

Alginate beads containing water treatment residuals for arsenic removal from water—formation and adsorption studies

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Received: 30 January 2016 / Accepted: 26 April 2016 / Published online: 10 May 2016
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Abstract Water treatment residuals (WTRs) produced in large quantities during deironing and demanganization of infiltration water, due to high content of iron and manganese oxides, exhibit excellent sorptive properties toward arsenate and arsenite. Nonetheless, since they consist of microparticles, their practical use as an adsorbent is limited by difficulties with separation from treated solutions. The aim of this study was entrapment of chemically pretreated WTR into calcium alginate polymer and examination of sorptive properties of the obtained composite sorbent toward As(III) and As(V). Different products were formed varying in WTR content as well as in density of alginate matrix. In order to determine the key parameters of the adsorption process, both equilibrium and kinetic studies were conducted. The best properties were exhibited by a sorbent containing 5 % residuals, formed in alginate solution with a concentration of 1 %. In slightly acidic conditions (pH 4.5), its maximum sorption capacity was 3.4 and 2.9 mg g⁻¹ for As(III) and As(V), respectively. At neutral pH, the adsorption effectiveness decreased to 3.3 mg As g⁻¹ for arsenites and to 0.7 mg As g⁻¹ for arsenates. The presence of carboxylic groups in polymer chains impeded in neutral conditions the diffusion of anions into sorbent beads; therefore, the main rate-limiting step of the adsorption, mainly in the case of arsenates, was intraparticle diffusion. The optimal condition for simultaneous removal of arsenates and arsenites from water by means of the obtained composite sorbent is

slightly acidic pH, ensuring similar adsorption effectiveness for both arsenic species.

Keywords Calcium alginate · Arsenic adsorption · Water treatment residuals · Metal oxides · Hybrid polymer

Introduction

Arsenic is considered as one of the most toxic and carcinogenic naturally occurring contaminants of drinking water supplies. Since the long-term ingestion of water or food containing even small quantities of arsenic causes a variety of diseases, in many countries, its maximum contaminant level in drinking water has been revised from 0.05 to 0.01 mg L⁻¹ in accordance with WHO recommendations. The problem of elevated concentrations of arsenic compounds in water intended for human consumption concerns many regions of the world including rural areas in Bangladesh and India, some European countries, and the USA (Karagas et al. 2015). Therefore, development of efficient and cost-effective technologies for arsenic removal from water is a subject of intensive research. Among different techniques used for this purpose the most promising is adsorption, which is highly valuable for the removal of contaminants present in water at low concentrations, simultaneously enabling their reduction to significantly lower, recommended levels of several µg L⁻¹.

For arsenic removal from water, different adsorbents have been used such as reactive polymers, activated carbon, and various biosorbents obtained from living or dead waste biomass (Mohan and Pittman 2007; Pandey et al. 2009). However, the most effective and selective toward arsenic species are adsorbents based on metal oxides including ferric oxides, aluminum oxides, manganese oxides, and cupric oxides (Giles et al. 2011; Hua et al. 2012; Manning et al. 2002;

Responsible editor: Angeles Blanco

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Reddy et al. 2013). The adsorption of arsenic species on the surface of metal oxides occurs via electrostatic interactions usually followed by formation of inner sphere complexes, which ensures the high selectivity of arsenic removal. Therefore, the pH_{pzc} of the sorbent and pK_{a} of the arsenate acid are crucial parameters determining the effectiveness of the process (Cornell and Schwertmann 2003). Due to significant difference in pK_{a} values of the two acids ($\text{pK}_{\text{a As(III)}}=9.2$ and $\text{pK}_{\text{a As(V)}}=2.2$), which causes As(III) and As(V) to occur in natural water in different forms, molecular and ionic respectively, As(V) species are removed with higher efficiency (Gibbons and Gagnon 2011). The adsorption processes therefore sometimes require a preoxidation step. This inconvenience can be overcome by using adsorbents with simultaneous sorptive and oxidative properties toward arsenic. Comparative studies suggested that among metal oxides, iron oxides showed the highest affinity toward arsenates—both (III) and (V)—and also certain oxidative properties. However, the best results were obtained when mixtures of iron and manganese oxides were used, since the manganese component plays the role as a very efficient oxidant of As(III) to As(V) (Jacukowicz-Sobala et al. 2013; Lakshminathiraj et al. 2006; Tresintsi et al. 2013; Zhang et al. 2007; Zhu et al. 2015).

Metal oxides for adsorption purposes are synthesized in different shapes and sizes using physical and chemical methods such as high-energy ball milling, inert gas condensation, microemulsion synthesis, and controlled co-precipitation (Hua et al. 2012). An alternative solution for metal oxides synthesized *de novo* is application of low-cost adsorbents obtained as waste materials, which is in accordance with the current approach of industrial waste management. The most widely studied groups of industrial waste materials containing iron oxides used for arsenic removal from water are red mud from bauxite processing, fly ashes from coal and biomass incineration, and water treatment residuals from coagulation, deironing, and demanganization processes (Jacukowicz-Sobala et al. 2015). These materials besides iron oxides usually also contain large quantities of aluminum oxides, titanium oxides, or silica, which are less specific toward arsenic species (Li et al. 2012; Zhou and Haynes 2012). The exception is residuals from deironing and demanganization of underground or infiltration water treatment processes, whose main constituents are iron and manganese oxides—the desired components of effective and selective adsorbents for both As(III) and As(V) compounds (Gibbons and Gagnon 2010).

The application of metal oxide adsorbents is usually restricted by their physical form of nanoparticles or microparticles. While their surface area to volume ratio is advantageous for adsorption processes, the application of the process in the fixed-bed systems is excluded due to their tendency to aggregate, resulting in a large drop in hydraulic pressure and in consecutive clogging of the bed. Great efforts have been made to modify the physical form of the metal oxide adsorbents, usually by their encapsulation within the porous structure of a bulk supporting materials such as zeolites,

silica, activated carbon, and reactive polymers (Hua et al. 2012; Sarkar et al. 2012; Westerhoff et al. 2006). The simplest method of obtaining adsorbents of this type is synthesis of metal oxides *in situ* within the structure of supporting material, which enables uniform dispersion of the metal oxide throughout the grains or beads of the porous material (Jacukowicz-Sobala et al. 2013, 2014; Sarkar et al. 2012). However, the deposition of earlier prepared metal oxides such as waste iron and manganese sludge from water treatment processes requires an opposite approach—synthesis or formation of the supporting material in the presence of metal oxide particles. Considering the simplicity of the process, the best choice for metal oxide encapsulation is linear biopolymers such as alginate or chitosan, which are soluble in aqueous solutions and after cross-linking forms a porous, polymeric support for inorganic deposits (Elwakeel and Guibal 2015; Fundueanu et al. 1999; Kamaruddin et al. 2014; Liu et al. 2010). This method of encapsulation of metal oxide waste materials for obtaining adsorbents has been used in very few studies. To date, solid wastes containing Fe(III) and Ni(II) hydroxides from an electroplating plant entrapped in calcium alginate beads and fly ash entrapped within the structure of chitosan have been used for arsenic adsorption (Adamczuk and Kołodźńska 2015; Escudero et al. 2009). Alginate is a highly advantageous material for this purpose due to its low price and simplicity of cross-linking with CaCl_2 solution (Ca^{2+} cations bind two carboxyl groups of guluronic residues in alginate chains). Therefore, this polymer has been widely used for waste biomass or zero valent iron or magnetic iron oxide nanoparticle encapsulation (Bezbaruah et al. 2009; Escudero et al. 2006; Hassan et al. 2014; Lim et al. 2009).

Our preliminary studies revealed that water treatment residuals obtained from the deironing and demanganization process in drinking water production are an efficient adsorbent for arsenic species with sorption capacity of $132 \text{ mg As(III) g}^{-1}$ and $77 \text{ mg As(V) g}^{-1}$ (Ociński et al. 2016). Based on these results, the aim of the present study was to evaluate an arsenic adsorbent combining high sorption capacity and advantageous physical form of the beads which can be easily separated after exhaustion of their sorption capacity. This purpose was achieved by chemical and thermal treatment of iron and manganese oxide waste sludge and then its immobilization within the matrix of calcium alginate beads. Finally, basic adsorption properties toward arsenic species of the obtained sorbent were studied.

Materials and methods

Materials

Raw water treatment residuals (WTRs) were supplied by the “Na Grobli” water treatment plant, Wrocław, Poland. This material was a by-product formed during deironing and

demanganization of infiltration water for drinking water production. The sludge, collected from the sedimentation tank, was washed with distilled water, dried for 72 h at 25 °C, grinded in a mortar, sieved to remove large particles, and stored in a desiccator for further analysis and experiments. The dried WTRs were composed mainly of iron oxides and oxo-hydroxides (25 % Fe) and manganese oxides (5 % Mn). The material had a high surface area ($120 \text{ m}^2 \text{ g}^{-1}$) and was mainly amorphous, with small fractions of ferrihydrite and Mn_2O_3 . The maximum sorption capacities toward both forms of arsenic were $132 \text{ mg As(III) g}^{-1}$ and $77 \text{ mg As(V) g}^{-1}$.

All chemicals were of analytical grade, and all solutions were prepared with deionized water ($18.3 \text{ M}\Omega \text{ cm}^{-1}$; Barnstead, EASYpure RF). The As(III) and As(V) stock solutions (1 mg As mL^{-1}) were prepared by dissolving sodium (meta)arsenite NaAsO_2 (Sigma-Aldrich, 99 %) and disodium hydrogen arsenate $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (Sigma-Aldrich, 98 %) respectively in deionized water. These solutions were subsequently diluted to the concentrations required in adsorption experiments. Alginate acid, sodium salt from brown algae (Sigma-Aldrich), was used as a hydrocolloid gelling material. Calcium chloride solutions used in the gel synthesis were prepared by dissolving anhydrous calcium chloride (Chempur, Poland, 97 %) in deionized water. Acetic buffers were obtained by mixing appropriate amounts of 0.1 M acetic acid (Stanlab, Poland, 99.9 %) and 0.1 M sodium acetate $\text{C}_2\text{H}_3\text{NaO}_2 \cdot 3\text{H}_2\text{O}$ (Chempur, Poland, 99 %) solutions.

Chemical and thermal pretreatment of raw WTRs

Chemical modification of raw WTRs consisted of treating 1 g of the substrate with 25 mL of an appropriate solution (deionized water, 3 % H_2O_2 , 0.05–1.0 M HCl) for 25 min, filtration, washing, and drying at 50 °C for 24 h. The obtained product was ground in a mortar, sieved, and stored for further experiments. Thermal modification of both raw and chemically modified WTR consisted of heating 1 g of the substrate at a temperature in the range of 100–700 °C for 2 h, cooling to room temperature, grinding, and sieving.

Alginate bead formation

Sodium alginate solutions (1–4 % w/w) were prepared by dissolving the appropriate mass of sodium alginate in 30 mL of distilled water at a temperature of about 45 °C. The mixture was vigorously stirred for 30 min to allow the complete dissolution of the polymer and then left at room temperature for the next 30 min to degas the viscous polymer solution. The desired amount of modified WTRs was added to 10 mL of deionized water under constant magnetic stirring, and the mixture was sonicated in an ultrasonic bath (10 min) to eliminate particle aggregation. The resulting

suspension was then added to alginate solution under continuous stirring and, when homogeneity was achieved, dropped into 0.1 M CaCl_2 solution for gel formation. Depending on the suspension concentration, the obtained beads contained 1, 2, 3, or 5 % w/w of the WTRs. In order to ensure constant process parameters, a peristaltic pump (Gilson MiniPuls3) was used, equipped with a micropipette tip 0.5 mm in diameter placed at the end of the dispensing tube. The formed gel beads (2.5–mm diameter) were retained in the same calcium chloride solution for 48 h for hardening and then rinsed several times with distilled water. The beads were then stored in distilled water before use.

Sorption experiments

The experiments were carried out in a batch regime, separately on As(III) and As(V) solutions, at room temperature in Erlenmeyer flasks. The sorbent beads in the appropriate number (20–130) were contacted with arsenic solutions for 24 h using a control shaker (IKA KS–260). After this time, the concentration of As(III) or As(V) and pH of the solutions were measured. All calculated parameters, both in kinetic and equilibrium studies, were expressed in relation to the mass of the wet sorbent beads, not to its number. Due to the narrow size distribution of the formed spherical beads, the weight of a single bead was determined and used each time for unit conversion. The mass of a single bead was determined as follows: 100 of the beads, separated from the water, were gently blotted using bibulous paper and weighed. This procedure was repeated five times, and the average mass (with standard error) of a single bead was determined as $8.9 \pm 0.07 \text{ mg}$. The same set of beads were then dried for 24 h at 60 °C and weighed, and the mass of a single dry bead was determined as $0.8 \pm 0.02 \text{ mg}$. The content of WTRs in dry alginate beads was 55.6 %. The kinetic study of arsenic adsorption was conducted by shaking 130 sorbent beads (1.16 g) with 100 mL of solutions with concentration of 10 or 25 mg As L^{-1} . The changes of arsenic concentration were analyzed in appropriate time intervals. Adsorption isotherm studies were carried out by contacting 50 sorbent beads (0.45 g) with 40 mL of arsenic solutions with various initial concentrations (3–200 mg As(V) L^{-1} or 5–200 mg As(III) L^{-1}) for 24 h. The influence of pH on arsenic adsorption efficiency was investigated by stirring 25 sorbent beads (0.22 g) with 20 mL of As(III) or As(V) solutions with concentration of 20 mg As L^{-1} with pH in the range from 4.5 to 7.5. Due to buffering properties of the WTRs, the acidic pH of the solutions was maintained using acetate buffers.

Analytical methods

Arsenic concentrations in solutions were determined using the spectrophotometric molybdenum blue method (Specord 210,

Analytical Jena, Germany). Arsenate ions formed a colorless antimonyl–arsenomolybdate complex, which was reduced with ascorbic acid, producing a blue species. The absorbance measurement was taken at 880 nm. Since arsenite does not form a molybdenum complex, prior to the analysis, an oxidizing agent (potassium iodate) was used to convert As(III) into As(V). In order to determine the iron content in raw and modified WTRs, 0.05 g of dried material was treated for 24 h with 20 mL of 2 M H₂SO₄. The obtained solutions, after dilution, were analyzed for Fe(III) content using the spectrophotometric thiocyanate method. The pH_{pzc} (point of zero charge) of the formed alginate beads containing WTRs was determined by means of the drift method. A measured amount of the sorbent (15 beads, 0.134 g) was contacted for 24 h with 0.1 M KCl solutions at different initial pH in the range of 2–11. After that time, the final pH of the solutions was measured and a graph of the initial pH versus ΔpH was plotted. The point at which the curve crossed the pH axis determined the pH_{pzc} of the sorbent.

Results and discussion

Preparation of WTRs

Preparation of metal oxide waste materials for adsorption processes usually requires preliminary processing in order to improve their sorption properties. This stage is significantly important when bauxite residuals are used as adsorbents (Jacukowicz-Sobala et al. 2015). Since WTRs exhibit neutral pH and trace amounts of heavy metal content, their treatment before use is much simpler. In this work, the first step of WTRs preparation was chemical pretreatment with distilled water or 3 % H₂O₂ solution or HCl solutions in order to dissolve from its surface compounds of heavy metals co-precipitated during the water deironing process. Moreover, acid treatment can develop a positive surface charge due its protonation which in consequence is favorable for anionic species adsorption. To assess the optimal conditions of chemical treatment, two parameters were controlled: content of Fe in relation to Fe content of raw WTRs and weight loss during the treatment. As can be seen from Figs. 1 and 2, the highest increase of Fe content

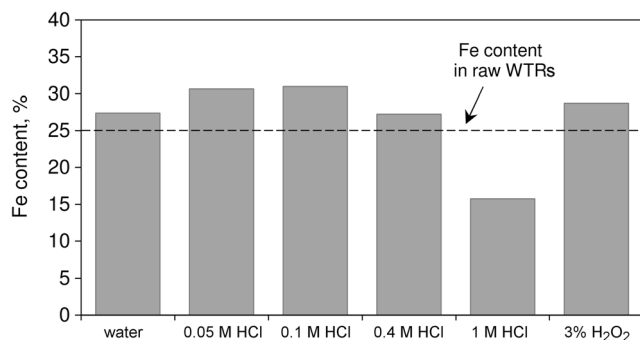


Fig. 1 Fe content in WTRs pretreated with various solutions

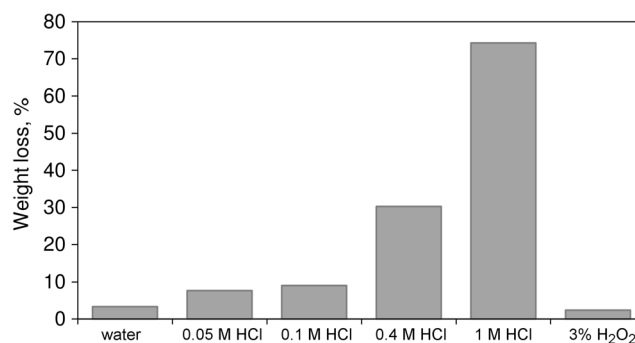


Fig. 2 Weight loss of WTRs during pretreatment with various solutions

and simultaneously an acceptable weight loss were obtained when the sludge was treated with 0.05 M HCl solution.

In the next step, we studied the influence of thermal pretreatment of WTRs on its sorption capacity. Thermal modification of metal oxide residuals may lead to stabilization of the waste sludge, changes in crystalline structure and chemical properties of the surface, and sometimes to an increase in the surface area resulting from release of gaseous products. Figure 3 presents the efficiency of As(III) and As(V) removal from aqueous solutions using WTRs after 2 h of thermal treatment at different temperatures in the range of 20–700 °C. Thermal treatment caused a decrease of sorption capacity of WTRs. The results revealed that heating up to 100 °C resulted in insignificant loss of arsenic sorption efficiency. At this temperature, there probably occurs reversible removal of physisorbed water from the surface of the sorbent. The treatment at temperatures equal to and higher than 200 °C caused an explicit decrease of arsenic removal which was presumably due to irreversible changes in the WTRs structure such as surface-bound hydroxyl removal and then changes in crystalline structure of iron and manganese oxides, leading to their better structurally ordered forms (Dose and Donne 2011; Cornell and Schwertmann 2003). This observation is in accordance with literature data indicating that amorphous iron oxides exhibit higher sorption capacity in comparison to crystalline

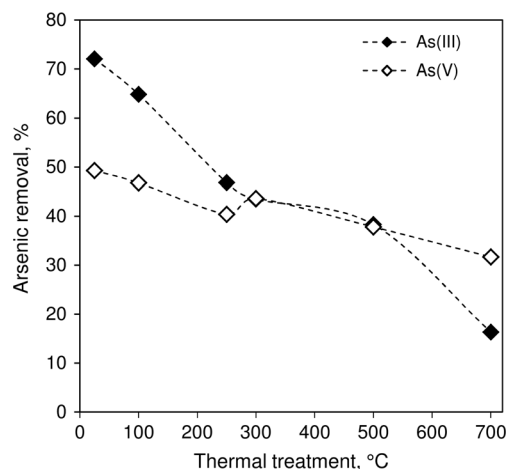


Fig. 3 Efficiency of arsenic removal by means of WTRs modified by thermal pretreatment at various temperatures

forms (Boggaard 1983). Simultaneously, the more intensive drop of adsorption efficiency with the increase of pretreatment temperature in the case of As(III) species is probably due to transformation of crystalline structure of manganese oxides.

The final procedure of WTRs pretreatment was chosen by comparison of As(V) removal efficiency using as the adsorbent raw WTRs (dried at 25 °C), WTRs after treatment with 0.05 M HCl solution and drying at 50 °C, and WTRs after treatment with 0.05 M HCl solution and thermal treatment at 300 °C. The concentration of used HCl solution as well as the temperature of thermal treatment was chosen based on the results presented on Figs. 1, 2, and 3. The determined efficiency of arsenite removal was respectively as follows: 50.2, 53.6, and 35.9%. Therefore, for further studies, encapsulation of WTRs within the matrix of alginate was conducted using the waste sludge pretreated with 0.05 M HCl solution and dried at 50 °C.

Formation of calcium alginate beads with WTRs deposit

In order to obtain spherical and uniformly sized particles of calcium alginate, a dripping technique was chosen. The spherical droplets of sodium alginate solution were introduced into the CaCl₂ solution, which played the role of a cross-linking agent. According to literature data, the increasing concentration of polymeric solution resulting in increased viscosity affected the shape and quality of the beads (Fundueanu et al. 1999). Therefore, the concentration of sodium alginate solutions used for bead formation was studied in the range of 1–4 %. As can be seen (Fig. 4), the particles obtained using

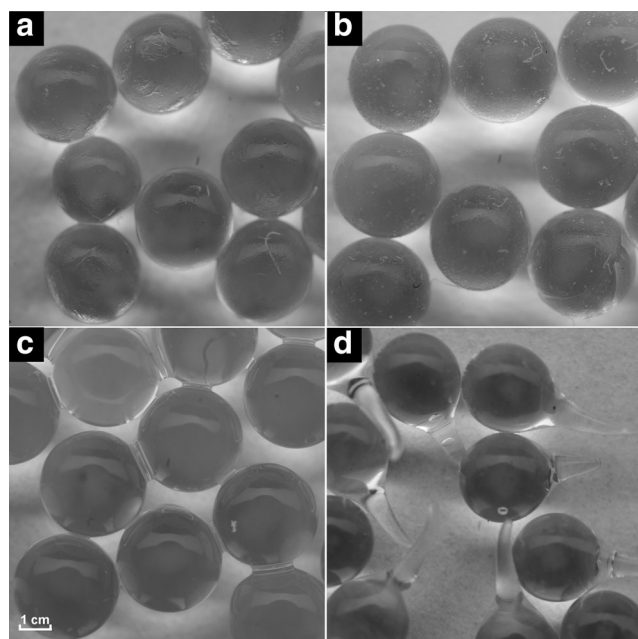


Fig. 4 Image of alginate beads formed using alginate solutions with different concentrations (% w/w): **a** 1 %, **b** 2 %, **c** 3 %, and **d** 4 %

polymeric solution with concentrations of 1, 2, and 3 % showed symmetric, spherical shape with uniform surface and size ranging from 2.4 to 2.6 mm with an average of 2.5 mm. In contrast, the particles obtained using polymeric solution with a concentration of 4 % exhibited a deformed spherical shape with tails and irregular sizes. Since sodium alginate solution may also influence the density of polymeric gel of the beads, which may affect the diffusion of sorbate during the adsorption process, introduction of the WTRs load was carried out using polymeric solutions with concentrations of 1 and 3 %.

Encapsulation of chemically prepared WTRs within the structure of calcium alginate beads was carried out according to the scheme shown in Fig. 5. A dispersion of WTRs particles after ultrasonication was introduced into the sodium alginate solution. Then, obtained dispersions containing 1.0, 2.0, 3.0, and 5.0 % WTRs particles in polymeric solutions with concentrations of 1.0 and 3.0 % were dripped into CaCl₂ solutions. Optimum operational parameters of the process of adsorbent bead formation were as follows: Distance between orifice of the micropipette tip and surface of CaCl₂ solution was 2 cm, flow rate of WTRs dispersion in polymeric solution was 0.6 mL min⁻¹, and concentration of CaCl₂ solution was 0.1 M. Obtained materials are shown in Fig. 6. For comparison, the beads were also formed by introduction of dried WTRs solid directly into polymeric solutions (Fig. 7). As can be seen, ultrasonication ensured fine dispersion of WTRs sludge within the matrix of calcium alginate beads and constricted its agglomeration. Due to this, the beads show a

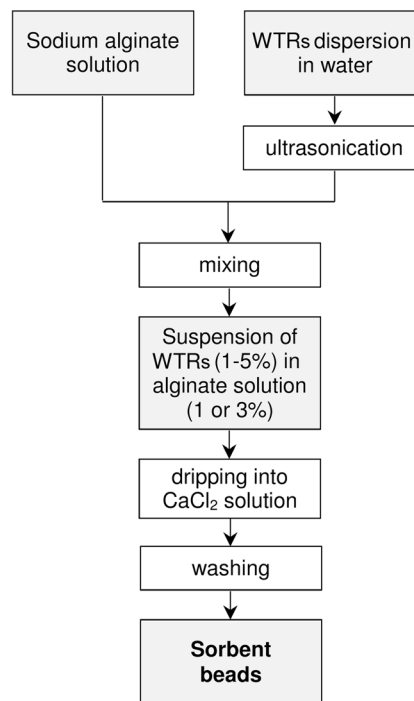
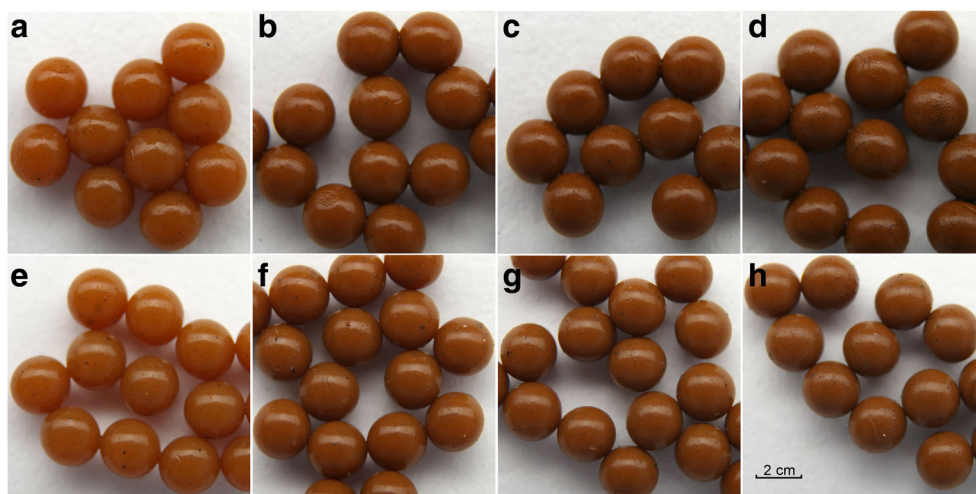


Fig. 5 Scheme of formation of WTRs-loaded alginate beads

Fig. 6 Image of two series of WTRs-loaded alginate beads formed using polymer solutions with different concentrations: 1 % (a–d) and 3 % (e–h) containing 1 % (a, e), 2 % (b, f), 3 % (c, g), and 5 % (d, h) of pretreated WTRs



uniform and smooth surface, in contrast to the beads obtained using dry WTRs.

Arsenic adsorption preliminary study

Eight obtained samples varying in WTRs content and density of polymer bead structure were used for As(III) removal from aqueous solutions under neutral pH. The results (Fig. 8) revealed that both factors influenced their adsorption capacity. The increase of WTRs content resulted in higher adsorption capacity due to the higher number of active sites on the surface of immobilized iron and manganese oxides. However, the effect of polymer concentration was much more significant. The adsorbent beads obtained using more concentrated polymer solutions with lower WTRs load (1–3 %) showed a very low adsorption capacity, which was probably the result of the dense polymeric matrix of the beads. Since alginic acid is a polymer of mannuronic and guluronic acids, increasing the polymer concentration content of carboxyl groups results in a higher cross-linking degree and diffusional barrier for arsenic species within its matrix. Therefore, for further studies, material with the highest WTRs load encapsulated

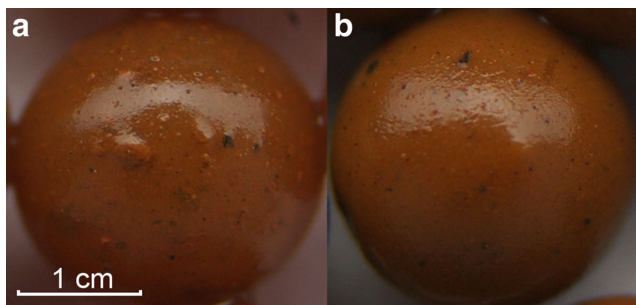


Fig. 7 Image of WTRs-loaded alginate beads formed using a dry WTRs and b ultrasonicated aqueous suspension of WTRs

within alginate beads obtained using polymer solutions with a concentration of 1 % was chosen.

Influence of pH on As(III) and As(V) adsorption

The pH of treated solution is a crucial factor determining the adsorption efficiency of arsenic oxyanions on iron oxide-based adsorbents. Depending on the pH, the surface charge of iron oxides becomes negative, considerably diminishing anion adsorption due to their repulsion from active sites, or the surface charge becomes positive, which favors arsenate adsorption. Thus, an important parameter of the sorbent is pH_{pzc} , below which there are favorable conditions for anion binding. The adsorption capacity of iron oxides toward arsenate ($pK_{a1}=2.2$) is usually the highest in slightly acidic conditions and decreases sharply above pH_{pzc} . Such a dependence is different for arsenites, which occur in acidic conditions in the form of undissociated, uncharged molecules ($pK_{a1}=9.2$). This is the reason for the lower adsorption capacity of iron oxide-based adsorbents toward arsenites under these conditions. The use of mixed iron and manganese oxides, due to their capacity for simultaneous oxidation of As(III) and adsorption of As(V), enables one to obtain similar removal

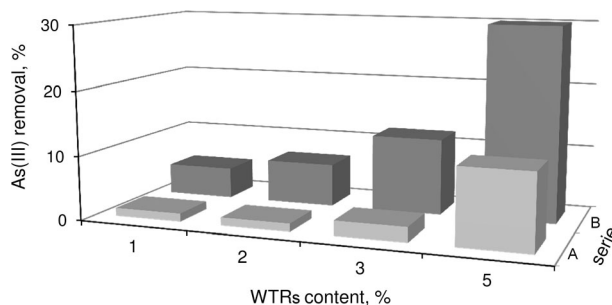


Fig. 8 Efficiency of arsenite removal by means of WTRs-loaded alginate beads containing different WTRs deposit, formed using polymer solutions with different concentrations, 3 % (series A) or 1 % (series B)

effectiveness for As(III) and As(V) (Jacukowicz-Sobala et al. 2013; Lakshmipathiraj et al. 2006; Zhu et al. 2015). The simplified scheme of As(III) and As(V) adsorption mechanisms on Fe–Mn binary oxides is presented in Fig. 9.

Moreover, oxidation of As(III) by means of manganese dioxide is accompanied by release of Mn^{2+} cations and their adsorption on a negatively charged sorbent surface, which finally improves adsorption of arsenate anions in neutral and slightly alkaline conditions (Zhang et al. 2007; Saleha et al. 2011). The effect of pH on arsenic adsorption efficiency by WTRs-loaded alginate beads (pH_{pzc} of the obtained product was determined as 6.2) is shown in Fig. 10.

As can be seen, the increase of pH from 4.5 to 7.5 negatively influenced the adsorption capacity of the sorbent, especially toward As(V). This agrees with previous studies and literature data, although in comparison with adsorption on raw water treatment residuals (not entrapped in alginate beads), the decrease in process efficiency was more noticeable. This can be explained by chemical properties of calcium alginate. The negatively charged carboxylic groups with $pK_a=3.4-4.4$ (depending on the ratio of mannuronate and guluronate units in the polymer) impeded the diffusion of arsenate anions into sorbent beads. Moreover, the negative charge of arsenates increased with the increase of solution pH, due to the higher contribution of $HAsO_4^{2-}$ divalent ions ($pK_{a2}=7.1$). Simultaneously, the diffusion limitations affected the adsorption of uncharged arsenite molecules to a lesser degree, resulting in a lower decrease in arsenic(III) removal efficiency with pH increase. Furthermore, adsorption of As(III) was additionally

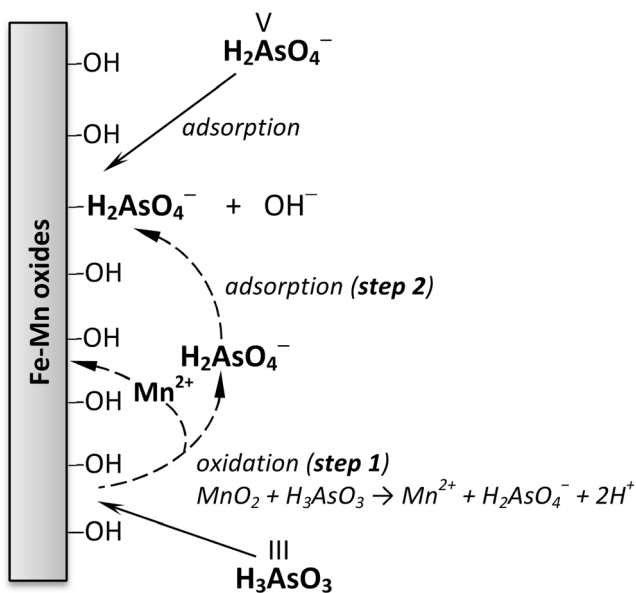


Fig. 9 The scheme of As(V) adsorption and As(III) oxidation and adsorption on Fe–Mn binary oxides

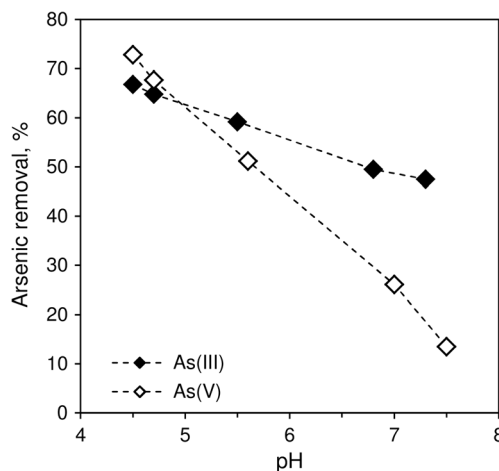


Fig. 10 Effect of pH on arsenic removal by selected WTRs-loaded alginate beads (5 % WTRs, 1 % alginate solution)

enhanced by the presence of Mn^{2+} cations, being released during reductive dissolution of manganese dioxide.

Kinetic studies of As(III) and As(V) adsorption

The effect of contact time on As(III) and As(V) adsorption at different initial concentrations (10 and 25 mg As L^{-1}) and different pH conditions is shown in Fig. 11a, b. Since WTRs-loaded alginate beads revealed buffering properties similarly as WTRs sludge maintained neutral pH of the treated solution, the adsorption process at $pH=4.5$ was conducted in acetate buffer. As can be seen, the adsorption of both arsenic forms is not a rapid process, especially in comparison to iron oxide nanoparticles or microparticles, and the equilibrium was reached after exceeding 24 h (Lakshmipathiraj et al. 2006; Zhang et al. 2007). In every case, the process began with initial fast arsenic uptake followed by gradual slowdown before achieving an equilibrium. Distinctive differences were observed between As(III) and As(V) adsorption at different pH, which confirmed the more significant influence of pH on arsenate(V) adsorption.

In order to understand the mechanism of the process, determine its rate, and identify rate-limiting steps, experimental kinetic data were evaluated using pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic reaction models, as well as an intraparticle diffusion (ID) model (Qiu et al. 2009). The pseudo-first-order kinetic model considers that the adsorption rate is proportional to the number of unoccupied sites. It can be expressed as

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{1}$$

The pseudo-second-order model can be applied for the description of chemisorption, where covalent or ionic bonds

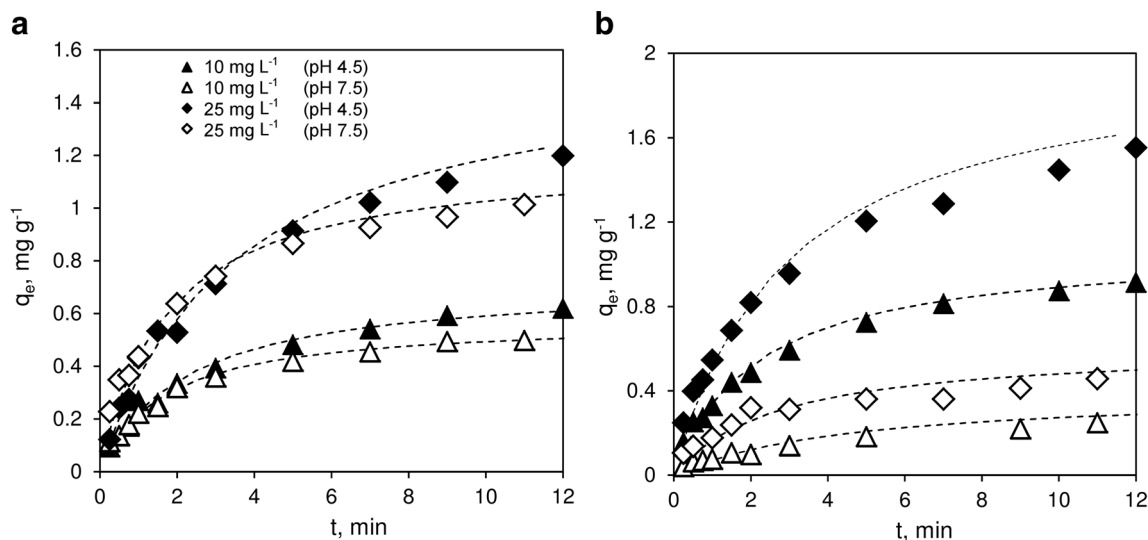


Fig. 11 Kinetics of arsenite (a) and arsenate (b) adsorption on the selected WTRs-loaded alginate beads at various concentrations and pH (the dashed lines are the plots of the pseudo-second-order kinetic model)

between adsorbate and adsorbent are formed. The equation may be expressed in the form

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (2)$$

$$h_0 = k_2 q_e^2 \quad (3)$$

where k_1 and k_2 are the equilibrium rate constants of the PFO and PSO adsorption respectively, q_e is the amount of adsorbate adsorbed at equilibrium, q_t is the amount adsorbed at time t , and h_0 is the initial rate of adsorption.

The intraparticle diffusion model describes the adsorption from a mechanistic point of view, allowing the identification of the steps involved in this process. It can be expressed as a function of the square root of time:

$$q_t = k_i t^{0.5} + C \quad (4)$$

where k_i is the intraparticle rate constant and C is the intercept. If the plot of q_t versus $t^{0.5}$ is a straight line and the intercept C passes through the origin, the sole rate-limiting step during the adsorption process is the pore diffusion. Otherwise, if the intercept differs from zero, the adsorption kinetics is also controlled by film diffusion.

The parameters calculated from PFO, PSO, and ID models are listed in Tables 1 and 2. In all four As(III) adsorption experiments, the data fitted well the PSO model, which considers an adsorption mechanism based on chemical interactions between sorbate and adsorbent surface. This confirms literature data on the mechanism of As(III) adsorption on the iron and manganese oxide surface (Zhang et al. 2007; Saleha et al. 2011). However, in the case of As(V), this model described better only data obtained from the kinetic study conducted at the initial concentration of 10 mg As(V) L⁻¹ at acidic pH. Fitting of the other data (25 mg As(V) L⁻¹, pH=4.5 and

7.5) was ambiguous, and the data obtained at a concentration of 10 mg As(V) L⁻¹ at pH=7.5 surprisingly followed the PFO model. This result may imply that chemisorption of As(V) at neutral pH is not the rate-limiting step. Presumably, in this case, diffusion of arsenates throughout the matrix of alginate beads to the WTRs particle surface comprises a significant barrier determining the rate of the process. The confirmation of this supposition is the result of analysis of experimental data using the ID model equation (Fig. 12). Adsorption of

Table 1 Kinetic parameters for arsenic adsorption from solutions with initial concentration of 10 mg L⁻¹

Parameter	As(III)		As(V)	
	pH 4.5	pH 7.5	pH 4.5	pH 7.5
Pseudo-second-order kinetic equation				
k_2 (g mg ⁻¹ h ⁻¹)	0.63	1.06	0.42	0.55
q_e (mg g ⁻¹)	0.72	0.57	1.09	0.40
q_e experimental	0.66	0.54	1.01	0.36
h_0 (mg g ⁻¹ h ⁻¹)	0.33	0.35	0.49	0.09
r^2	0.998	0.999	0.998	0.939
Pseudo-first-order kinetic equation				
k_1 (h ⁻¹)	0.10	0.11	0.11	0.10
q_e (mg g ⁻¹)	0.48	0.35	0.74	0.35
r^2	0.884	0.887	0.947	0.982
Intraparticle diffusion kinetic equation				
k_{id1} (mg g ⁻¹ h ^{-0.5})	0.25	0.22	0.33	0.072
C (mg g ⁻¹)	-0.028	-0.01	0.004	0.008
r^2	0.954	0.973	0.990	0.994
k_{id2} (mg g ⁻¹ h ^{-0.5})	0.16	0.11	0.15	-
r^2	0.997	0.996	0.979	-

k_{id1} and k_{id2} are equilibrium rate constants for the first and the second stage of adsorption process

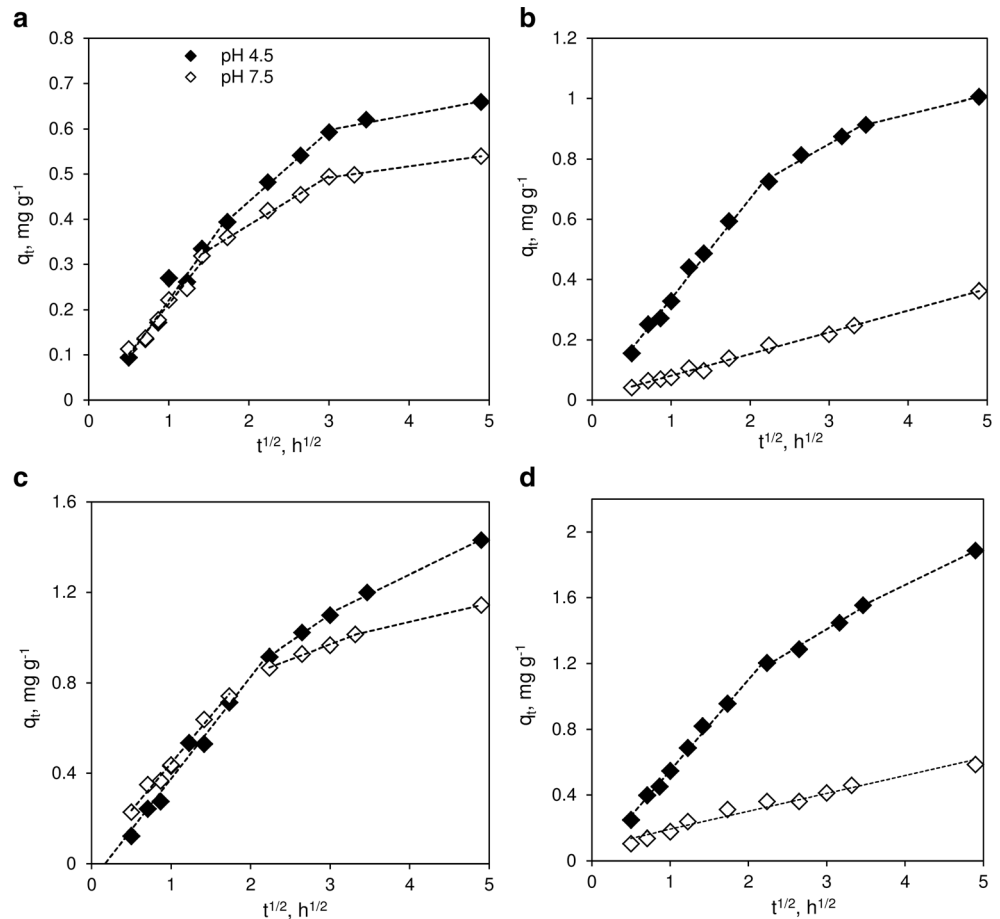
Table 2 Kinetic parameters for arsenic adsorption from solutions with initial concentration of 25 mg L⁻¹

Parameter	As(III)		As(V)	
	pH 4.5	pH 7.5	pH 4.5	pH 7.5
Pseudo-second-order kinetic equation				
k_2 (g mg ⁻¹ h ⁻¹)	0.18	0.48	0.17	0.61
q_e (mg g ⁻¹)	1.59	1.2	2.02	0.61
q_e experimental	1.43	1.14	1.89	0.58
h_0 (mg g ⁻¹ h ⁻¹)	0.46	0.7	0.69	0.23
r^2	0.994	0.997	0.987	0.969
Pseudo-first-order kinetic equation				
k_1 (h ⁻¹)	0.092	0.12	0.10	0.12
q_e (mg g ⁻¹)	1.25	0.77	1.59	0.48
r^2	0.967	0.951	0.989	0.972
Intraparticle diffusion kinetic equation				
k_{id1} (mg g ⁻¹ h ^{-0.5})	0.45	0.42	0.58	0.11
C (mg g ⁻¹)	-0.07	0.025	-0.034	0.08
r^2	0.98	0.989	0.994	0.969
k_{id2} (mg g ⁻¹ h ^{-0.5})	0.24	0.13	0.29	–
r^2	0.997	0.997	0.989	–

k_{id1} and k_{id2} are equilibrium rate constants for the first and the second stage of adsorption process

As(III) at various concentrations and pH values is a three-stage process—first controlled by external diffusion, the second step controlled by intraparticle diffusion, and the third step corresponding to equilibrium stabilization. In the case of As(V), the same shape of the ID curve was obtained only for a concentration of 10 mg L⁻¹ at acidic pH, while for a higher concentration under the same pH, adsorption of arsenic was a two-stage process. The first step was probably controlled by intraparticle diffusion, since intercept C for this curve is close to 0.0. Simultaneously, adsorption of As(V) at neutral pH without regard to concentration is only controlled by intraparticle diffusion. Kinetic studies conducted at different pH values have been useful for elucidating the mechanism of As(III) and As(V) adsorption. The kinetics of As(III) adsorption were more affected by its concentration than pH, in contrast to As(V) adsorption kinetics, which were strongly influenced by pH of treated solutions. Due to the low dissociation degree of As(III) species at the studied pH range, its adsorption was solely driven by the concentration gradient. Therefore, the initial adsorption rate was higher for a higher arsenic concentration, while the overall adsorption rate was higher for a lower concentration, since

Fig. 12 Plots of the intraparticle diffusion model for arsenic adsorption on selected WTRs-loaded alginate beads: **a** 10 mg As(III) L⁻¹, **b** 10 mg As(V) L⁻¹, **c** 25 mg As(III) L⁻¹, and **d** 25 mg As(V) L⁻¹ at different pH



more available active sites on the outer sphere of the beads were sufficient for fewer portions of the sorbate. Although overall adsorption rates of As(III) were higher in comparison to As(V) under respective conditions, at acidic pH, the initial rates of As(V) adsorption surpassed these values determined for As(III). This phenomenon was due to the one-step mechanism of arsenate adsorption and electrostatic attraction of the positively charged surface of WTRs below $pH_{pzc} = 6.2$, which was the driving force of the process under these conditions. Summing up the kinetic studies, the rate of arsenite adsorption was controlled by chemical reactions occurring on the WTRs surface (oxidation and inner sphere complex formation), while the arsenate adsorption rate was determined by its diffusion within the polymeric matrix of calcium alginate beads.

Equilibrium studies of As(III) and As(V) adsorption

The fitting of experimental data to theoretical models allows one to determine key parameters describing the adsorption

process. The results of equilibrium studies of arsenate and arsenite adsorption on WTRs-loaded calcium alginate beads are presented in Fig. 13. Experimental data were analyzed using Langmuir (4,6) and Freundlich (5,7) isotherm models:

$$q_e = \frac{q_m K_L c_e}{1 + K_L c_e} \tag{5}$$

$$q_e = K_F c_e^{\frac{1}{n}} \tag{6}$$

where q_m and q_e are the maximum and equilibrium sorption capacities, c_e is the equilibrium concentration, K_L is the Langmuir isotherm constant expressing the affinity of binding sites, K_F is the Freundlich isotherm constant related to the adsorption capacity, and $1/n$ is the heterogeneity factor. Fitting of experimental data to theoretical models was conducted using linearized forms of equations:

$$\frac{c_e}{q_e} = \frac{1}{K_L q_m} + \frac{c_e}{q_m} \tag{7}$$

$$\log q_e = \log K_F + \frac{1}{n} \log c_e \tag{8}$$

Fig. 13 Adsorption isotherms of **a** As(III) at pH=7.5, **b** As(III) at pH=4.5, **c** As(V) at pH=7.5, and **d** As(V) at pH=4.5 on selected WTRs-loaded alginate beads. The lines are the plots of theoretical isotherm models

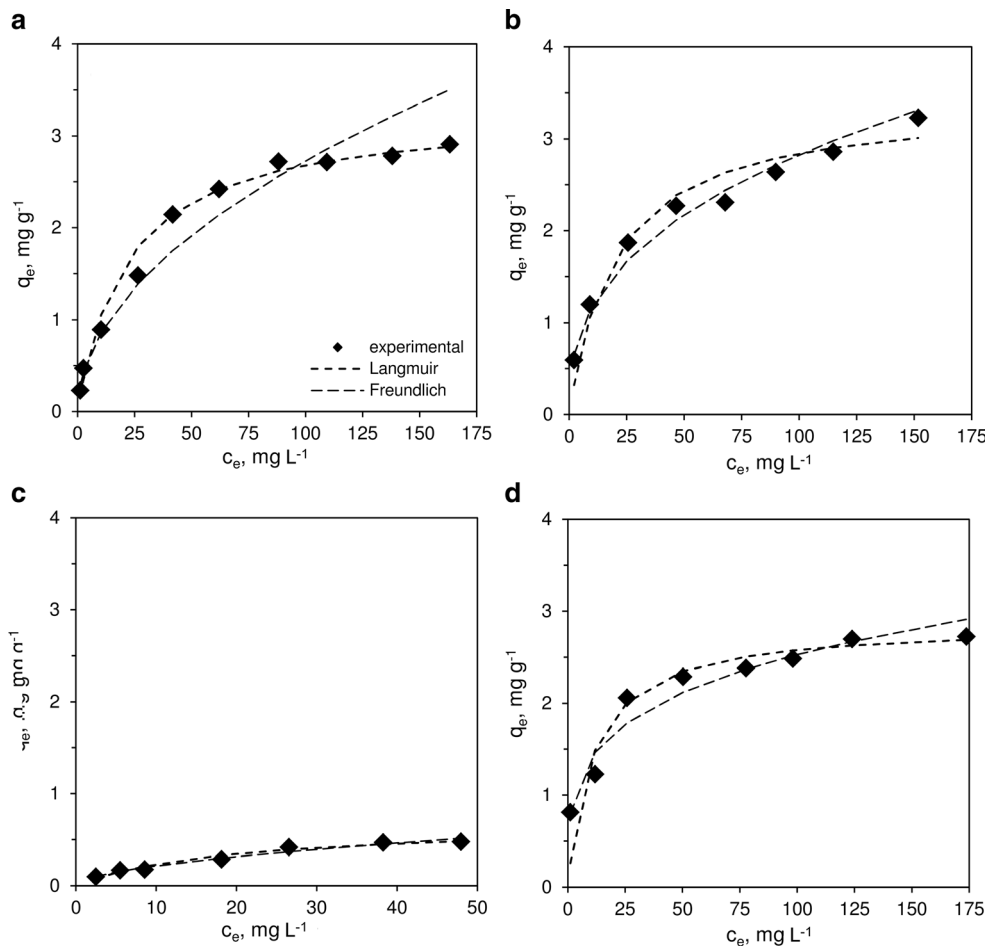


Table 3 Langmuir and Freundlich isotherm parameters for arsenic sorption on WTRs-loaded alginate beads

Isotherm model	As(III)		As(V)	
	pH 4.5	pH 7.5	pH 4.5	pH 7.5
Langmuir				
q_m (mg g ⁻¹)	3.40	3.26	2.86	0.67
K_L (L mg ⁻¹)	0.050	0.046	0.092	0.053
R^2	0.977	0.992	0.994	0.948
Freundlich				
K_F (L g ⁻¹)	0.49	0.26	0.78	0.06
$1/n$	0.38	0.51	0.26	0.55
R^2	0.985	0.975	0.953	0.981

The determined isotherm parameters for As(III) and As(V) adsorption are presented in Table 3. The calculated correlation coefficients as well as the shapes of plotted isotherms (Fig. 13a, c, d) showed better fit of experimental data by a Langmuir type of equation than Freundlich, with the exception of adsorption of As(III) in acidic pH. Under these conditions, the shape of the plotted isotherm (Fig. 13b) is typical for a power-type function without a plateau. This might be caused by the release of Mn²⁺ cations (during arsenite oxidation), which are adsorbed on the sorbent surface, creating new adsorption sites. Thus, the higher the initial concentration of arsenite was, the more new active sites were created. At neutral pH, this mechanism was also essential.

However, owing to the fact that some of the arsenites were dissociated at higher pH, their diffusion into sorbent beads was suppressed by the negative charge of alginate chains. As a consequence, the saturation of the sorbent beads occurred at a lower solution concentration, and the isotherm reached a plateau. Nonetheless, due to the preoxidation mechanism, the calculated adsorption capacities were much higher for

As(III) than for As(V) in neutral conditions. Above the pH_{pzc} of the sorbent, the adsorption of arsenate anions decreased fourfold in comparison with the values obtained in acidic conditions. Nevertheless, the calculated values of K_L constant indicate that the affinity of binding sites was the highest for As(V) adsorption in an acidic environment. The feasibility of the adsorption process can also be predicted by the value of the separation factor (R_L):

$$R_L = \frac{1}{1 + K_L c_0} \tag{9}$$

where K_L is the Langmuir constant and c_0 is the initial concentration of the solution. The adsorption is favorable when the R_L values are between 0 and 1, unfavorable if $R_L > 1$, and irreversible if $R_L = 0$. The calculated values of the separation factor were in the range of 0.05–0.52 for As(V) adsorption at pH 4.5 and 0.1–0.85 for other conditions. This might be explained by the ability of direct formation of inner sphere complexes (the most thermodynamically stable) of arsenates on the iron oxide surface below pH_{pzc} . The values of maximum sorption capacity of the studied sorbent were in acidic conditions 3.4 and 2.9 mg g⁻¹ for As(III) and As(V), respectively. Due to hydrogel matrix of alginate beads containing over 90 % of water, in order to compare their adsorptive properties with that of raw WTRs as well as of other sorbents, the maximum sorption capacity was also expressed in relation to the dry mass of the sorbent, which was 38.2 mg As(III) g⁻¹ and 32.6 mg As(V) g⁻¹. The obtained values were comparable with sorption capacity of synthetic materials containing binary Fe–Mn oxides such as modified graphene or hybrid polymers based on ion exchangers (Table 4). However, they are significantly lower than sorption capacity of inorganic materials containing Fe–Mn oxides as main constituents—both synthetic (Zhang et al. 2007) and waste materials (raw WTRs) (Ociński et al. 2016). Lower sorption capacity of obtained product is a result of the presence of polymeric support, which does not exhibit adsorption capacity and

Table 4 Comparison of sorption capacity of different Fe/Mn oxides containing materials

Adsorbent	q_{max} (mg g ⁻¹)		Reference
	As(III)	As(V)	
Graphene modified by Fe–Mn binary oxide	47.05	49.01	Zhu et al. 2015
Fe–Mn binary oxide	119.12	69.70	Zhang et al. 2007
Mn-substituted iron oxo-hydroxide	4.58	5.72	Lakshmipathiraj et al. 2006
Tetravalent manganese ferroxhyte	6.70	11.70	Tresintsi et al. 2013
Macroporous anion exchanger-supported Fe–Mn binary oxide	44.91	13.17	Li et al. 2012
Anion exchanger containing Fe/Mn oxides	40.20	86.5	Jacukowicz-Sobala et al. 2014
Hybrid polymer containing Fe/Mn oxides	13.5	14.5	Jacukowicz-Sobala et al. 2013
Water treatment residuals containing Fe/Mn oxides (raw WTR)	132.17	76.73	Ociński et al. 2016
Water treatment residuals (containing Fe/Mn oxides) entrapped in calcium alginate	3.40 (38.2) ^a	2.86 (32.6) ^a	This study

^a Values calculated for dry mass of the sorbent

hinders active sites on WTRs surface. Simultaneously, its presence ensures desired hydraulic and mechanical properties which are important in fixed-bed adsorption processes. Considering the content of WTRs in formed alginate beads (55.6 % w/w of dry mass of the sorbent), sorption capacity calculated for dry WTRs was 68.7 mg As(III) g⁻¹ and 58.63 mg As(V) g⁻¹, and the degree of utilization of their adsorption capacity was about 52 % for As(III) and 76 % for As(V).

Conclusions

Entrapment of water treatment residuals into calcium alginate polymer allowed us to obtain an effective sorbent for arsenite and arsenate removal from water. The proposed method consisting of mixing of WTRs suspension, after its sonication, with sodium alginate solution allowed us to obtain homogeneous, spherical beads with a narrow size distribution. The chemical pretreatment of WTRs was performed by rinsing it with 0.05 M HCl solution, in order to dissolve compounds of heavy metals co-precipitated during the water deironing process. Preliminary studies showed that the best adsorptive properties were exhibited by a product containing 5 % WTRs within the polymer matrix, formed using one percentile alginate solution. This material, in the form of spherical beads with a diameter of 2.5 mm, is free of the main drawback of raw residuals composed from micro-sized particles difficult to separate from treated solution. The maximal adsorption capacity, toward As(III) and As(V) species, of the obtained sorbent was smaller (3.4 and 2.9 mg g⁻¹, respectively) than that of raw WTRs, but considering its content in formed alginate beads, the degree of utilization of the WTRs adsorption capacity amounted to 52 and 76 %. Since hydrogel matrix of alginate beads contained over 90 % of water, maximal sorption capacity calculated for a dry mass of the sorbent was 38.2 mg As(III) g⁻¹ and 32.6 mg As(V) g⁻¹. Entrapment of WTRs into alginate polymer slowed down the arsenic adsorption rate in comparison with their raw form. Due to the presence of negatively charged carboxylic groups in alginate polymer chains, the slowdown distinctly affected arsenate removal, especially in neutral pH conditions. The main rate-limiting step of As(V) adsorption was intraparticle diffusion, whereas adsorption of arsenites was controlled mainly by the two-step binding mechanism of As(III) on the surface of iron oxides. The influence of pH on the adsorption effectiveness was crucial, especially for arsenate removal. The increase of pH from 4.5 to 7.5 resulted in a drop of adsorption capacity from 2.9 to 0.7 mg g⁻¹. For arsenites, the adsorption capacity decreased in these conditions from 3.4 to 3.3 mg g⁻¹. The only slight influence of pH on arsenite removal efficiency resulted from its high dissociation constant (pK_{a1} = 9.2) and different, two-step mechanism of As(III) adsorption in the presence of manganese dioxide being a constituent of WTRs. Further

investigations have to be carried out in order to gain a complete characterization of the adsorption process conducted in a dynamic regime. Since entrapment of WTRs into alginate beads slowed down the adsorption rate, it is essential to find optimal fixed-bed parameters, including the diameter of the beads, which would enable the high adsorption rate to be combined with low hydraulic resistance of the bed.

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