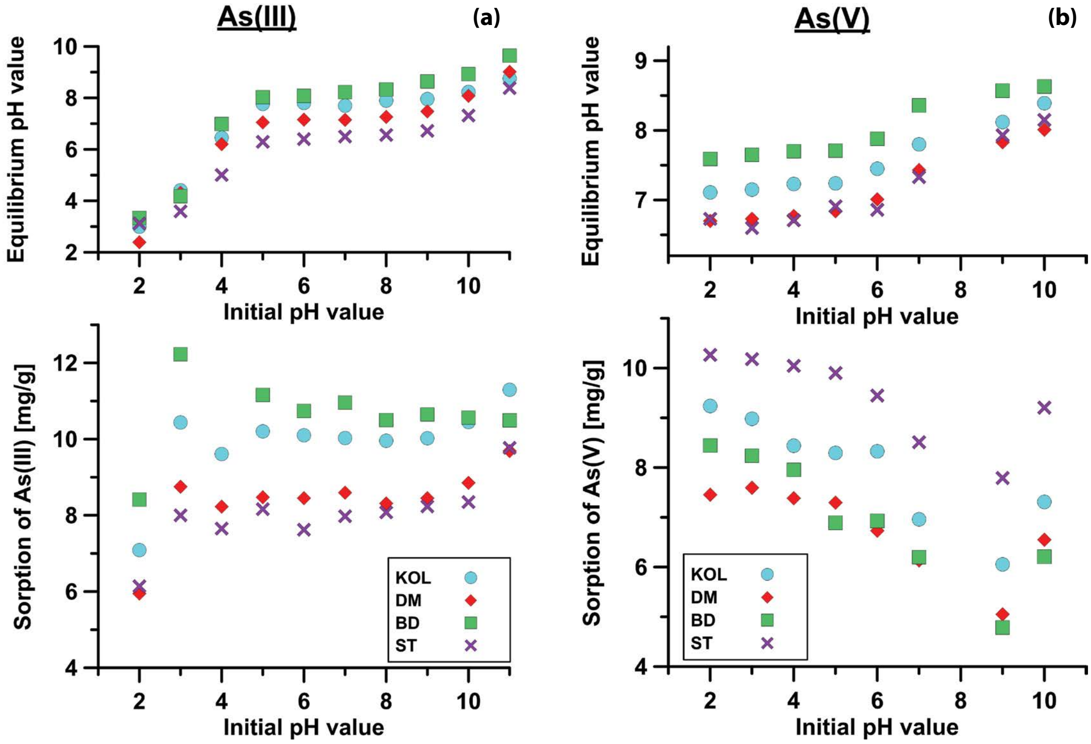

Fig. 3. (a) Sorption of As(III) as a function of initial pH value, and (b) Sorption of As(V) as a function of initial pH value. (bottom plots – As(III) or As(V) sorption depending on the initial pH values; top plots – the equilibrium pH values of the solutions after sorption depending on the initial pH values).

the sorption capacity is clearly lower at very low pH, whereas, at higher pH values, the sorption capacity seems almost independent of the acidity of the solution. On the other hand, the efficiency of As(V) adsorption (Fig. 3b) is higher in a low pH environment, clearly decreasing with pH increase.

The effect of pH on As removal was much more pronounced for As(V) than for As(III). The differences between the sorption capacity in different pH conditions could also be associated with the speciation of As(III) and As(V) and the surface charge of the adsorbent. In the range of pH used in this study (2–11), dominant speciations are $HAsO_4^{2-}$ or $H_2AsO_4^-$ for As(V) and $H_3AsO_3^0$ for As(III), thus changing of the surface charge do not have a significant impact for behavior of zero-valent speciation of As(III), but on the other hand increasing pH may cause competition between anionic forms of As(V) and OH^- groups. [1,14,42,43]. The maximum As(V) sorption capacity observed at low pH is probably related to the partial dissolution of ferrihydrite below pH 3.0. It is theorized that dissolved iron precipitates with As(V) again, entrapping As(V) [44–47]. The microscopic characterization analysis and the macroscopic adsorption experiments conducted by Jiang et al. [48] revealed that the removal of As(V) by IO proceeds mainly via both surface complexation and surface precipitation [37]. However, the contribution of surface precipitation decreases with an increase in pH of the solution. It is estimated that precipitation occurs at pH 3.0–6.0. This is probably the main reason for higher removal of As(V) under low pH conditions. Adsorption of As(III) in the pH range 3–11 is not strongly dependent on pH. Clearly, lower removal at pH 2 could be attributed to the substantial dissolution of IO, which results in a reduction in the number of active sites to which arsenic ions may attach [49].

3.2. Competitive adsorption of As(III) and As(V)

Fig. 4 shows that the sorption efficiency strongly depends not only on the concentration of arsenic but also on the molar ratio of As(III) to As(V). Removal of As(III) from a single-component solution is the most effective for medium concentrations (5–0.25 mM; Fig. 4a). At high concentrations of As (20 mM), the presence of As(V) positively affects the sorption of As(III), regardless of the molar ratio of these ions. However, the higher the molar ratio of As(V), the less effective As(III) immobilization. For medium concentrations (0.5 and 0.25 mM), removal of As(III) is slightly enhanced by a small addition of As(V); however, the more As(V) in the solution, the less effective the sorption of As(III). At the lowest concentration (0.025 mM), sorption is the least effective in both single- and two-component solutions.

Removal of As(V) is also more effective at medium concentrations (0.5 and 0.25 mM; Fig. 4b). At high concentrations (20 mM), sorption effectiveness of As(V) increases with an increase in the amount of As(III). For medium concentrations (5, 0.5, and 0.25 mM), a small amount of As(III) causes a significant decrease in As(V) removal. Nevertheless, the more As(III) ions, the greater As(III) immobilization.

The results suggest that the predominant sorption mechanisms of As(III) and As(V) are different. The surface of IO contains adsorption sites that are accessible to both species and adsorption sites that are species-exclusive [50]. Competitive adsorption can take place only at sites available for both As(III) and As(V); however, it is possible that sorption of As on species-exclusive sites modify the surface of the sorbent, creating new adsorption sites.

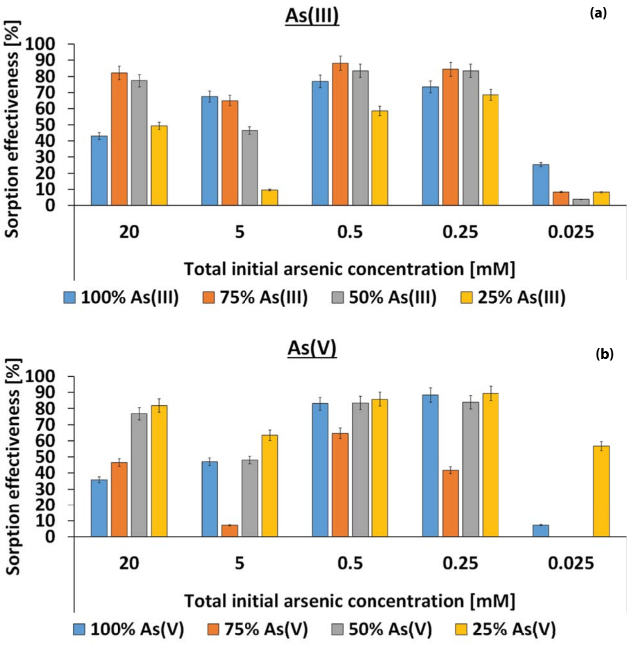

Fig. 4. (a) Effectiveness of As(III) sorption depending on the ratio of As(III) to As(V) for BD sample and (b) Effectiveness of As(V) sorption depending on the ratio of As(V) to As(III) for BD sample.

The relative affinity of arsenate and phosphate for IO is pH dependent and tended to be similar at neutral pH indicating that these two species may compete for similar surface sites, so the presence of As(III) may enhance ligand exchange between As(V) and phosphate [36]. This could explain why the presence of As(III) has a positive impact on As(V) sorption. Conversely, the presence of As(V) ions could have a negative effect on the binding of As(III), because of strong competition between these two species. However, detailed studies are required to unequivocally prove the mechanisms of positive impact of As(III) on As(V) sorption.

3.3. Sorption competitiveness between As and heavy metals

Fig. 5a shows that sorption of As(III) is almost independent of the concentration of Pb(II), Zn(II), Cd(II), and Cu(II). Higher total concentrations of the cations only slightly enhanced the effectiveness of As sorption. Cd(II) has a high affinity for bog iron ores, which results in the effectiveness of sorption at 100% for a wide range of concentrations. However, at low As and metals concentration, removal efficiency was significantly lower for three bog iron ores. Zn(II) sorption shows the highest variation. At higher metal concentrations (0.25 mM), the effectiveness of sorption is about 70% regardless of the As(III) concentration. However, at low metal concentrations, increasing the quantity of As(III) causes a decrease in Zn(II) sorption. Immobilization of Pb(II) is closely dependent on the concentration of cations and

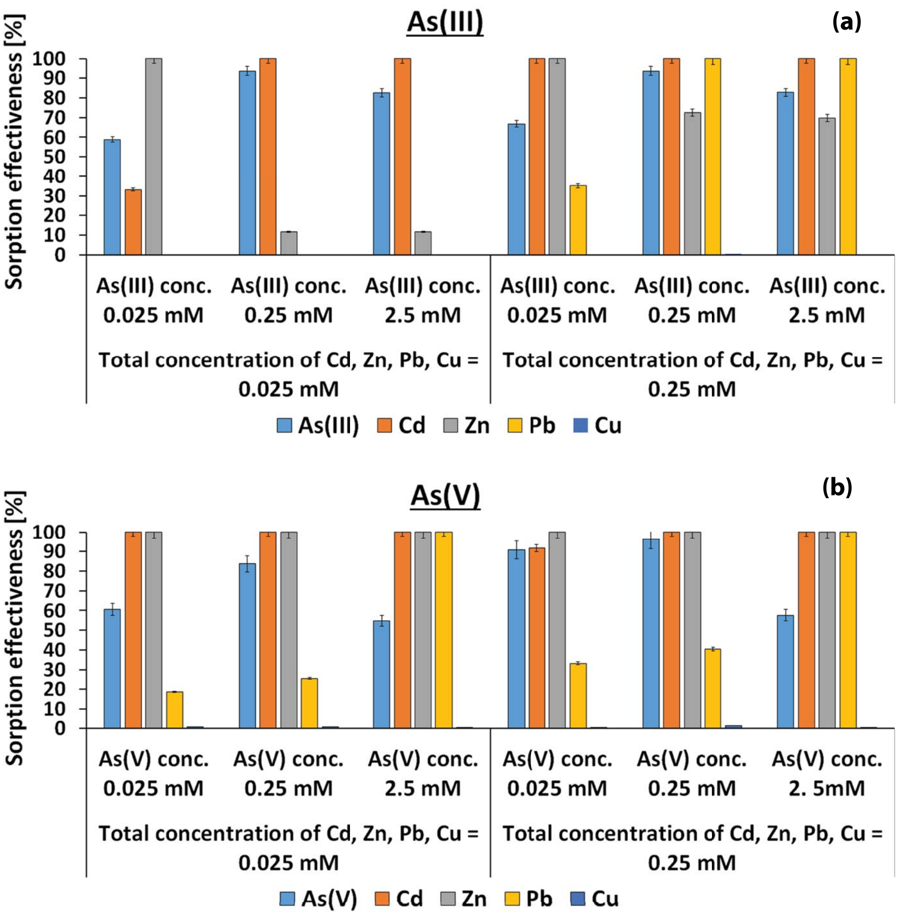

Fig. 5. (a) Sorption efficiency of As(III) and heavy metals for BD sample and (b) Sorption efficiency of As(V) and heavy metals for BD sample.

anions. When the total concentration of cations is 0.025 mM, sorption processes do not occur. However, when the heavy metal concentration is higher, the sorption efficiency varies from 30% to 100% depending on the anion concentrations. The higher the concentration of As(III), the more effective is Pb(II) sorption. Removal of Cu(II), regardless of the concentration of As and other cations, does not occur at all, or its effectiveness is less than 1%.

The removal of As(V) appears to be almost independent of the presence of the cations in the solution (Fig. 5b). Immobilization of Cd(II) occurs with 100% efficiency in almost all conditions. The immobilization of Pb(II) is significantly higher at high As(V) concentration. The effectiveness of Zn(II) sorption is extremely high. The removal efficiency does not depend on the concentration of ions in the solution and in each case, it is 100%. Cu(II) sorption does not occur at all, whatever the concentration of ions in the solution.

A previous study on sorption properties of bog iron ores regarding Cu(II), Zn(II), and Pb(II) ions sorbed from single-component solutions conducted at comparable conditions [7] revealed that these cations can be effectively immobilized. Sorption efficiencies were in the range 85%–99%. However, our results clearly show that sorption from multi-component solutions affects the removal efficiency. Cadmium is most effectively sorbed regardless of the presence of other ions in the solution. In each case, 100% removal efficiency was obtained. This indicates that cadmium cations have the highest affinity for the surface of bog iron ores. In contrast, copper, whatever the concentration of itself or other components, is not removed from the solution. The reason is probably the seizure of active centers that can sorb Cu(II) by other ions present in the solution or/and creation of zero valent species with arsenates (such as $Cu_3(AsO_4)_2$). The sorption of lead and zinc strongly depends on whether the As(III) or As(V) anions were sorbed at the same time; it can be assumed that As affect the number of active sites to which Pb and Zn have an affinity. Moreover, the presence of Cd(II) has a favorable impact on immobilization of Pb(II) [51], what is more perceivable in the case of sorption from As(III)-containing solutions. At a higher concentration of heavy metals, removal of Pb(II) ions is more efficient. As coexisting with Pb(II) appears to enhance sorption of lead. The reason may be the creation of insoluble arsenates such as mimetite or could be related to the different processes of removal of arsenic ions (ligand exchange, oxidation of As(III) with simultaneous reduction of Fe(III) to Fe(II), or dissolution of ferrihydrite and repeated precipitation) that may cause the formation of new active centers that could entrap Pb(II). However, it is debatable and unconfirmed by other literature data.

pH value of the solution has a significant impact on the removal of cations by IO. Depending on the pH value, heavy metals occur in different chemical species. At pH 4 analyzed cations appear mostly in form of Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} [52,53]. At low pH, the surface of the most IO has a positive charge, which causes repulsion of the cations. At pH 4 the charge of the surface of the complex materials containing IO usually becomes negatively charged (or less positively charged) [33] however, the amount of suitable active centers could be insufficient for cations concentrations proposed in this study. The formation of the complexes between the surface of the sorbent and each cation require a different kind of linkages between corners, edges, or faces. Ponthieu et al. [54] proved that each cation has its own coordination and form different surface structures. However, these surface structures strongly depend on the type of IO that participate in the process of adsorption. Zinc does not have the same geometry when adsorbed on goethite and ferrihydrite surfaces. It can have a sixfold coordination geometry when adsorbed on goethite [55–57] and a fourfold one when adsorbed on ferrihydrite [57,58]. Lead adsorbed onto goethite formed either a square [56,59] or a trigonal pyramid [60,61]. The cadmium and copper both have sixfold coordination and form similar surface complex structures [54], which could be the main reason for ineffective adsorption of Cu onto analyzed bog iron ore. The immobilization of Cd instead of Cu may be probably related to their reactivity – the position of these elements in electrochemical series indicate the higher reactivity of Cd than Cu. Results implicate that analyzed cations may form similar surface complex structures and due to an insufficient amount of active centers suitable for cations, a strong competitive effect occur. However, more detailed studies are required to confirm these predictions.

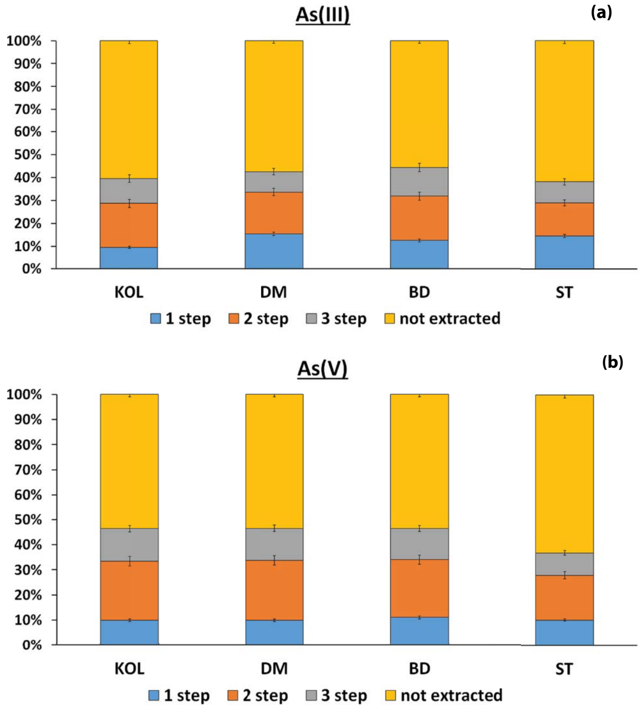

Fig. 6. (a) Sequential extraction of As(III) and (b) Sequential extraction of As(V).

3.4. Sequential extraction experiment

The results of As(III) and As(V) sequential extraction (Figs. 6a and b, respectively) revealed that it is possible to recover no more than half the previously absorbed As. Based on these results, one can infer the potential bond strength between sorbent and sorbate. In the first stage of sequential extraction, relatively few ions previously absorbed were removed. It is assumed that NaCl extractant causes the removal of ionically exchangeable As [26]. At this step, chloride is exchanged for arsenate, but the formation of Na–arsenate complexes is possible as well [25]. Ions adsorbed by physical sorption are more easily extracted, while those bound to the surface by chemical bonds require more aggressive reagents. The amount of As extracted at stages 2 and 3 is relatively high. The extractions at both stages were performed using 1 M K_2HPO_4 solution at pH 5. The As liberated by the PO_4 extractant is most likely that which is strongly complexed by either IO or humic acids [26]. Thus the application of sequential extraction procedure provides information about the potential mobility of As in sediments. In the case of bog iron ores, As is mainly immobilized by IO. With this type of bonds, there is a risk of arsenic remobilization under extremely acidic, alkaline, or extremely anaerobic conditions, as well as due to dissolution by bacteria or during phase transformation of ferrihydrite and goethite [62]. The amounts of As(III) and As(V) extracted from bog iron ores obtained in this study are lower than those reported by Debiec et al. [13]. They were able to extract about 70% of both As(III) and As(V) previously absorbed on the bog iron ore. It could be related to the processes of As removal. To mobilize arsenic precipitated with IO, more effective reagents, such as HCl or ammonium oxalate/oxalic acid, should be used [26]. Therefore, the low efficiency of extraction was obtained.

4. Conclusions

The sorption capacity of bog iron ores relative to As (III, V) varies, depending on the type of adsorbed compound, bog iron ore and pH value. The highest percentage reduction of As were obtained at moderate initial concentrations: 0.25–5 mM As(III) and 0.25–0.5 mM As(V). Depending on the pH value, different mechanisms of immobilization are present. It is assumed that in addition to absorption, dissolution and re-precipitation of iron oxides also occurs at pH 3.0–6.0. Re-precipitation of IO may cause entrapping and immobilization of As. In addition, at low pH the surface of IO is positively charged, which enhance the anions absorption. Therefore, removal of As is the most effective in acidic conditions. The sorption of arsenic is also dependent on the presence of heavy metals (Pb(II), Zn(II), Cd(II) and Cu(II)) in the solution. Removal of As(V) is almost insensitive to the presence of heavy metals, however, the immobilization of As(III) was slightly enhanced by the higher total cations concentration (0.25 mM) and at low concentration (0.025 mM), removal efficiency was significantly lower for most bog iron ores. The sequential extraction experiment shows that it is likely to recover no more than 50% of the absorbed arsenic from bog iron ores. More reactive extractants (such as HCl or ammonium oxalate/oxalic acid) are required to release arsenic precipitated with IO. Research has shown that despite the disparity of results caused by the chemical, physical, and mineralogical diversity, the bog iron ores are effective sorbents of heavy metal(loid)s. Such properties combined with the widespread presence and the ease of their extraction should stimulate further research on the use of bog iron ores as sorbents. Research proved that arsenic and some cations such as cadmium, lead, and zinc can be effectively removed at the same time. These properties are extremely valuable because natural water contains a wide range of contaminants and their simultaneous removal could reduce the costs and the number of used sorbents. It can be especially useful in industrial applications, where it is important to remove as many different contaminants from water as possible. Due to the ubiquity of bog iron ores, the cost of sorbent production is relatively low and its granulation is already tested and proven to be effective in As and Zn removal. Bog iron ores can be used as natural filters retaining As and heavy metals in industrial, domestic, agricultural, and technological applications. Thus, is necessary to conduct more detailed research to fully recognize the potential of bog iron ores in the removal of heavy metals from water.

Acknowledgments

This work was supported by the Statutory Grant of AGH-UST, Project No. 11.11.140.158 and National Centre for Research and Development (Poland) grant number LIDER/043/403/L-4/12/NCBR/2013.

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