

## Powder iron-containing adsorbents for arsenic removal: influence of heating

Marta Litynska \*, Roman Antoniuk, Nataliia Tolstopalova, Igor Astrelin

National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute", 37 Peremohy pr., Kyiv, 03056, Ukraine

### ARTICLE INFO

#### Article history:

Received 8 October 2017

Received in revised form 30 October 2017

Accepted 1 November 2017

#### Keywords:

Arsenic removal

Adsorption

Iron (III) oxyhydroxide

Arsenate

Arsenite

### ABSTRACT

There is a variety of treatment methods for arsenic-containing waters, but adsorption is one of the most popular among them, providing the removal of arsenic compounds from aqueous phase. For sorption experiments, two iron (III)-containing adsorbents with different drying and roasting modes were used. Adsorbent roasted at 250°C demonstrated better As(V) removal properties than adsorbent dried at 18°C. For all discovered impurities (Na<sub>2</sub>HAsO<sub>4</sub>, Na<sub>3</sub>AsO<sub>3</sub> and C<sub>16</sub>H<sub>13</sub>N<sub>2</sub>O<sub>11</sub>S<sub>2</sub>As) adsorbent dried at 18°C demonstrated worth sorption efficiency than the one processed at 250°C. Thus, the heating increases arsenic removal efficiency of iron-containing adsorbents, while the drying of iron (III) hydroxide at low temperatures gives insufficient result.

© 2017 Process Engineering Journal.

## 1. Introduction

Arsenic occurs in nature in different oxidation states from –3 to +5, but in natural waters +3 and +5 forms are predominant. Drinking water with arsenic content more than 10 µg/L is dangerous for consumption, causing different health problems. Arsenic compounds occur in natural waters of many countries (Iran, China, India, Chile, Mexico, Taiwan, Italy, etc.) and its concentration is often much higher than normative content [1]. Consequently, for these countries arsenic removal is one of the most important stages in drinking water treatment.

Speciation of arsenic compounds depends from geochemical and climatic conditions; type of water body; chemical, hydrological and biological processes in water body; source of arsenic compound; pathways, etc. There are different natural and anthropogenic ways for arsenic compounds to get into natural waters (Fig. 1).

In natural waters arsenic can occur in organic or inorganic form, +5 or +3 oxidation state. In groundwaters, both inorganic As(III) and As(V) may occur, but presence of As(III) is more frequent [2]. For surface water bodies, As(V) is more characteristic than As(III) due to aerobic conditions. Sometimes, especially during the warm period, arsenic is in organic forms, i.e. monomethylarsonic acid or

dimethylarsinic acid. Microbiological activity is the main reason of these transformations. In addition, As(V) can replace P(V) in different biological processes and after decompositions of aquatic plants, fishes and other organisms, arsenic enters water in organic form. Besides, arsenic can form soluble complexes with humic compounds, which take place in humus layer of soil, peat bogs or in water bodies with high humic content [3].

There are a lot of treatment methods (reverse osmosis, ion exchange, coagulation, electrocoagulation, adsorption, etc.) for arsenic-containing waters and all of them have advantages and disadvantages. Reverse osmosis has high energy consumption and is ineffective in As(III) removal, but doesn't require big amount of chemicals and has small physical footprint. Ion exchange also doesn't need a lot of space, but produces arsenic-containing water after regeneration, which requires utilization. Coagulation by iron (III)-containing coagulants can effectively remove As(III), As(V) and organic matter, but has high chemicals consumption and high space requirements. Now adsorption is one of the most popular methods of arsenic compounds removal from aqueous phase. This method has small physical footprint and doesn't need permanent dosage of chemicals. Some adsorbents can effectively purify water from all forms of arsenic and many other pollutants. Also, it is possible to apply different type of adsorbents in one filter [3].

\* Corresponding author. E-mail address: maril91@mail.ru

© 2017 Process Eng. J. Process Engineering Journal is licensed under a "Creative Commons Attribution-NonCommercial 4.0 International License (CC BY-NC 4.0)".

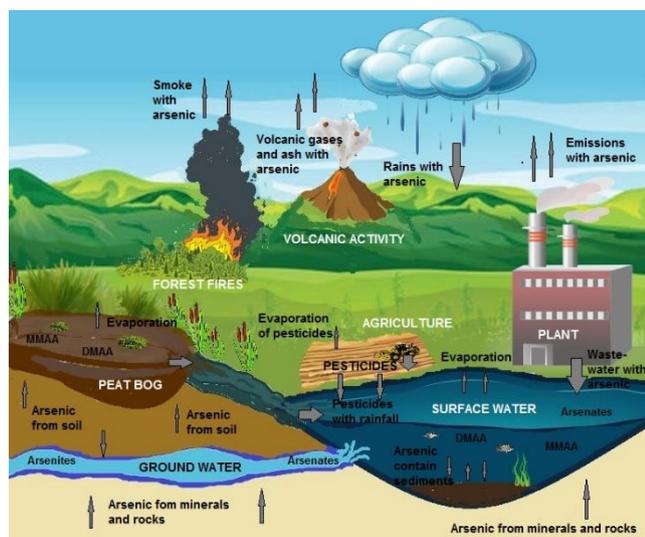


Fig. 1 - Sources and pathways of arsenic compounds getting into natural waters.

Different types of adsorbents can be used for arsenic removal, such as: ferric hydroxide, iron (III) oxyhydroxide, iron (III) oxide, magnetite, aluminium oxide, chitosan-based sorbents, CuO, zero-valent iron, zirconium compounds, zeolites, TiO<sub>2</sub>, Mn<sub>2</sub>O<sub>4</sub>, activated carbons, different wastes and by-products, etc [1, 4-11].

In addition, different combinations of these adsorbents can be used, for instance: TiO<sub>2</sub>-impregnated chitosan bead, natural zeolite (clinoptilolite type) modified by magnetite, Fe-sericite composite powder, porous silica modified by bis(3-triethoxysilylpropyl) tetrasulfide, multiwall carbon nanotube doped by zero valent iron, hydrogel-biochar composite, zirconium-doped activated carbon fiber, egg shells coated by manganese oxide, aluminum oxyhydroxide-poly[(4-vinylbenzyl)trimethylammonium chloride] hybrid sorbent, zirconium oxide on alginate beads, Fe-Mn binary oxide impregnated chitosan bead, chitosan/Cu(OH)<sub>2</sub> and chitosan/CuO composites, etc [12-23].

However, iron-containing sorbents are cheap, easy synthesized and eco-friendlier than any other adsorbents. That's why they are still very popular for arsenic removal. NaOH solution is usually used for precipitation of iron (III) hydroxide, but in our case ammonia solution was used. It is well known that precipitation pH, concentration and type of reagents and drying mode have very great influence on the properties of iron compounds, but low-temperature drying (under approximately room temperature) was never previously discovered. Theoretically, this adsorbent can be more hydrated and have better adsorbent properties than sorbents with high-temperature drying. But different processes can take place and affect adsorption characteristics. Thus, the comparison of two heating modes (18°C and 250°C) can give interesting results.

## 2. Materials and methods

### 2.1. Synthesis of iron-containing powder sorbents

Iron (III) hydroxide was precipitated from concentrated FeCl<sub>3</sub> solution by 5% solution of NH<sub>4</sub>OH at pH 10. Hydroxide was

produced at incessant mixing by magnetic stirrer. After that slurry was filtered and rinsed on the filter by distilled water.

One portion of rinsed iron (III) hydroxide was dried to complete dryness in desiccator at the temperature of 18 °C and then powdered.

Other portion was dried at the temperature of 105 °C during 10 h. Then it was crushed and after that roasted during 1 h at 250°C. Cooled material was powdered.

### 2.2. Adsorption experiments

For sorption experiments, Na<sub>2</sub>HAsO<sub>4</sub>, Na<sub>3</sub>AsO<sub>3</sub> and C<sub>16</sub>H<sub>13</sub>N<sub>2</sub>O<sub>11</sub>S<sub>2</sub>As solutions were used. Portions (200 mL) of Na<sub>2</sub>HAsO<sub>4</sub> solution (initial concentration of As(V) was 500 µg/L) were placed in a conical flasks (volume of flask is 250 mL) with screw caps. Sorbent dose was 0.25 g/L. Sorbent was dosed into flasks. After that flasks are placed on the orbital shaker. Shaking durations were: 5, 10, 20, 40, 90 and 120 min. After sorption, solutions were filtered and analyzed.

As(V) concentration in filtrate was determined photometrically. The method is based on the methodology which applies ammonium molybdate and ascorbic acid with subsequent measurement of optical density at the wavelength of 840 nm [24].

For As(III) sorption, Na<sub>3</sub>AsO<sub>3</sub> solution (initial concentration of As(III) was 500 µg/L) was used. Other experimental conditions were the same. Filtrate was oxidized to transform As(III) into As(V). After that concentration was determined according to the previous procedure.

For experiments with organic arsenic compounds C<sub>16</sub>H<sub>13</sub>N<sub>2</sub>O<sub>11</sub>S<sub>2</sub>As solution was prepared. Initial content of C<sub>16</sub>H<sub>13</sub>N<sub>2</sub>O<sub>11</sub>S<sub>2</sub>As (Fig. 2) was 20 mg/L. Prepared solution has a red color.

Other conditions were analogical. Residual concentration was determined by the measurement of filtrate optical density at the wavelength of 500 nm [25].

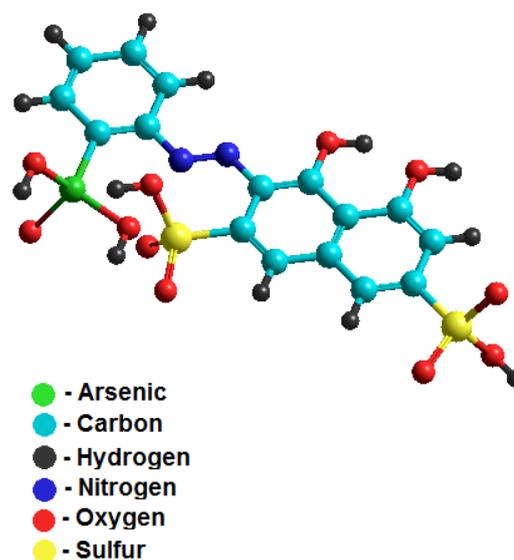


Fig. 2 - Structure of 5-hydroxy-3-[[2-[hydroxy(oxido)arsoryl]phenyl]hydrazinylidene]-4-oxonaphthalene-2,7-disulfonate.

### 3. Results and discussion

Adsorbent roasted at 250°C (A2) demonstrated better As(V) removal properties than adsorbent dried at 18°C (A1) (Fig. 3). During 120 min sorption, A2 reduced As(V) concentration from 500 to 115 µg/L (77% removal), but in A1 case, As(V) content decreased only to 207 µg/L (58.6% removal).

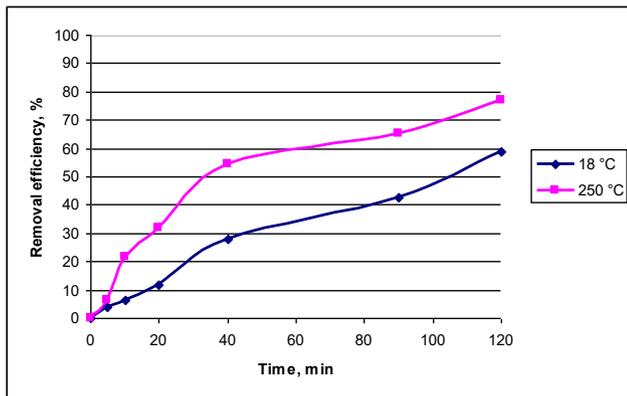


Fig. 3 - As(V) removal by adsorbent roasted at 250°C (A2) and adsorbent dried at 18°C (A1).

A1 needed too much time (about 5 days) to dry at the temperature of 18°C. Therefore, different stabilization processes could take place, which could quite efficiency reduce the sorption of the adsorbent. After 2 h sorption, capacities of adsorbents were 1.17 and 1.54 mg As(V)/g for samples dried at 18°C and 250°C, respectively. But equilibrium capacity could be much higher. According to Ref. [26], some materials had worth or better adsorption properties, for example, iron oxide coated sands had lower As(V) capacity (0.008–0.043 mg/g), ferrihydrite capacity was 0.25–111.02 mg/g (conditions had very big influence), but TiO<sub>2</sub> was more effective (4.65–37.46 mg/g). Thus, A1 and A2 adsorption efficiency was comparable with other popular adsorbents for arsenic removal.

Also, these two samples had different structure. A1 was much more amorphous than A2, because A1 didn't undergo thermal decomposition. During the heating, iron (III) hydroxide lost water and became more crystalline due to the formation of FeO(OH) and Fe<sub>2</sub>O<sub>3</sub>. But in the case of As(III), the difference was not so significant (Fig. 4).

During the first phase (10–15 min), A1 showed better results than A2, but later A2 reduced arsenic concentration more significantly than A1. During 120 min sorption, A2 removed 71.6% (residual arsenic concentration was 142 µg/L) and A1 removed only 63.8% (residual content was 181 µg/L). These adsorbents demonstrated same As(III) capacities (1.28 and 1.43 mg/g for A1 and A2, respectively), which were comparable with such sorbents as iron oxide coated sands (0.028–0.136 mg/g), nanoscale zero-valent iron (2.47 mg/g), modified calcined bauxite (1.37 mg/g), etc. [26].

A1 and A2 removed C<sub>16</sub>H<sub>13</sub>N<sub>2</sub>O<sub>11</sub>S<sub>2</sub>As very effectively and demonstrated the extent levels for water treatment (Fig. 5).

During 120 min of sorption, A1 reduced concentration of C<sub>16</sub>H<sub>13</sub>N<sub>2</sub>O<sub>11</sub>S<sub>2</sub>As from 20 to 1.21 µg/L and A2 reduced content to

0.91 µg/L with removal efficiencies of 94% and 95.5%, respectively. But even after 5 min of the adsorption, both sorbents showed high efficiency (91.7% for A1 and 92.4% for A2).

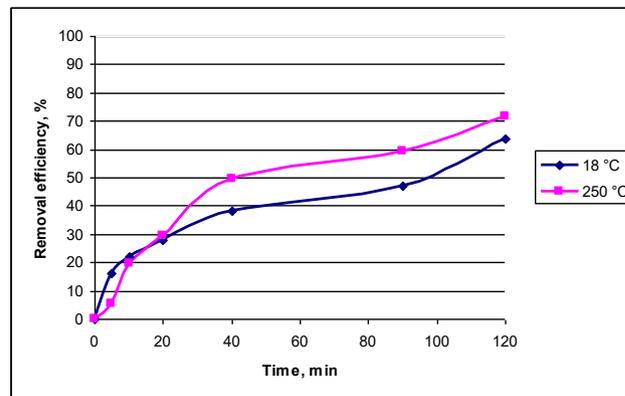


Fig. 4 - As(III) elimination by adsorbent roasted at 250°C (A2) and adsorbent dried at 18°C (A1).

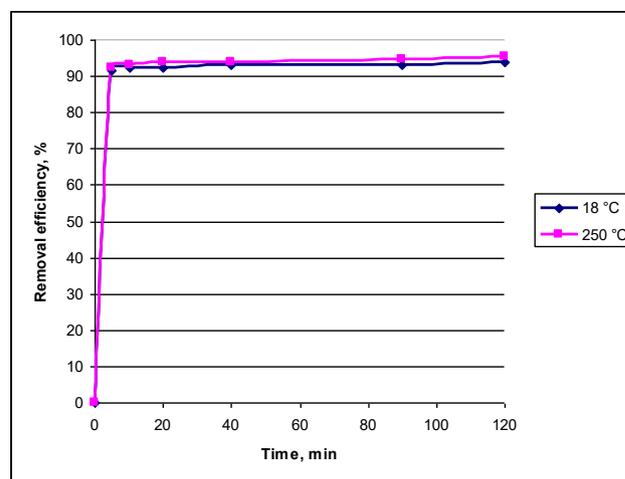


Fig. 5 - C<sub>16</sub>H<sub>13</sub>N<sub>2</sub>O<sub>11</sub>S<sub>2</sub>As removal by adsorbent roasted at 250°C (A2) and adsorbent dried at 18°C (A1).

Thus, heating mode during adsorbent preparation had very significant influence on sorption of inorganic As(III) and As(V), but for arsayl compound the difference was mitigated. During heating, precipitated amorphous ferrihydrite lost water and changed its structure. It became more crystalline and iron content increased in sorbent with decreasing of water and OH-group content. Consequently, in this case for As(III) and As(V), high iron content was more important than availability of OH-groups. But OH-groups were perspective in terms of ion exchange (OH<sup>-</sup> and arsenate or arsenite anions could be interchanged). Thus, it is expediently to continue experiments with other drying temperatures, for example, 50 or 75°C. Amorphous iron (III) hydroxide continues to be amorphous after these heating modes, but exsiccation is quicker, hence influence of different stabilization processes can be lower.

#### 4. Conclusion

Two iron (III)-containing adsorbents with different drying and roasting modes were used for arsenic removal from aqueous solutions. Adsorbent roasted at 250°C (A2) demonstrated better As(V) removal properties than adsorbent dried at 18°C (A1). During 120 min sorption, A2 reduced As(V) concentration from 500 to 115 µg/L (77% removal), but in A1 case As(V) content decreased only to 207 µg/L (58.6% removal). But in the case of As(III), the difference was not so significant. During 120 min sorption, A2 removed 71.6% (residual arsenic concentration was 142 µg/L) and A1 removed only 63.8% (residual content was 181 µg/L).

A1 and A2 removed C<sub>16</sub>H<sub>13</sub>N<sub>2</sub>O<sub>11</sub>S<sub>2</sub>As very effectively and demonstrated the same results. During 120 min sorption, A1 reduced concentration of C<sub>16</sub>H<sub>13</sub>N<sub>2</sub>O<sub>11</sub>S<sub>2</sub>As from 20 to 1.21 mg/L and A2 reduced content to 0.91 mg/L with removal efficiencies of 94 and 95.5%, respectively. But even after 5 min of the adsorption, both sorbents showed high efficiency (91.7% for A1 and 92.4% for A2).

Consequently, in the case of all discovered impurities (Na<sub>2</sub>HAsO<sub>4</sub>, Na<sub>3</sub>AsO<sub>3</sub> and C<sub>16</sub>H<sub>13</sub>N<sub>2</sub>O<sub>11</sub>S<sub>2</sub>As), adsorbent dried at 18°C (A1) demonstrated worth sorption efficiency than the adsorbent roasted at 250°C (A2). There were different explanations for this. A1 needed quite much time (about 5 days) to get dried at the temperature of 18°C. As a result, different stabilization processes could take place. It could reduce sorption efficiency of the adsorbent. Also, these two samples had different structure. A1 was much more amorphous than A2, because A1 did not undergo thermal decomposition. During heating, iron (III) hydroxide was dehydrated and became more crystalline due to the formation of FeO(OH) and Fe<sub>2</sub>O<sub>3</sub>.

Thus, the heating increases arsenic removal efficiency applying iron-containing adsorbents and the drying of iron (III) hydroxide at low temperatures gives insufficient result.

#### REFERENCES

- [1] M. Litynska, N. Tolstopalova, I. Astrelin, Neutralization of arsenic pollutants, contained in natural waters: The theoretical analysis of solubility of some arsenates and optimization of the processes, *Journal of Water and Environmental Nanotechnology* 2 (2017) 1-8.
- [2] H. Garelick, H. Jones, A. Dybowska, E. Valsami-Jones, Arsenic pollution sources, *Reviews of Environmental Contamination* 197 (2009) 17-60.
- [3] M. Litynska, I. Astrelin, N. Tolstopalova, Ways of Arsenic Compounds Getting into Natural Waters, *Modern Environmental Science and Engineering* 3 (2017) 50-60.
- [4] B. Xie, M. Fan, K. Banerjee, Modeling of arsenic(V) adsorption onto granular ferric hydroxide, *American Water Works Association* 99 (2007) 92-102.
- [5] K. Debiec et al., The influence of thermal treatment on bioweathering and arsenic sorption capacity of a natural iron (oxyhydr)oxide-based adsorbent, *Chemosphere* 188 (2017) 99-109.
- [6] R. Brion-Roby, J. Gagnon, J.-S. Deschênes, B. Chabot, Development and treatment procedure of arsenic-contaminated water using a new and green chitosan sorbent: kinetic, isotherm, thermodynamic and dynamic studies, *Pure and Applied Chemistry* 89 (2017) 840-852.
- [7] K. McDonald, K.J. Reddy, N. Singh, R.P. Singh, S. Mukherjee, Removal of arsenic from groundwater in West Bengal, India using CuO nanoparticle adsorbent, *Environmental Earth Sciences* 73 (2015) 3593-3601.
- [8] O. Eljamal, K. Sasaki, S. Tsuruyama, T. Hirajima, Kinetic Model of Arsenic Sorption onto Zero-Valent Iron (ZVI), *Water Quality, Exposure and Health* 2 (2011) 125-132.
- [9] R. Vera, C. Fontas, E. Anticó, Titanium dioxide solid phase for inorganic species adsorption and determination: the case of arsenic, *Environmental Science and Pollution Research* 24 (2017) 10939-10948.
- [10] K. Babaeiveli, A.P. Khodadoust, D. Bogdan, Adsorption and removal of arsenic (V) using crystalline manganese (II,III) oxide: Kinetics, equilibrium, effect of pH and ionic strength, *Journal of Environmental Science and Health Part A Toxic/Hazardous Substances & Environmental Engineering* 49 (2014) 1462-1473.
- [11] S. Fiore, T. Marengo, C. Briens, F. Berruti, Arsenic removal from drinking water by means of low-cost biochars derived from miscanthus and coconut shell, *Conference: Biochar: Production, Characterization and Applications* (2017) 25-30.
- [12] S.M. Miller, M.L. Spaulding, J.B. Zimmerman, Optimization of capacity and kinetics for a novel bio-based arsenic sorbent, TiO<sub>2</sub>-impregnated chitosan bead, *Water Research* 45 (2011) 5745-5754.
- [13] M. Vaclavikova, Magnetic Zeolite as Arsenic Sorbent. In Stefusova et al (Eds), *Water Treatment Technologies for the Removal of High-Toxicity Pollutants* (2009), (pp. 51-59).
- [14] J. Kim, C. Lee, S.M. Lee, Lalhmunsiam, J. Jung, Chemical and toxicological assessment of arsenic sorption onto Ferrocite composite powder and beads, *Ecotoxicology and Environmental Safety* 147 (2017) 80-85.
- [15] H. Vojoudi, A. Badiie, S. Bahar, G.M. Ziarani, F. Faridbod, M.R. Ganjali, Post-modification of nanoporous silica type SBA-15 by bis(3-triethoxysilylpropyl)tetrasulfide as an efficient adsorbent for arsenic removal, *Powder Technology* 319 (2017) 271-278.
- [16] H. Alijani, Z. Shariatnia, Effective aqueous arsenic removal using zero valent iron doped MWCNT synthesized by in situ CVD method using natural α-Fe<sub>2</sub>O<sub>3</sub> as a precursor, *Chemosphere* 171 (2016) 502-511.
- [17] M.L. Sanyang, W.A.W.A.K. Ghani, A. Idris, M. Bin Ahmad, Hydrogel biochar composite for arsenic removal from wastewater, *Desalination and Water Treatment* 57 (2016) 3674-3688.
- [18] D. Zhao, Y. Yu, J.P. Chen, Fabrication and testing of zirconium-based nano-particle doped activated carbon fiber for enhanced arsenic removal in water, *RSC Advances* 6 (2016) 27020-27030.
- [19] S. Mubarak, M. Zia-ur-Rehman, M.N. Chaudhry, Modified Eggshells as Cost Effective Adsorbent for the Treatment of Arsenic(III) Contaminated Industrial Effluents, *Asian Journal of Chemistry* 27 (2015) 1995-2000.
- [20] J. Pérez, L. Toledo, C.H. Campos, J. Yañez, B.L. Rivas, B.F. Urbano, Arsenic sorption onto an aluminum oxyhydroxide-poly[(4-vinylbenzyl)trimethylammonium chloride] hybrid sorbent, *RSC Advances* 6 (2016) 28379-28387.
- [21] O.H. Kwon, J.O. Kim, D.W. Cho, R. Kumar, S.H. Baek, M.B. Kurade, B.H. Jeon, Adsorption of As(III), As(V) and Cu(II) on zirconium oxide immobilized alginate beads in aqueous phase, *Chemosphere* 160 (2016) 126-133.
- [22] J. Qi, G. Zhang, H. Li, Efficient removal of arsenic from water using a granular adsorbent: Fe-Mn binary oxide impregnated chitosan bead, *Bioresource Technology* 193 (2015) 243-249.
- [23] K.Z. Elwakeel, E. Guibal, Arsenic(V) sorption using

- chitosan/Cu(OH)<sub>2</sub> and chitosan/CuO composite sorbents, Carbohydrate Polymers 134 (2015) 190–204.
- [24] State Standard 4152-89. Drinking water. Determination of arsenic mass concentration (in Russian). <http://www.internet-law.ru/gosts/gost/19530/>.
- [25] M. Litynska, R. Antoniuk, N. Tolstopalova, I. Astrelin, Application of arsenic aromatic compounds in modeling of arsenic-containing waters (in Ukrainian), Young Scientist 9 (2017) 270-281.
- [26] D. Mohan, C. U. Pittman Jr, Arsenic removal from water/wastewater using adsorbents - A critical review, Journal of Hazardous Materials 142 (2007) 1–53.

**Please cite this article as: M. Litynska, R. Antoniuk, N. Tolstopalova, I. Astrelin, Powder iron-containing adsorbents for arsenic removal: influence of heating, Process Eng. J. 1 (2017) 68–72.**