



Arsenic removal from water using low-cost adsorbents – a comparative study

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Abstract: Inorganic arsenic removal from water using low-cost adsorbents is presented in this paper. Selective removal of As(III) and As(V) from water was performed with natural materials (zeolite, bentonite, sepiolite, pyrolusite and limonite) and industrial by-products (waste filter sand as a water treatment residual and blast furnace slag from steel production); all inexpensive and locally available. Kinetic and equilibrium studies were realized using batch system techniques under conditions that are likely to occur in real water treatment systems. The natural zeolite and the industrial by-products were found to be good and inexpensive sorbents for arsenic while bentonite and sepiolite clays showed little affinity towards arsenic. The highest maximum sorption capacities were obtained for natural zeolite, 4.07 mg As(V) g⁻¹, and waste iron slag, 4.04 mg As(V) g⁻¹.

Keywords: adsorption; arsenic removal; arsenic remediation; low cost sorbents.

INTRODUCTION

The presence of arsenic in natural waters has become a worldwide problem in the past decades. Arsenic pollution from natural sources was recently reported in China, Taiwan, India, Bangladesh, USA, Canada, Mexico, Chile, Argentina, New Zealand, Poland, Hungary, Croatia, Serbia and Romania.^{1–5}

Arsenic is widely found in the Earth's crust in oxidation states of –3, 0, +3 and +5, often as sulfides or metal arsenides or arsenates.³ In water, it is mostly present as arsenate (+5) but under anaerobic conditions, it is likely to be present as arsenite (+3).⁴ It usually occurs in natural waters at concentrations of less than 1 or 2 μg L⁻¹.² However, in natural groundwater reservoirs where there are

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sulfide mineral deposits and sedimentary deposits derived from volcanic rocks, the concentrations can be significantly increased (up to 12 mg L^{-1}).²

Increased risks of arsenic related diseases have been reported to be associated with ingestion of drinking-water at concentrations of $<50 \text{ } \mu\text{g L}^{-1}$.^{3,5} However, considering the significant uncertainties surrounding the risk assessment for arsenic carcinogenicity and the practical difficulties in removing arsenic from drinking-water, a provisional guideline value for arsenic was set by the WHO at a limit of 0.01 mg L^{-1} in the 1993 Guidelines. In view of the scientific uncertainties, the guideline value is designated as provisional. A new maximum concentration limit of 0.01 mg L^{-1} for arsenic in drinking water was set by the US EPA in 2001⁶ and EU law⁷ in 2003, requiring public water supply systems to reduce arsenic in drinking water by not later than January 2006. In the Republic of Serbia, the new arsenic concentration limit was set in 1998.⁸

Toxicological review

The most important routes of arsenic exposure are through food and drinking water. Arsenic is found in food, particularly in fish and shellfish, in which it is found mainly in the less toxic organic form.⁹ Arsine is considered the most toxic form, followed by arsenites, then arsenates and organic arsenic compounds.^{4,5}

Environmental exposure to arsenic through drinking-water has been associated with skin cancer.¹⁰ Acute arsenic intoxication associated with the ingestion of water containing a very high concentration of arsenic (21.0 mg L^{-1}) was reported.³ Moreover, it was concluded that long-term exposure to arsenic in drinking water is causally related to increased risks of cancer in the skin, lungs, bladder and kidney, as well as other skin changes, such as hyperkeratosis and pigmentation changes.¹¹ Epidemiological studies^{12,13} in areas with different frequencies of black-foot disease and where drinking water contained $0.35\text{--}1.14 \text{ mg L}^{-1}$ arsenic revealed elevated risks for cancers of the bladder, kidney, skin, lung, liver and colon. Dermal lesions were the most commonly observed symptom occurring after minimum exposure periods of approximately 5 years.^{12,13}

Arsenic removal technologies

It is technically feasible to achieve arsenic concentrations of $10 \text{ } \mu\text{g L}^{-1}$ or lower using any of the following treatment technologies: oxidation/precipitation,^{5,14} coagulation/coprecipitation,¹⁴ sorption^{15,16}, ion-exchange¹⁷ and membrane technologies.¹⁸ Among them, adsorption is considered to be a relatively simple, efficient and low-cost arsenic removal technique, especially convenient for application in rural areas.⁴ A wide range of sorbent materials for aqueous arsenic removal is available nowadays: biological materials, mineral oxides, different soils, activated carbons and polymer resins.¹⁸ Nevertheless, finding inexpensive and effective sorbents for arsenic removal from water is still highly desired.

Natural materials such as clay minerals, zeolites and metal oxides are widespread and abundant in terrestrial environments. Clay minerals and zeolites adsorb cationic, anionic and neutral metal species.¹⁸ As reported in recent papers, certain agricultural and industrial by-products, such as waste tea fungal biomass,¹⁹ rice husks,²⁰ red mud,¹⁸ fly ash,²¹ *etc.*, were found to be good and inexpensive arsenic sorbents. In addition, application of industrial wastes in water treatment follows the reuse-recycle concept.

The aim of this study was to investigate and compare natural materials (zeolite, bentonite, sepiolite, pyrolusite and limonite) and industrial by-products (blast furnace slag and waste filter sand), inexpensive and all locally available, as potential sorbents for arsenic.

EXPERIMENTAL

Reagents and apparatus

An As(V) stock solution (100 mg L⁻¹) was prepared by dissolving 416.5 mg of sodium arsenate (Na₂HAsO₄·7H₂O, Analar analytic reagent) in 1 L of distilled water, which was preserved with 0.5 % HNO₃. An As(III) stock solution (3750 mg L⁻¹) was prepared by dissolving sodium arsenite (0.05 mol NaAsO₂, Riedel-de-Haen (4.946 g As₂O₃ + 1.3 NaOH in 1 L)) in distilled water in a 1 L volumetric flask, which was preserved with 0.5 % HNO₃.

Arsenic was analyzed using the ICP-MS method, according to Standard methods,²² using an Agilent 7500ce spectrometer equipped with octopole reaction system (ORS). Calibration was realized using external standards (2, 4, 20, 40, 80 and 100 µg L⁻¹), which were prepared by appropriate dilution of a 1000 µg L⁻¹ stock standard solution. Working standards, as well as blank solutions, were prepared with high purity HNO₃. The concentrations of the investigated samples were adjusted to the concentration range 5–100 µg L⁻¹. The experimental data measurements were accepted as reasonable data in cases of less than 5 % relative standard deviation (RSD). In order to amplify the consistency of the results, the experiments were performed in triplicate and the mean values considered. The limit of detection was 0.1 µg L⁻¹. A laboratory pH meter (Metrohm 827) was used for pH measurements. The accuracy of the pH meter was ±0.01 pH units.

Materials and characterization techniques

Zeolite (Z), natural clay minerals, bentonite (B) and sepiolite (S), and natural metal oxide minerals, limonite (L) and pyrolusite (P) were selected as the natural materials while waste iron slag (WIS) and waste filter sand (WFS) were selected as the waste materials to be tested within the scope of the presented investigations. The natural materials were obtained from natural deposits located in Serbia and Bosnia. The industrial by-products were obtained from local industrial facilities: blast furnace slag from the steel production plant US Steel Serbia (Smederevo, Serbia) and waste filter from groundwater treatment plant “Bežanija” in Belgrade, Serbia. The physical properties and chemical composition of all materials are presented in the further text.

The microstructure of the analyzed material samples was examined by scanning electron microscopy (SEM) using a Jeol JSM 5800 instrument (operated at 25 kV). The BET specific surface areas were determined by the technique of nitrogen adsorption¹⁷ using a Sorptomatic 1990 Thermo Finning instrument. The chemical composition of the materials was determined by standard silicate analysis.^{23,24}

Kinetic and equilibrium studies

Kinetic batch experiments were performed for As(III) and As(V), with an initial As concentration $c_0 = 0.5 \text{ mg L}^{-1}$. The experiments were performed in different time intervals, up to $\tau = 24 \text{ h}$. During each set of conducted kinetic batch experiments, it was observed that absolute equilibrium was not reached even after 24 h. In each set of experiments, $\tau = 6 \text{ h}$ was found to be the turning point after which the sorption rate was significantly lower and thus changes in sorption efficiency were far less rapid. Moreover, the rapid sorption rate range (0–6 h) was found to be the most interesting for detailed examination in terms of the potential application of waste materials. Finally, the adsorption isotherm experiments were performed under different initial arsenic, As(III) and As(V) concentrations (0.500, 1.00, 5.00, 10.0, 50.0 and 100.0 mg L^{-1}) for a contact time $\tau = 6 \text{ h}$, at pH 7.

RESULTS AND DISCUSSION

Characterization

Chemical composition. The chemical compositions of the selected natural and waste materials are summarized in Table I. The main accessory minerals in the zeolite were quartz, feldspar and carbonate. The clinoptilolite content in the zeolite was 85 %. Bentonite is a clay material consisting mostly of montmorillonite (95 %) with some accessory quartz, calcite, feldspar, muscovite and biotite. Sepiolite is a natural hydrous magnesium silicate. The chemical analyses results indicated that the sepiolite sample consisted of 98 % pure mineral (based on the SiO_2 content). Limonite is a natural ore comprised of hydrated iron(III) oxides, mostly made up of goethite ($\alpha\text{-FeOOH}$). Elemental analysis of the limonite ore indicated that the iron content was 45.5 %. Pyrolusite is a mineral consisting essentially of manganese dioxide (MnO_2) and is important as a manganese ore. The content of manganese in the natural pyrolusite was 51.8 %. The dominant constituent of the waste filter sand was quartz (SiO_2) coated by metal oxide layer

TABLE I. Chemical composition (%) of the studied natural and waste materials (Z – zeolite, B – bentonite, S – sepiolite, L – limonite, P – pyrolusite, WFS – waste filter sand, WIS – waste iron slag)

| Material | Deposits location | SiO_2 | Fe_2O_3 | FeO | Al_2O_3 | CaO | MgO | TiO_2 | Na_2O | K_2O | Fe | Mn |
|----------|------------------------|----------------|-------------------------|-------|-------------------------|-------|-------|----------------|-----------------------|----------------------|-------|-------|
| Z | Vranjska Banja, Serbia | 66.57 | 2.30 | – | 13.13 | 3.85 | 1.27 | – | 1.27 | 1.17 | – | – |
| B | Birač, Zvornik, Bosnia | 54.97 | 6.83 | – | 16.82 | 2.0 | 2.6 | 1.3 | 0.38 | 0.15 | – | – |
| S | Antići, Čačak, Serbia | 56.68 | 0.04 | – | 0.03 | 0.27 | 28.6 | – | 0.15 | 0.096 | – | – |
| L | Majdanpek, Serbia | 2.85 | 59.19 | – | 8.12 | 0.028 | 2.19 | – | – | – | 45.5 | – |
| P | Majdanpek, Serbia | 3.1 | 3.9 | – | 2.5 | 0.1 | 0.3 | – | – | – | – | 51.8 |
| WFS | – | 65.16 | 3.68 | 0.82 | – | 1.14 | 21.23 | – | – | – | 3.93 | 15.66 |
| WIS | – | 23.82 | 13.02 | 15.73 | 7.70 | 26.5 | 11.13 | 0.08 | – | – | 21.20 | – |

consisting of iron (Fe) and manganese (Mn) deposits. The content of Mn was four times higher than that of Fe. The results of the chemical analyses showed that the waste iron slag was a complex heterogeneous material, mainly composed of silica, and iron and calcium oxides.

Physical properties. Clays are natural materials known for their highly developed surface area. The bentonite (B) clay from the Birač deposits exhibited the highest specific surface area of all the investigated materials ($593 \text{ m}^2 \text{ g}^{-1}$) (Table II), two times higher than the sepiolite (S) clay ($286 \text{ m}^2 \text{ g}^{-1}$). The other natural materials exhibited moderate to low specific surface areas. The relatively high surface area obtained for the waste filter sand (WFS) was assigned to the iron and manganese oxides layer which coats the original quartz grain of the sand.²⁵

TABLE II. Physical properties of the studied natural and waste materials

| Material | Grain size, mm | BET specific surface area, $\text{m}^2 \text{ g}^{-1}$ |
|-------------------------|----------------|--|
| Zeolite (Z) | 0.4–0.8 | 45.7 |
| Bentonite (B) | <0.074 | 593.0 |
| Sepiolite (S) | <0.074 | 286.0 |
| Limonite (L) | 1–2 | 1.7 |
| Pyrolusite (P) | 1–2 | 1.2 |
| Waste filter sand (WFS) | 1.25 | 94.1 |
| Waste iron slag (WIS) | 0.470 | 2.9 |

The porous microstructures with pores of different size and shape could be observed from all micrographs (Fig. 1). The limonite microstructure (Fig. 1d) shows that this porous natural material was composed of particles in the size range from approximately a few hundred nanometers to a few microns. The microstructure of the pyrolusite (Fig. 1e) was also porous with particles of different shape and size. Rod-shaped particles were also observed in the pyrolusite microstructure. SEM micrograph in Fig. 1c shows a fibrous texture, typical for the structure of sepiolite. The bentonite microstructure was also porous and shapeless pores a few microns in size can be observed in Fig. 1b.

Batch system investigations

Preliminary investigations. A continuously mixed batch system was employed. The kinetic batch experiments were performed for As(III) and As(V), using initial As concentrations 0.500 and 10.0 mg L^{-1} , respectively, for the time interval $\tau = 2 \text{ h}$. Despite their high specific surface area, the natural mineral clays, bentonite and sepiolite, exhibited low or no affinity towards As(III) and As(V) (Fig. 2). The highest sorption capacity was obtained for sepiolite, $5 \mu\text{g g}^{-1}$ of As(V).

The natural Fe and Mn oxide minerals, limonite and pyrolusite, exhibited low sorption capacities of up to $30 \mu\text{g g}^{-1}$ of As(V) only under high initial arsenic concentrations. At low initial arsenic concentrations, limonite and pyrolusite showed no affinity towards As(III) and As(V).

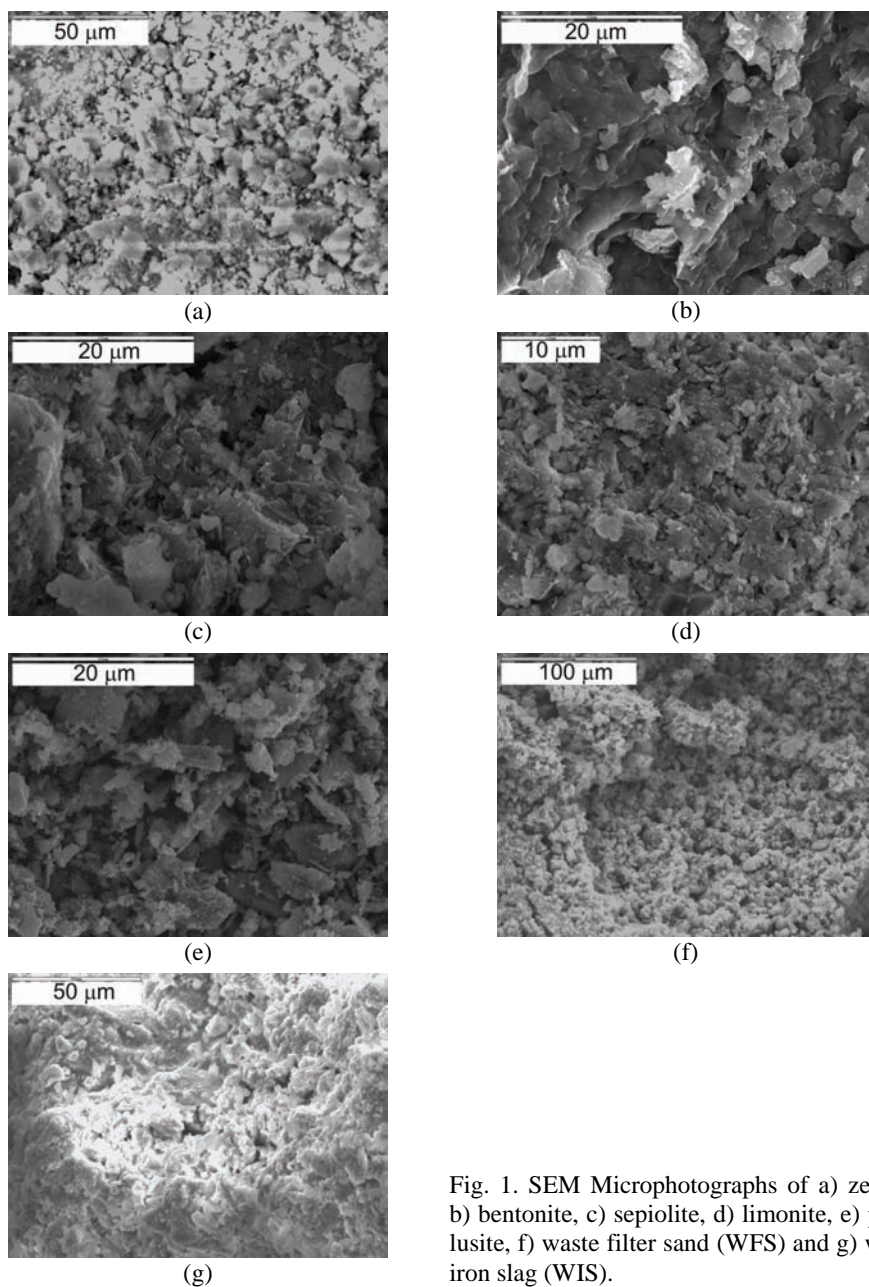


Fig. 1. SEM Microphotographs of a) zeolite, b) bentonite, c) sepiolite, d) limonite, e) pyrolusite, f) waste filter sand (WFS) and g) waste iron slag (WIS).

In the first set of preliminary experiments, only natural the zeolite of all the tested natural materials exhibited certain sorption features, while the waste materials proved to be good arsenic sorbents. Therefore, further detailed examinations were focused on these three materials only.

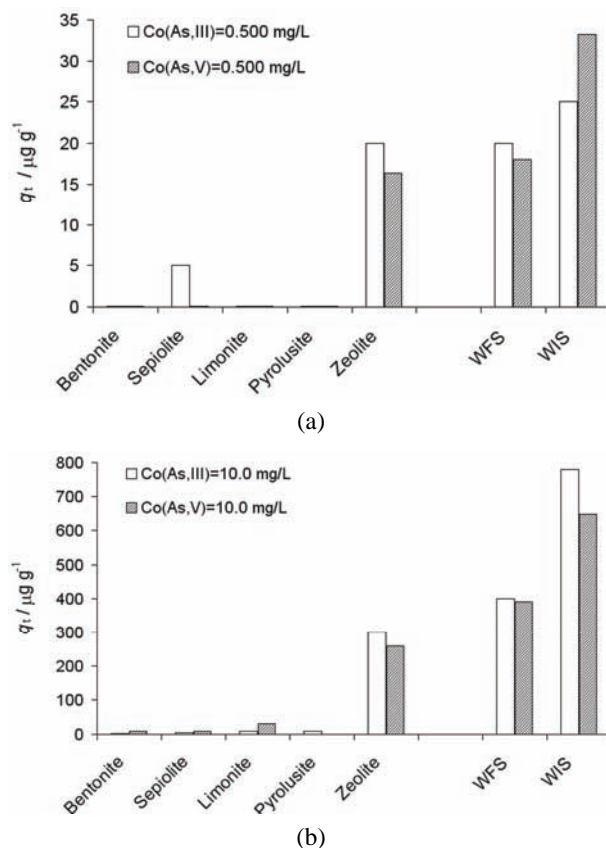
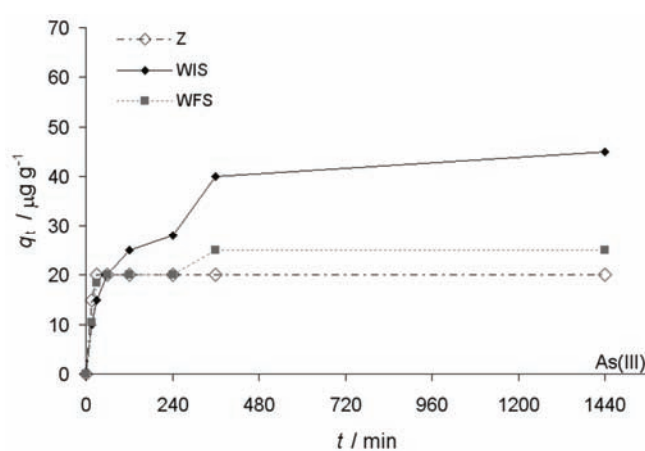


Fig. 2. Preliminary batch experiments for As(III,V) sorption. Conditions: $c_{\text{As(III,V)}} = 0.500$ (a) and 10.0 mg L^{-1} (b), $m = 1.00 \text{ g}$, $t = 20 \text{ }^\circ\text{C}$, $V = 100 \text{ mL}$, $\tau = 2 \text{ h}$.

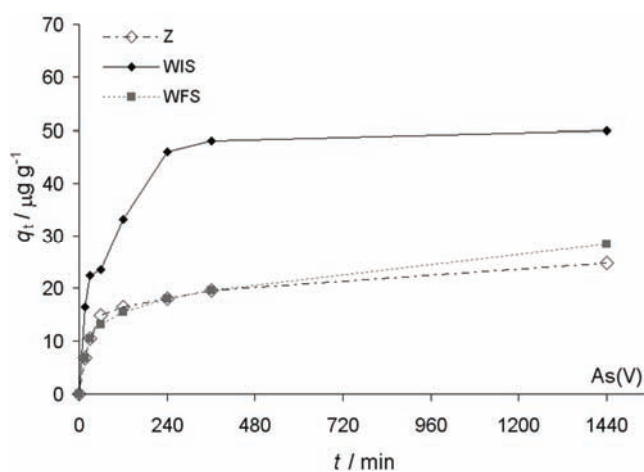
Sorption kinetic studies. The sorption kinetics of As(III) and As(V) onto the natural zeolite and the waste materials are presented in Fig. 3. The waste slag, WIS, exhibited substantial sorption capacities. It was found that the WIS adsorbed $10 \mu\text{g g}^{-1}$ of As(III) and $16.4 \mu\text{g g}^{-1}$ of As(V) in the first 15 min, reaching $45 \mu\text{g g}^{-1}$ for As(III) and $50 \mu\text{g g}^{-1}$ for As(V) after the equilibrium contact time (6 h). The kinetic performance of the natural zeolite was nearly as good as that of the waste filter sand (WFS). In 24 h, the WFS adsorbed $25 \mu\text{g g}^{-1}$ As(III) and $29 \mu\text{g g}^{-1}$ As(V), while in the first 15 min it adsorbed $10.5 \mu\text{g g}^{-1}$ As(III) and $6.8 \mu\text{g g}^{-1}$ As(V).

Several model equations have been established to describe sorption kinetics. The Lagergren First Order and the Pseudo-Second-Order sorption kinetic models are the most frequently used. These models were thoroughly discussed in a recent paper²⁶ and, hence, they are only summarized here (Table III). In Table III, q_t is sorption capacity at time t ($\mu\text{g g}^{-1}$), q_e the equilibrium sorption capacity ($\mu\text{g g}^{-1}$),

k_2 the rate constant of sorption ($\text{g } \mu\text{g}^{-1} \text{ min}^{-1}$), h the initial sorption rate ($\mu\text{g g}^{-1} \text{ min}^{-1}$) and k_L the Lagergren rate constant (min^{-1}). The experimental results were fitted to the pseudo-second-order and the Lagergren First Order model, applying non-linear regression analysis using MS Office 2000 Excel spreadsheets. The correlation coefficients, R , were calculated in order to quantify the applicability of the applied kinetic models. Values of the model parameters obtained from the regression analyses are presented in Table IV.



(a)



(b)

Fig. 3. Sorption kinetics of As(III) (a) and As(V) (b) onto the natural and waste materials. Conditions: $c_{\text{As(III,V)}} = 0.500 \text{ mg L}^{-1}$, $m = 1.00 \text{ g}$, $t = 20 \text{ }^\circ\text{C}$, $V = 100 \text{ mL}$, $\tau = 24 \text{ h}$.

The regression analyses showed that the pseudo-second-order equation is the most appropriate kinetic model for arsenic sorption onto the investigated mate-

rials, which indicates that chemisorption occurs. Although WFS would be presumed to be primarily a weak, physical sorbent, the high correlation coefficient obtained for the pseudo-second-order model, indicating chemisorption, is assumed to result from the presence of iron and manganese oxides on the surface of the sand grains (Table I). Effective arsenic sorption onto the surface of iron oxides has already been reported.²⁷ Depending on the pH, various forms of hydrated iron oxide exist on solid surfaces in contact with water: FeOH₂⁺, FeOH and FeO⁻. At neutral pH, FeOH₂⁺ and FeOH forms are predominant and they are responsible for the selective binding of As(III) and As(V). The sorption process in neutral conditions occurs owing to FeOH sites, which bond molecular forms of As(III) (HAsO₂), and FeOH₂⁺ sites, which bond ionic forms of As(V) (H₂AsO₄⁻ and HAsO₄²⁻).

TABLE III. Adsorption kinetic models and their linear forms

| Type | Non-linear form | Linear form | Plot |
|---------------------|---|---|---|
| Pseudo-second-order | $\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t$ | $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$ | $\frac{t}{q_t}$ vs. t |
| Lagergren | $q_t = q_e (1 - e^{-k_L t})$ | $\ln\left(1 - \frac{q_t}{q_e}\right) = -k_L t$ | $\ln\left(1 - \frac{q_t}{q_e}\right)$ vs. t |

TABLE IV. Kinetic model parameters and correlation coefficients for As(III) and As(V) sorption

| Model equation | Parameter | Z | | WIS | | WFS | |
|---------------------|---|---------|----------|---------|---------|---------|---------|
| | | As(III) | As(V) | As(III) | As(V) | As(III) | As(V) |
| Pseudo-second order | $q_e / \mu\text{g g}^{-1}$ | 20.02 | 25.7 | 47.6 | 51.7 | 25.4 | 29.8 |
| | $k_2 / \text{g } \mu\text{g}^{-1} \text{ min}^{-1}$ | 0.0481 | 0.000593 | 0.00023 | 0.00043 | 0.00157 | 0.00033 |
| | $h / \mu\text{g g}^{-1} \text{ min}^{-1}$ | 1.93 | 0.39 | 0.53 | 1.14 | 1.01 | 0.29 |
| | R | 0.999 | 0.998 | 0.997 | 0.999 | 0.999 | 0.995 |
| Lagergren | $k_L / \text{g } \mu\text{g}^{-1} \text{ min}^{-1}$ | 0.00062 | 0.00154 | 0.00204 | 0.00203 | 0.00135 | 0.00169 |
| | R | 0.3334 | 0.934 | 0.944 | 0.828 | 0.721 | 0.979 |

The two times higher sorption capacities obtained with the WIS (47.6 $\mu\text{g g}^{-1}$) compared to WFS (25.4 $\mu\text{g g}^{-1}$) contribute to the assumption that chemisorption occurs, since slag material exhibit significantly lower BET specific surface area (Table II), which is a crucial characteristic that enhances the sorption properties of a material. Further insight into the chemical composition of the examined materials (Table I) revealed that the WIS exhibited higher sorption capacities due to the five times higher iron and iron oxides content compared to the WFS, despite its lower BET surface area. The contribution of manganese (15.66 %) in WFS to the sorption mechanism is probable since the low iron content in the metal oxide layer (3.93 %) hinders the WFS from being an efficient sorbent for arsenic. WIS exhibited similar specific arsenic removal efficiencies, $\approx 220 \mu\text{g As g}^{-1} \text{ Fe}$. Ap-

plied to the WFS containing 39.3 mg g^{-1} Fe, the contribution of iron to arsenic removal was expected to be $9 \text{ } \mu\text{g As g}^{-1}$ WFS. The obtained q_e values (25.4 and $29.8 \text{ } \mu\text{g g}^{-1}$ for As(III) and As(V), respectively) suggest that iron was not the only active component in the WFS. Although these results can not be directly correlated (due to the chemical and physical properties), the higher efficiency of the WFS could be assigned to manganese activity. Assuming the difference between the contribution iron to the sorption and the total q_e values is the consequence of manganese activity only, the specific arsenic removal efficiency of manganese was estimated to be $115 \text{ } \mu\text{g As g}^{-1}$ Mn.

The experimental plots of As(III) and As(V) sorption on the waste materials with time initially increase rapidly, which is followed by a very slow increase in the sorption capacity over longer periods (Fig. 3).

The Lagergren First Order model was found to be the less suitable for describing the kinetics of arsenic sorption on the investigated materials. However, the Lagergren rate constants (k_L) were comparable to rate constants of the pseudo-second order model (k_2).

Equilibrium studies. Adsorption isotherms are important for the description of how molecules of a sorbate interact with the sorbent surface and for the prediction of the extent of sorption. The Langmuir isotherm model was derived under the assumption that the sorbate is sorbed in a one molecule layer. The Freundlich isotherm is a consecutive layer model which does not predict any saturation of the sorbent by sorbate. The isotherm model equations and their linear forms are presented in Table V.

TABLE V. Sorption isotherm models and their linear forms

| Type | Non-linear form | Linear form | Plot |
|------------|--|---|-------------------------------------|
| Langmuir | $q_e = \frac{q_{\max} K_L c_e}{1 + K_L c_e}$ | $\frac{1}{q_e} = \frac{1}{q_{\max} K_L} \frac{1}{c_e} + \frac{1}{q_{\max}}$ | $\frac{1}{q_e}$ vs. $\frac{1}{c_e}$ |
| Freundlich | $q_e = K_F c_e^{1/n}$ | $\ln q_e = \ln K_F + \frac{1}{n} \ln c_e$ | $\ln q_e$ vs. $\ln c_e$ |

In Table V, q_e is the amount of solute sorbed per gram of sorbent (mg g^{-1}), c_e the equilibrium concentration of solute (mg L^{-1}), K_L a constant related to the energy of sorption (L mg^{-1}) (Langmuir model), q_{\max} the maximum amount of solute sorbed per gram of sorbent (mg g^{-1}), K_F the Freundlich constant (mg g^{-1}) and n is a constant related to the sorption intensity of the sorbent.

Values of the isotherm model parameters obtained from regression analyses are presented in Table VI. A dimensionless separation factor constant, R_L , was proposed to estimate the feasibility of the Langmuir isotherm:²⁸

$$R_L = \frac{1}{1 + K_L c_0} \quad (1)$$

Accordingly,²⁸ R_L values in the $0 < R_L < 1$ range indicates favorable sorption. The R_L values for all the tested materials and for the complete c_0 range (0.500–100.0 mg L⁻¹ As) were $0.150 < R_L < 0.973$.

TABLE VI. Langmuir and Freundlich isotherm parameters for the studied natural zeolite and waste materials

| Model equation | Parameter | Z | | WIS | | WFS | |
|----------------|-------------------------------|---------|--------|---------|--------|---------|--------|
| | | As(III) | As(V) | As(III) | As(V) | As(III) | As(V) |
| Langmuir | $q_{\max} / \text{mg g}^{-1}$ | 0.9691 | 4.07 | 0.82 | 4.04 | 0.55 | 0.77 |
| | $K_L / \text{L mg}^{-1}$ | 0.0565 | 0.0137 | 13.22 | 12.71 | 0.37 | 1.18 |
| | R | 0.9902 | 0.9997 | 0.9666 | 0.9986 | 0.7899 | 0.9738 |
| Freundlich | $K_F / \text{L mg}^{-1}$ | 50.703 | 55.106 | 0.567 | 3.010 | 0.110 | 0.157 |
| | $n^{-1} / \text{L g}^{-1}$ | 0.884 | 1.003 | 0.519 | 0.591 | 0.843 | 0.727 |
| | R | 0.9902 | 0.9989 | 0.9635 | 0.8341 | 0.9618 | 0.9218 |

The highest maximum sorption capacities, q_{\max} , were found for natural zeolite, Z: 0.97 and 4.07 mg g⁻¹ for As(III) and As(V), respectively. The Z and WIS exhibited significantly higher q_{\max} values for As(V) compared to As(III), while the WFS attained nearly equal values for both As forms. The differences in the q_{\max} values for As(III) and As(V) might suggest that the arsenic species present under neutral conditions (As(III) in the molecular form while As(V) in the ionic form) influence the sorption efficiency of Z and WIS. The higher sorption capacities of the Z and WIS (4 and 5 times, respectively) for As(V) suggest that molecular arsenic was less efficiently bound to the slag materials than its ionic forms. While iron was the main active component in the slag materials, manganese was dominant in the WFS. The low content of iron in the WFS is presumed responsible for its lower As(V) sorption capacity. The maximum specific As(V) uptake onto the slag materials, derived from the q_{\max} values, was 15.4 mg As(V) g⁻¹ Fe. The calculated difference between the iron responsible (0.62 mg As(V) g⁻¹ WFS) and exhibited q_{\max} value (0.77 mg As(V) g⁻¹ WFS), $\Delta = 0.15$ mg As(V) g⁻¹ WFS, indicates again the presence of a second active substance in the WFS, *i.e.*, manganese. In addition, the same difference of 0.41 mg As(III) g⁻¹ WFS obtained for the trivalent arsenic form suggests that manganese has a greater affinity toward molecular arsenic forms than iron.

The Langmuir constant, K_L , is a function of the sorption strength: the larger the K_L value, the stronger is the sorption bond. The significantly lower K_L values obtained for the WFS and Z (Table VI), indicating weak sorption bonds, confirms the assumption that physical sorption was dominant for these materials. In addition, the relatively strong sorption bonds, indicated by the high K_L value, suggest that chemisorption was dominant for the WIS. However, the complexity of the experimental results requires further examination of the nature of the sorption processes.

Further insight into the nonlinear Langmuir plots (Fig. 4) revealed that the sorption process continued beyond q_{\max} for the industrial waste materials, WIS and WFS, suggesting that the sorption process continued after monolayer saturation. Likewise, applying the subsequent Freundlich Monolayer Model (Fig. 5) also suggests that arsenic uptake continues after the calculated monolayer saturation.

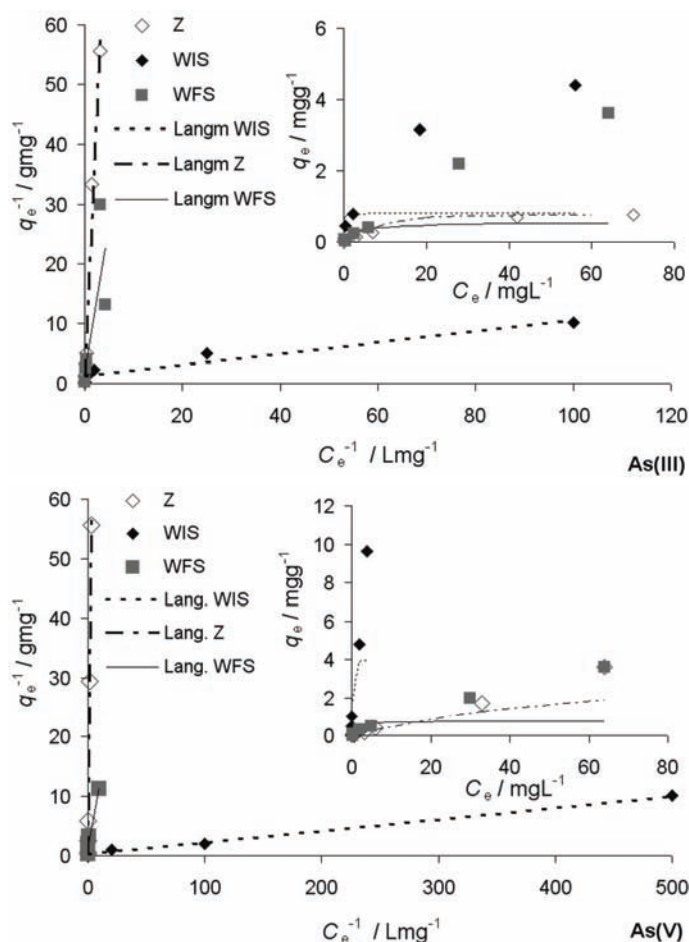


Fig. 4. Langmuir isotherm plots (linear and non-linear) for As(III) and As(V) sorption onto the natural zeolite and the industrial by-products.

These findings might be supported by the complexity of the examined materials in terms of their physico-chemical composition. The presence of active substances, such as iron and manganese (for WFS), and the increased specific surface area contributed to the complex nature of sorption process for all the examined materials.

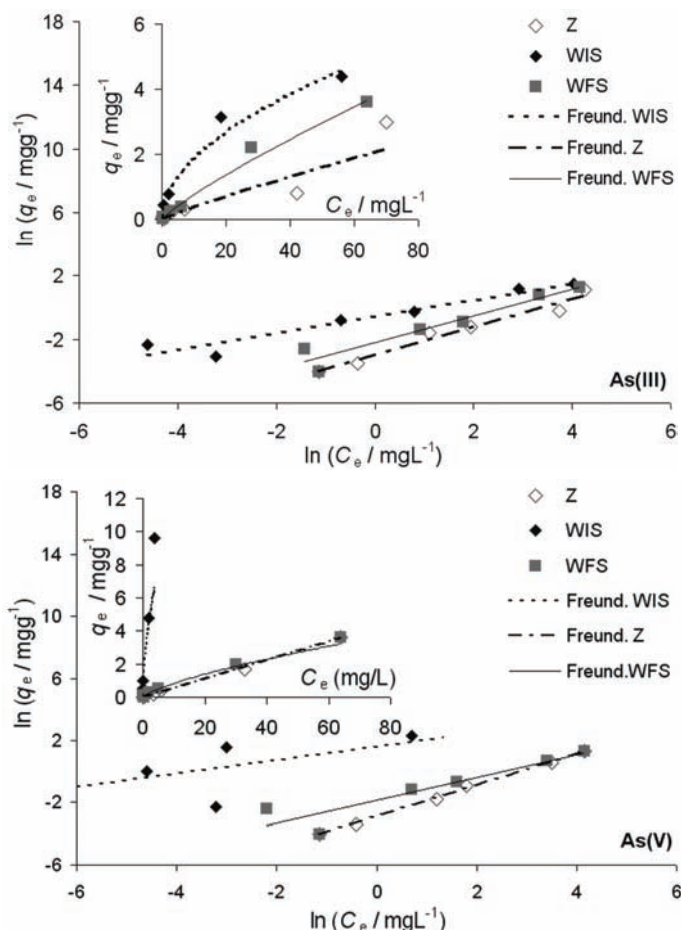


Fig. 5. Freundlich isotherm plots (linear and non-linear) for As(III) and As(V) sorption onto the natural zeolite and the industrial by-products.

The capacities of various low-cost adsorbents reported in recent papers are summarized in Table VII. Although bentonite and sepiolite clays are found to be frequently used for the removal of metal ions from aqueous solution, there was no data available for arsenic removal. Kaolinite clay was reported to be efficient for As(V) removal with 0.23 mg g^{-1} maximum sorption capacity. Zeolite tuffs were reported to exhibit $0.002\text{--}0.0167 \text{ }\mu\text{g As(III) g}^{-1}$ and $0.006\text{--}0.100 \text{ }\mu\text{g As(V) g}^{-1}$ which is significantly lower compared to values obtained for natural zeolite within the scope of this study (0.97 and 4.07 mg g^{-1} for As(III) and As(V), respectively). It is assumed that higher sorption capacities obtained for natural zeolite were due to its higher specific surface area and the higher initial concentration range. A low specific surface area is assumed to contribute to the low sorption capacities obtained for limonite and pyrolusite, although iron (hematite) and

manganese ores are reported to be efficient in As sorption. The lower specific surface area probably contributed to lower sorption efficiencies of WIS for As(III) compared to the values reported in the literature. However, the As(V) sorption capacity obtained by the WIS was 4.07 mg g⁻¹. The WFS obtained the lowest sorption capacities of all tested materials. However, its availability and inexpensiveness makes this waste material an equally valuable alternative for arsenic removal from water.

TABLE VII. Comparative evaluation of various low cost adsorbents for arsenic removal

| Adsorbent | pH | Concentration range | Specific surface area m ² g ⁻¹ | t / °C | Model used to calculate adsorption capacity | Capacity mg g ⁻¹ | | Ref. |
|------------------------|---------|--------------------------------|--|--------|---|-----------------------------|-------|------|
| | | | | | | As(III) | As(V) | |
| Natural materials | | | | | | | | |
| Kaolinite | 5.5 | 10–1000 mg L ⁻¹ | 8.5 | 25 | Langmuir | – | <0.23 | 18 |
| Zeolitic tuff ZH | 4 | 0.1–4 mg L ⁻¹ | – | 22 | Langmuir. | 0.002 | 0.006 | 29 |
| Zeolitic tuff ZMS | 4 | 0.1–4 mg L ⁻¹ | 28 | 22 | Langmuir. | 0.0167 | 0.100 | 29 |
| Goethite | 9.0 | 0–60 mg L ⁻¹ | 39 | 22 | – | 22 | 4 | 18 |
| Mixed rare earth oxide | 6.5 | 50 mg L ⁻¹ | 6.75 | 29 | Langmuir. | – | 2.95 | 18 |
| Manganese ore | 6.3–6.5 | – | – | – | Langmuir | 0.53 | 15.38 | 18 |
| Hematite | 4.2 | 133.5 μmol L ⁻¹ | 14.4 | 30 | Langmuir | – | 0.2 | 18 |
| Feldspar | 4.2 | 133.5 μmol L ⁻¹ | 10.25 | 30 | Langmuir | – | 0.18 | 18 |
| Waste materials | | | | | | | | |
| Bauxol | 4.5 | 0.8–32.00 mM | – | 23±1 | Langmuir | – | 1.081 | 18 |
| Blast furnace slag | 7.1 | 0–1000 mg L ⁻¹ | 12.56 | 25 | Langmuir | 1.4 | – | 30 |
| Orange juice residue | 2–11 | – | – | 30 | Langmuir | 70.43 | 67.43 | 18 |
| Tea fungal biomass | 7.2 | 0.9–1.3 mg L ⁻¹ | – | 30 | Freundlich | 1.11 | 4.95 | 18 |
| Human hair | – | 0.090–0.360 mg L ⁻¹ | – | 22 | Langmuir | – | 0.012 | 18 |

CONCLUSIONS

Preliminary investigations showed that natural zeolite and industrial by-products (blast furnace slag and waste filter sand) exhibit substantial arsenic sorption properties. Natural clay minerals (bentonite and sepiolite) and iron and manganese minerals (limonite and pyrolusite) showed very little affinity towards inorganic arsenic species, below 2 μg g⁻¹ in a 2-h contact time, under the conditions that are likely to occur in real water treatment systems. The complex nature of the sorption processes in the selected natural zeolite and industrial by-products, including both chemisorption and physical sorption, was revealed by the equilibrium studies. The sorption capacities for As(V) compared to As(III) were signifi-

cantly higher for the natural zeolite and the blast furnace slag, while the waste filter sand exhibited similar removal efficiencies for both arsenic species. The arsenic sorption process on the natural zeolite followed the monolayer saturation (Langmuir) model, reaching a maximum sorption capacity of 0.97 mg g^{-1} and 4.07 mg g^{-1} for As(III) and As(V), respectively. However, with the waste materials, sorption continued after monolayer saturation (following the Freundlich isotherm model). The blast furnace slag exhibited the highest equilibrium sorption efficiency of 0.05 mg g^{-1} under the conditions that occur in real water treatment systems, while natural zeolite and waste filter sand reached $0.02\text{--}0.03 \text{ mg g}^{-1}$. Comparing to the equilibrium sorption efficiency of 0.05 mg g^{-1} obtained for granular ferric hydroxide, a commercial arsenic sorbent, these results indicate that the application of natural zeolite and the industrial by-products is feasible in real water treatment systems.

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ИЗВОД

ПРЕГЛЕД САВРЕМЕНИХ МЕТОДА ЗА УКЛАЊАЊЕ АРСЕНА ИЗ ВОДЕ

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У овом раду су приказани резултати испитивања ефикасности природних и отпадних материјала за уклањање арсена из воде. Ефикасност уклањања арсена, As(III, V) испитана је у шаржном систему. Као сорбенти коришћени су природни материјали (зеолит, бентонит, сепиолит, пиролузит и лимонит) и отпадни материјали (отпадни филтарски песак са постројења за пречишћавање вода и отпадна шљака из производње челика). Испитивања су показала да отпадни материјали могу ефикасно уклонити и As(III) и As(V) из воде, али да се ефикасност разликује и зависи од валентног стања арсена, почетне концентрације и рН вредности воде. Експерименти на основу којих су добијене криве кинетике сорпције и сорпционе изотерме су рађени у условима какви владају у реалним системима за пречишћавање воде. Природни зеолит о отпадни материјали су се показали као релативно добри материјали за уклањање арсена из воде док су бентонит, сепиолит, лимонит и пиролузит показали слаб афинитет према арсену. Највећи максимални сорпциони капацитет су показали природни зеолит ($4.07 \text{ mgAs(V) g}^{-1}$), и отпадна шљака ($4.04 \text{ mgAs(V) g}^{-1}$).

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