Research Article

Arsenic Removal from Water Using Industrial By-Products

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In this study, removal of arsenic ions using two industrial by-products as adsorbents is represented. Removal of As(III) and As(V) from water was carried out with industrial by-products: residual from the groundwater treatment process, iron-manganese oxide coated sand (IMOCS), and blast furnace slag from steel production (BFS), both inexpensive and locally available. In addition, the BFS was modified in order to minimise its deteriorating impact on the initial water quality. Kinetic and equilibrium studies were carried out using batch and fixed-bed column adsorption techniques under the conditions that are likely to occur in real water treatment systems. To evaluate the application for real groundwater treatment, the capacities of the selected materials were further compared to those exhibited by commercial sorbents, which were examined under the same experimental conditions. IMOCS was found to be a good and inexpensive sorbent for arsenic, while BFS and modified slag showed the highest affinity towards arsenic. All examined waste materials exhibited better sorption performances for As(V). The maximum sorption capacity in the batch reactor was obtained for blast furnace slag, 4040 μgAs(V)/g.

1. Introduction

Arsenic presence is detected in groundwaters in South Eastern Europe [1, 2], Asia, North, and South America [3] as a natural and anthropogenic contaminant. Arsenic occurs in natural waters in both inorganic and organic forms, but inorganic species are predominant in natural waters. The valence and species of inorganic arsenic are dependent on the oxidation-reduction condition and pH of the water. Arsenite, the reduced trivalent form, exists in four forms in aqueous solution, depending on pH: H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{2-}$, and AsO_3^{3-}. Arsenate, the oxidized pentavalent form, exists in four forms in aqueous solution, also depending on pH: H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-} [4]. Most commonly, As(III) is found in groundwaters (assuming anaerobic conditions), while As(V) is found in surface waters (assuming aerobic conditions). However, this rule does not always apply for groundwaters. Some groundwaters have been found to have only As(III), others with only As(V), and still others with the combination of both As(III) and As(V) [3]. All arsenic compounds dissolved in water are toxic. Arsenic toxicity depends on its chemical formation. Inorganic arsenic compounds, most commonly present in natural waters, are the most toxic. In addition, inorganic As(III) is considered more toxic than inorganic As(V). Sea food (fish and shellfish) very often contains arsenic in significant amounts, but it is mainly in organic forms which are approximately 1000 times less toxic compared to inorganic forms [5, 6].

Increased risks of arsenic-related diseases have been reported to be associated with ingestion of drinking water at concentrations of <50 μg/L [7]. 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 WHO at the limit of 10 μg/L in the 1993 Guidelines. In view of the scientific uncertainties, the

guideline value is designated as provisional. A new maximum concentration limit of 10 μg/L for arsenic in drinking water was set by US EPA in 2001 [8] and EU law in 2003 [9] requiring public water supply systems to reduce arsenic in drinking water not later than January 2006. In the Republic of Serbia, the new arsenic concentration limit was set in 1998.

Available commercial arsenic removal technologies include adsorption, precipitation, and membrane processes. Among them, sorption is considered to be a relatively simple, efficient, and low-cost arsenic removal technique, especially convenient for application in rural areas. A wide range of sorbent materials for aqueous arsenic removal are available nowadays: biological materials [10], mineral oxides, different soils, activated carbons [11], and polymer resins [12, 13]. Nevertheless, finding inexpensive and effective arsenic sorbents is still highly desirable.

As reported in recent papers, certain agricultural and industrial by-products such as waste tea fungal biomass, rice husks, red mud, and fly ash were found to be good and inexpensive arsenic sorbents [14]. In addition, application of industrial wastes in water treatment follows the reuse-recycle concept. The aim of this paper is to investigate industrial by-products: BFS and IMOCS. The employed adsorbents are locally available and inexpensive which makes them suitable for application in rural areas of the developing world.

BFS is a typical industrial by-product from steel production factories. It is an inexpensive material, widely available, containing relatively high amounts of iron oxides which are efficient for arsenic removal. Disposed of after high temperature treatment during steel production, BFS is an environmentally safe material since the contained metals are tightly bound and cannot be easily leached. In addition, the thermal treatment at high temperatures enhances the physical properties of material which favour the sorption process (such as porosity and specific surface area). The reuse of slag residuals from steel production in road construction and building materials, and for ammonia and phosphorus uptake from aqueous solutions was investigated in recent studies [15]. However, the arsenic removal performances of the material and the potential side effects in terms of its application in water treatment systems have not been widely and thoroughly investigated. Quartz sand, most commonly used as a filter media in treatment of iron and manganese contaminated water, is coated by flocks of metal oxides after years of filter operation, and eventually the material requires replacement, while the metal oxide layer, built up over the years in the filter units and imposes negative features to the filter media, has been assumed beneficial for aqueous arsenic removal purposes. Although the idea of the reuse of waste materials has already been promoted, its application in potable water treatment is far from widely spread. This is presumably due to the wide gap between the purity of the final product and the impurity of the applied waste material. Both materials, BFS and IMOCS, were obtained from local industrial facilities. Additionally, blast furnace slag was modified (MBFS) to minimise its detrimental impact on raw water quality and, hence, ensure the safety of its use. Adsorption of both As(III) and As(V) was investigated under neutral conditions where the applied arsenic species are present in both molecular and ionic forms, which correspond to real groundwater conditions. The arsenic removal performances of the waste materials were further compared to those of commercial materials obtained under the same experimental conditions.

2. Materials and Methods

2.1. Materials and Characterization Techniques. BFS and IMOCS were selected as the waste materials to be tested within the scope of the presented investigations. BFS was obtained from the local steel mill "US Steel Serbia" (Smederevo, Serbia). IMOCS was obtained from the groundwater treatment plant WTP "Bežanija" in Belgrade, Serbia, just before replacement of the filter media after 7 years of use. The physical properties and chemical compositions of the waste materials are presented in the further text. The commercial materials, granular porous ferric hydroxide (GFH) and a hybrid polymeric anion exchange resin with nanoscale iron oxide particles (HIER), were examined under the same experimental conditions in order to compare their performances with those of the waste materials. The physicochemical properties of the commercial materials were obtained from the manufacturer's technical data sheets: GFH (grain size: 2.0–4.0 mm, BET specific surface area 300 m^2/g, iron (Fe^{3+}) content: min 40%, iron hydroxide content: min 70%); HIER (mean bead size: 0.35 mm, bulk density: 0.765 kg/L, functional group FeO(OH)).

The microstructure of the analyzed HFO-coated material samples was examined by scanning electron microscopy (SEM) using a Jeol JSM 5800 instrument (Tokyo, Japan) (operated at 25 kV). The Brunauer-Emmett-Teller (BET) specific surface areas were determined by standard techniques of nitrogen adsorption using a Sorptomatic 1990 Thermo Finningan (San Jose, California).

2.2. Reagents and Analytical Methods. An As(V) stock solution (100 mg/L) was prepared by dissolving 416.5 mg of sodium arsenate (Na$_2$ HAsO$_4 \cdot$ 7H$_2$O, Analar analytical reagent) in 1 L of distilled water, which was preserved with 0.5% HNO$_3 \cdot$ An As(III) stock solution (3750 mg/L) was prepared by dissolving sodium arsenite (0.05 mol NaAsO$_2$, Riedel-de Haen (4.946 g As$_2$O$_3$ + 1.30 g NaOH in 1 L)) in distilled water in a 1 L volumetric flask, which was preserved with 0.5% HNO$_3$.

Arsenic was analyzed using the ICP-MS method [16] using an Agilent 7500 ce spectrometer equipped with octopole reaction system (ORS). Calibration was realized using external standards (2, 4, 20, 40, 80, and 100 μg/L), which were prepared by appropriate dilution of a 1000 μg/L stock standard solution. Working standards, as well as blank solutions, were prepared with high purity HNO$_3$. The concentrations of the investigated samples were adjusted to the concentration range of 5–100 μg/L. 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. A laboratory pH meter (Metrohm 827) was used for pH measurements. The accuracy of the pH meter was ±0.01 pH units.

2.3. Sorption Experiments

2.3.1. Batch Experiments. Batch experiments were designed to investigate the efficiency of the waste materials for the removal of arsenic from water. The influence of contact time and initial arsenic concentration on the sorption by the selected waste materials were examined as the most crucial parameters which influence the sorption efficiency. The batch tests were performed under different As valence: As(III) and As(V). In order to meet the pH conditions in real groundwater sources, the pH of the model solutions was adjusted to pH 7 using HCl and NaOH prior to adsorption. Laboratory beakers containing 1 g of sorbent and 100 mL of model solution were placed on an orbital shaker (Rotamax 120, Heidolph Instruments) at room temperature. The beakers were shaken at 150 rpm. After agitation, each sorbent-solution suspension was left 1-2 min to settle. The supernatant water was carefully sampled, and the samples were filtered using filter paper for extremely fine precipitates (Macherey-Nagel, grade MN 619-de; average retention capacity 1-2 μm), and the filtrates were analyzed for arsenic. The pH of the model solutions was measured prior to and at the end of each batch test. The amount of arsenic sorbed per unit mass of adsorbent was calculated by (1):

$$q = \left(C_o - C_1\right)\frac{V}{m}, \tag{1}$$

where q (mg/g) is the amount of arsenic sorbed per unit mass of sorbent (sorption capacity), C_o (mg/L) and C_1 (mg/L) are the initial and final concentration of arsenic in solution, respectively, V (L) is the solution, volume, and m (g) is the sorbent mass.

2.3.2. Kinetics and Equilibrium Experiments. Sorption kinetic experiments were performed using batch experiments at different time intervals: 15 min–24 h, with an initial arsenic concentration C_o = 0.5 mg/L and pH = 7. The initial arsenic concentration and pH value were adopted to match the conditions in real groundwater supply systems. During each set of conducted kinetic batch experiments, it was observed that even 24 h are not sufficient to reach absolute equilibrium. In each set of experiments, τ = 6 h was found to be the breakthrough point after which sorption rate is significantly lower and thus changes in sorption efficiency far less rapid. Moreover, rapid sorption rate range (0–6 h) was found most interesting for detailed examination in terms of waste materials' potential application. Finally, the adsorption isotherm experiments were performed under different initial arsenic, As(III) and As(V) concentrations (0.5, 1.0, 5.0, 10.0, 50.0, and 100.0 mg/L) for a contact time τ = 6 h, at pH = 7. The volume of treated As solution was 100 mL.

2.3.3. Column Experiments. Column experiments were conducted in a fixed-bed downflow filtration unit as shown in Figure 1. The installation is designed so that it can examine the impact of different sorption-filtering parameters that affect the efficiency of sorption processes, such as contact time, surface hydraulic load, and granulometric composition of the material, on various sorbent materials. The laboratory/field installation (pilot model) consists of a transparent (Plexiglas) column, inner diameter of Ø56 mm, which is filled with an appropriate sorbent material. Column diameter is selected according to the recommended column diameter-grain diameter ratio, which should be at least 1 : 50 in order to minimise wall effect on the hydraulic performance of the filtration system. Overflow weir is installed in the upper part of the column to maintain constant pressure at the entrance of the downflow filtration unit. Sorbent material is placed at the bottom of the column, above a 2 cm thick layer of coarse sand and gravel. Under the coarse sand-gravel layer, an additional wire screen is installed to prevent penetration of fine particles further into the flow control unit. At the bottom of the column, a pressure monitoring device (piezometer) is installed.

3. Results and Discussion

3.1. Material Characterisation. Table 1 summarizes physical properties and chemical composition of the investigated waste materials-industrial by-products.

The dominant constituent of IMOCS was quartz (SiO$_2$) coated with metal oxide layers. The content of manganese (Mn) was 4 times higher than that of iron (Fe), also present in the metal oxide layer, which imparts a predominantly dark grey surface colour to the material. The results of the chemical analyses show that the BFS was a complex heterogeneous material, mainly composed of silica and iron and calcium oxides. During the first set of experiments, the pH measurements revealed that the BFS had a strong effect on the pH of the model solution. After addition of the BFS into the model solution, the pH drifted to 11.25. The explanation for the sudden pH increase was found in the presence of CaO in the original slag material, BFS, which dissolves in water forming Ca(OH)$_2$ causing a rapid pH increase (7 to 11.25). In order to minimise its deteriorating effect on the quality of the model solution, the BFS was modified to neutralize the CaO effect on the pH. The raw BFS samples were treated with sulphuric acid and dried in oven at 70°C for 24 h. After the modification, the pH was buffered (pH = 7.90). The physical structure of the modified material (MBFS) was influenced by the formed gypsum giving it a "powder" appearance. As a result of the applied modification, the strong effect on the pH was avoided, while the main components of the untreated material, such as iron and iron oxides supposed to be beneficial for arsenic sorption, remained at nearly the equal content (Table 1). Therefore, this new, modified material was subjected to further detailed examination together with the other selected waste materials.

The porous microstructure with pores of different size and shape could be observed from each SEM microphotograph (Figure 2). Relatively high surface areas obtained for the waste filter sand are assigned to the iron and manganese oxides layer which coats the original grain of quartz sand.
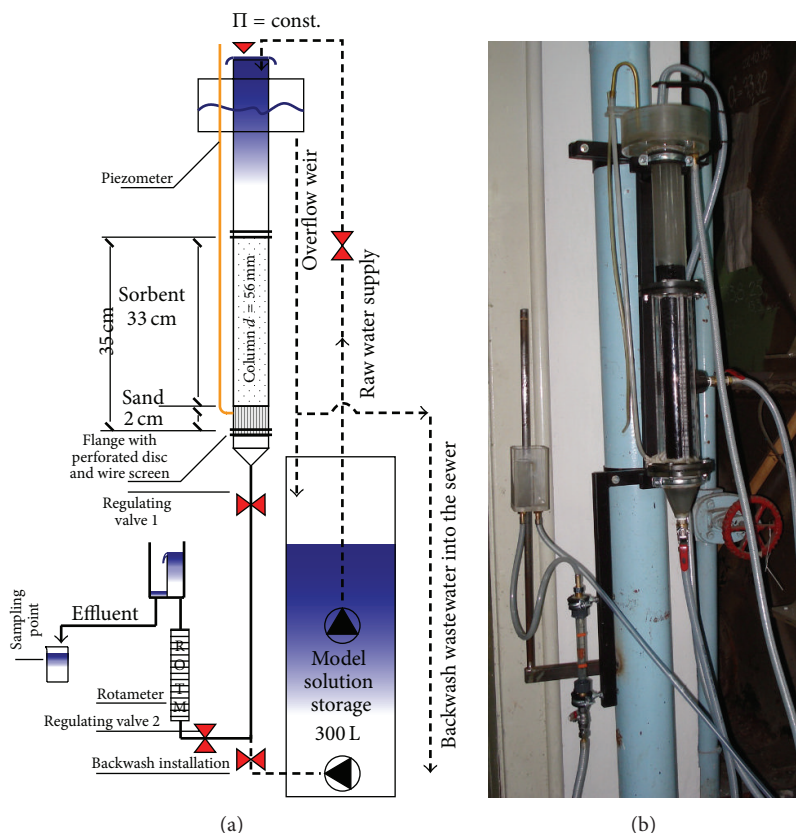
(a)

(b)

FIGURE 1: Experimental setup: pilot model of the sorption-filtration column for the arsenic removal from water.

TABLE 1: Chemical composition and physical properties of the industrial by-products.

Material	Chemical composition (%)								Physical properties	
	SiO_2	Fe_2O_3	FeO	Al_2O_3	CaO	MgO	Fe	Mn	Grain size (mm)	BET specific surface area (m^2/g)
IMOCS	65.16	3.68	0.82	—	1.14	21.23	3.93	15.66	1.25	94.1
BFS	23.82	13.02	15.73	7.70	26.5	11.13	21.20	—	0.470	2.9
MBFS	21.45	15.94	14.50	—	24.53	8.67	22.42	—	0.340	17.167

SEM microphotographs of the surface of the BFS revealed its highly porous structure (Figure 2(b)). The particles of BFS and MBFS were much larger, up to $20\,\mu$m, and they occurred in rounded (BFS) to needle-sharp forms (MBFS). Modification of the BFS was not detrimental to the porosity of the original material, causing only a sharpening of the pore edges (Figure 2(c)). Additionally, modification increased the BET specific surface area of the new, modified material ($17.167\,m^2$/g), which contributed to the efficiency of the sorption process.

3.2. Batch Kinetic and Equilibrium Studies.
Several model equations have been established to describe sorption kinetics, among which the pseudo-second-order (PSO) model is the most frequently used. In addition, the PSO model is found to be the most appropriate to describe the sorption process

of a chemical nature, chemisorption. The PSO model is described by (2):

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t, \qquad (2)$$

where q_t is sorption capacity at time t (μg/g), q_e the equilibrium sorption capacity (μg/g), and k_2 the rate constant of sorption (g/(μg·min)). The experimental results are fitted to the pseudo-second-order model, applying nonlinear regression analysis using MS Office 2000 Excel spreadsheets. The experimental and modelling results are presented in Figure 3. Values of the model parameters obtained from the regression analyses are presented in Table 2.

The two times higher sorption capacities obtained with the BFS ($47.6\,\mu$g/g) compared to IMOCS ($25.4\,\mu$g/g) contribute to the assumption that chemisorption occurs, since
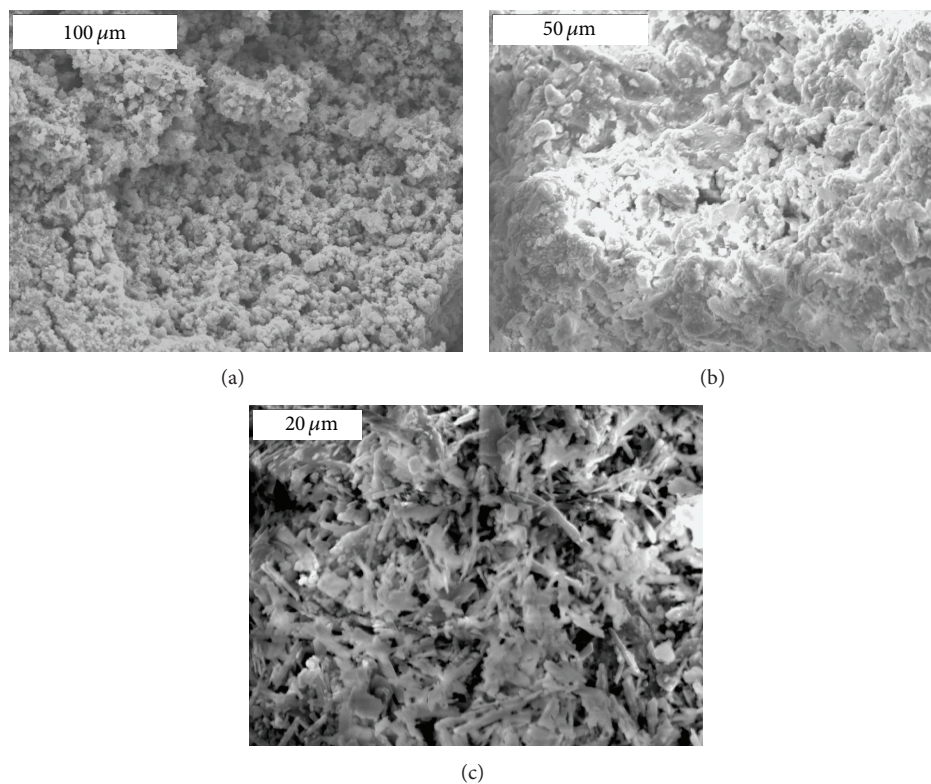
(a)

(b)

(c)

FIGURE 2: SEM microphotographs of (a) waste filter sand, (b) blast furnace slag, and (c) modified blast furnace slag.
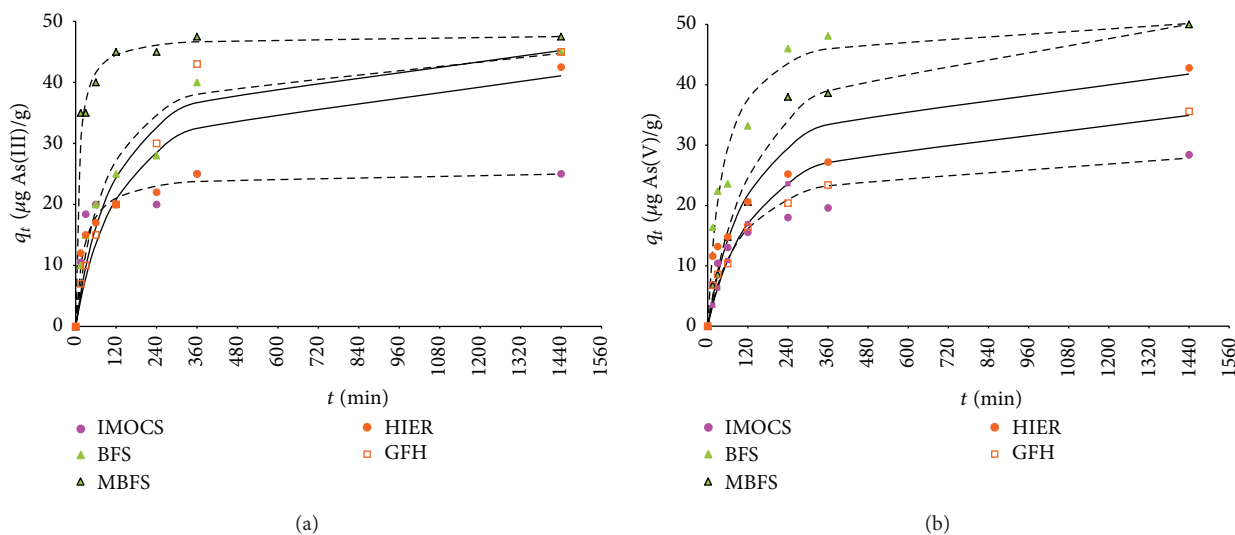

(a)

(b)

FIGURE 3: Sorption kinetics modelling of As(III) and As(V) on industrial by-products and commercial sorbents (pseudo-second-order model).

slag materials exhibit significantly lower BET specific surface area which is a crucial characteristic that enhances the sorption properties of a material. Further insight into the chemical composition of the examined materials (Table 1) revealed that the BFS exhibited higher sorption capacities due to the five times higher iron and iron oxides content compared to the IMOCS, despite their lower BET surface areas.

The contribution of manganese (15.66%) in IMOCS to the sorption mechanism is probable since the low iron content in the metal-oxide-layer (3.93%) hinders the IMOCS from being an efficient sorbent for arsenic. To evaluate contribution of manganese to arsenic sorption capacity of IMOCS specific arsenic removal, efficiency of iron has to be calculated first. Specific arsenic removal efficiency of iron is calculated from BFS since the iron is the dominant active substance assumed

TABLE 2: Pseudo-second-order kinetic model parameters for As(III) and As(V) sorption on industrial by-products.

Materials	As(III)			As(V)		
	q_e (μg/g)	k_2 (g/(μgmin))	R^2	q_e (μg/g)	k_2 (g/(μgmin))	R^2
IMOCS	25.4	0.001572	0.999	29.8	0.000329	0.989
BFS	47.6	0.000233	0.994	51.7	0.000427	0.999
MBFS	47.8	0.002334	1.000	55.2	0.000121	0.996
HIER	45.1	0.000158	0.965	45.6	0.000167	0.982
GFH	49.0	0.000168	0.994	38.7	0.000169	0.987

TABLE 3: Langmuir and Freundlich isotherm parameters for industrial by-products.

Material	Langmuir						Freundlich					
	As(III)			As(V)			As(III)			As(V)		
	q_{max} (mg/g)	K_L (L/mg)	R	q_{max} (mg/g)	K_L (L/mg)	R	K_F (L/mg)	$1/n$ (L/g)	R	K_F (L/mg)	$1/n$ (L/g)	R
BFS	0.82	13.22	0.97	4.04	12.71	0.99	0.567	0.519	0.96	3.010	0.591	0.83
MBFS	0.70	6.20	0.95	2.79	18.63	0.99	0.369	0.587	0.94	1.779	0.526	0.75
IMOCS	0.55	0.37	0.79	0.77	1.18	0.97	0.110	0.843	0.96	0.157	0.727	0.92
HIER	1.96	0.84	0.99	2.52	19.71	0.93	0.38	0.718	0.89	3.497	0.733	0.85
GFH	1.75	2.34	0.99	1.17	2.21	0.98	0.59	0.706	0.82	0.347	0.735	0.88

to be responsible for BFS sorption efficiency. According to experimental data, Fe content in BFS, 0.2120 gFe/gBFS (Table 1), and BFS equilibrium sorption capacity (Table 2), specific arsenic removal efficiency of iron present in BFS is estimated to 220 μgAs/gFe. Applied to the IMOCS containing 39.3 mg/g of Fe (Table 1), the contribution of iron to arsenic removal was expected to be 9 μgAs/gIMOCS (220 μgAs/gFe $\times$ 0.0393 gFe per unit mass of IMOCS). Higher values of q_e obtained for IMOCS (25.4 and 29.8 μg/g, for As(III) and As(V), resp.) suggest that iron was not the only active component in the IMOCS. Although these results cannot be directly correlated (due to the chemical and physical properties), the higher efficiency of IMOCS could be assigned to manganese activity. Assuming the difference between the contribution of iron to the sorption and the total q_e values is the consequence of manganese activity only, and the specific arsenic removal efficiency of manganese was estimated to be 115 μgAs/gMn.

In order to evaluate the applicability of the waste materials for the treatment of real arsenic-contaminated water treatment, these results were compared with those obtained for commercial materials. The same set of batch experiments was performed with commercial granular porous ferric hydroxide (GFH) and a hybrid ion exchange resin coated with nanoscale iron oxide particles (HIER). The obtained q_e values were 49.0 and 38.7 μg/g for GFH and 45.1 and 45.6 μg/g for HIER for A(III) and As(V), respectively. The capacities exhibited by the waste slag materials (Table 2) attained the values realized with the commercial materials for As(III), while the results were even slightly exceeded for As(V). The lower performances of the IMOCS compared to the commercial materials were assigned to its low iron content. However, sand filter media from other groundwater treatment plants were reported with different contents of iron (ranging from 15 to 330 mg/g) and manganese (0.2–50 mg/g) [23]. Previous findings on

specific arsenic removal efficiencies of active substances suggest that sand filter media containing a sufficient amount of iron (roughly estimated > 220 mg/g) can remove arsenic from aqueous solution equally efficiently as the examined commercial materials.

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 following is the Langmuir isotherm model (3):

$$q_e = \frac{q_{max}K_L C_e}{(1 + K_L C_e)}, \tag{3}$$

where q_e is the amount of solute sorbed per gram of sorbent (mg/g), C_e the equilibrium concentration of solute (mg/L), K_L a constant related to the energy of sorption (L/mg) (Langmuir model), q_{max} the maximum amount of solute sorbed per gram of sorbent (mg/g) which was derived under the assumption that the sorbate is sorbed in one molecule layer.

The following is the Freundlich isotherm model (4)

$$q_e = K_F C_e^{1/n}, \tag{4}$$

where K_F is the Freundlich constant (mg/g) and n, a constant related to the sorption intensity of the sorbent, is a consecutive layer model which does not predict any saturation of the sorbent by sorbate.

Table 3 summarises Langmuir and Freundlich isotherm model parameters for the examined industrial by-products and commercial sorbents.

The highest maximum sorption capacities were found for BFS: 0.82 mg/g and 4.04 mg/g for As(III) and As(V), respectively. The BFS and MBFS exhibited significantly higher q_{max} values for As(V) compared to As(III), while the IMOCS attained nearly equal values for both. The differences in the q_{max} values for As(III) and As(V) might suggest that the

TABLE 4: Comparative evaluation of various industrial by-products as adsorbents for arsenic removal.

Adsorbent	pH	Concentration/range	Surface area (m^2/g)	Temperature $(°C)$	Model used to calculate adsorption capacity	Capacity (mg/g)		Reference
						As(III)	As(V)	
Bauxsol	4.5	0.80–31.0 mM	—	23	Langmuir	—	1.081	[17]
Red mud	3.5 As(III) 7.25 As(V)	33.37–400.4 μmol/L	—	25	Langmuir	0.884	0.941	[18]
Rice husks	6.5	100 μg/mL	—	20	Column	0.020	0.007	[19]
Orange juice residue	7–11 As(III) 2–6 As(V)	—	—	30	Langmuir	70.43	67.43	[20]
Pine wood char	3.5	10–100 μg/L	2.73	25	Langmuir	0.0012	—	[21]
Oak wood char	3.5	10–100 μg/L	2.04	25	Langmuir	0.006	—	[21]
Oak bark char	3.5	10–100 μg/L	25.4	25	Langmuir	0.0074	—	[21]
Fe(III)/Cr(III) hydroxide waste from cooling water systems	4.0	20–100 mg/L	—	32	Langmuir	—	11.02	[22]

arsenic species present under neutral conditions As(III) in the molecular form, while As(V) in the ionic form influences the sorption efficiency of the waste slag materials. Although iron was found efficient for arsenic uptake, arsenic removal was found to be valence dependent making As(V) removal more effective than As(III). The higher sorption capacities of BFS and MBFS (5 and 4 times, resp.) 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 IMOCS. The low content of iron in the IMOCS is presumed responsible for its lower As(V) sorption capacity.

To evaluate the application for real groundwater treatment, the capacities of the obtained industrial by-products were further compared to those exhibited by commercial sorbents, which were examined under the same experimental conditions. At neutral pH value of arsenic aqueous solution, slag materials (BFS and MBFS) exhibited higher q_{max} values for As(V) than investigated commercial sorbents (GFH and HIER), indicating better performances of the waste slag materials (Table 3). The lower capacities of IMOCS compared to the commercial materials were assigned to its low iron content.

A range of industrial by-products and other low cost adsorbents are investigated for As(III) and As(V) removal. Reported adsorption capacities are summarised in Table 4. However, due to differences in experimental conditions (pH, temperature, ion interferences, and batch/column studies), initial arsenic concentrations and different arsenic speciation, and type of water treated, it is difficult to compare reported sorption capacities. It is obvious from the reported results that some low-cost adsorbents developed from industrial wastes exhibit significant capacities such as orange juice residue and Fe(III)/Cr(III) hydroxide waste from cooling water systems.

3.3. Column Studies

3.3.1. Hydraulic Characteristics of the Pilot Model.
Hydraulic and sorption-filtration characteristics of the pilot model were adopted to meet the operational range of similar reactors in real water treatment plants. Experimental investigations in batch system showed that the increase of contact time contributes to the increase in the efficiency of arsenic removal for all tested materials, including commercial materials. However, the practical application of sorption processes substantially limits the value of applied contact time in real reactors since the contact time is directly related to the dimensions of the reactor: the bigger the reactor, the higher the contact time. For this reason, the real reactors are designed for the contact time from 2.5 to 5 min. In the presented column examinations, the adopted empty bed contact time (EBCT) is 4 min. For the applied surface hydraulic load of 5 m/h, the calculated height of the adsorption filter media is 33 cm. Hydraulic characteristics of the pilot model are summarised in Table 5.

Arsenic sorption investigations in the continuous flow system were performed under the same experimental conditions as examinations of arsenic sorption kinetics in the batch reactor: $C_o = 0.5$ mg/L, pH neutral, and constant temperature of the solution. Breakthrough curves of As(III) and As(V) removal by IMOCS and BFS are shown in Figure 4.

The difference in the sorption kinetics of arsenite, As(III), and arsenate, As(V), on BFS in the continuous flow system is apparent. In the first 860 min, the effluent arsenate As(V) concentration changes slowly in low range arsenic concentrations (less than 50 mg/L). After this stage, the effluent arsenate concentration increases rapidly and media reaches 90% saturation in the next 13 h. In contrast, sorption of arsenite in the early stages of the experiment is less efficient. Arsenite concentration of 50 mg/L is exceeded after only

TABLE 5: Characteristics of the pilot model.

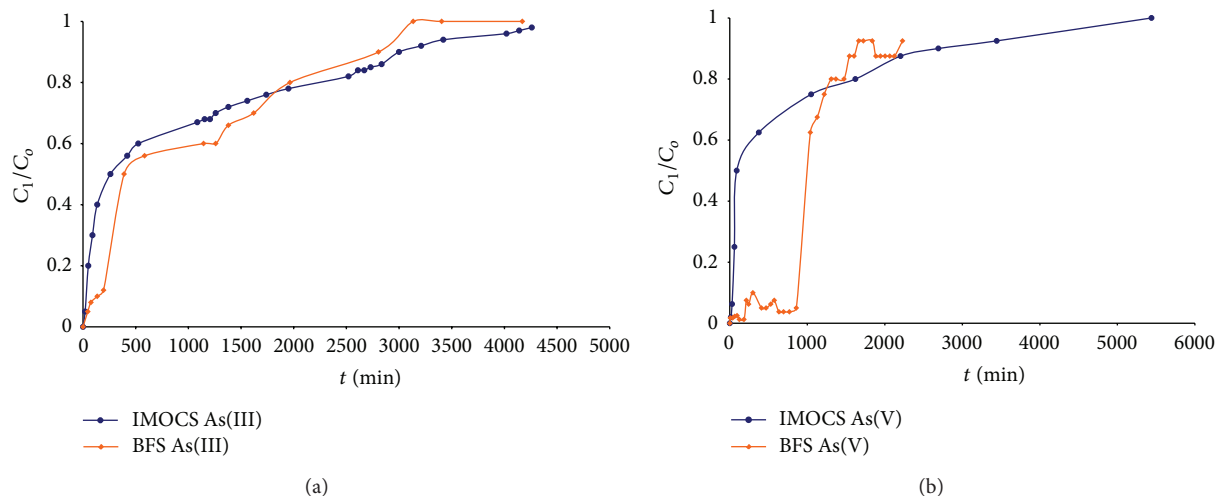| Hydraulic parameters			
Inner column diameter, D_k (mm)	56	Empty bed contact time, EBCT (min)	4
Mean grain diameter, d (mm)	1	Surface hydraulic load, v (m/h)	5
Height of the media, H_i (cm)	33	Hydraulic load, Q (L/h)	12.3
Height of the coarse gravel-sand layer, h_n (cm)	2	Backwash surface hydraulic load, v_{pf} (m/h)	50
Operating column volume, V_R (dm^3)	0.81	Backwash hydraulic load, Q_{pf} (L/h)	123.2

(a)

(b)

FIGURE 4: Breakthrough curves of As(III) and As(V) removal by IMOCS and BFS.

38 min. In the next 5.8 h, effluent arsenite concentration rapidly grows to 50% saturation after which it continues to increase slowly until the full saturation in the next 46 h. Unlike the slag material, breakthrough curves for As(III) and As(V) sorption on IMOCS are almost identical. This indicates that IMOCS exhibits the same performance in the sorption of both arsenic species in the continuous flow system.

Based on breakthrough curves, it could be concluded that IMOCS is not an efficient adsorbent for As(III) or As(V) and the breakpoint of the curve occurred quickly. On the other hand BFS seems to be more efficient than IMOCS for As removal in a column system. BFS adsorbent is also a more efficient adsorbent for As(V) removal than As(III) in a nonequilibrium column system too.

Arsenic sorption investigations in the continuous flow system were performed under the same experimental conditions as examinations of arsenic sorption kinetics in the batch reactor. In case of identical experimental conditions, equilibrium sorption capacity, q_e, obtained in batch experiments should correspond to the total sorbent capacity, K_E, obtained in the continuous flow reactor. Table 6 summarises the equilibrium capacity data from the batch tests and the total capacity of waste materials.

The values of equilibrium sorption capacity, q_e, are lower than total capacity, K_E, for all examined waste materials and both arsenic species. Hydraulic conditions in the batch reactor are favourable only for the development of the sorption process. However, continuous flow through the sorption-filtering unit enables development of several contaminant removal processes such as sorption, coagulation, flocculation, sedimentation, and filtration. The joint effects of all these contaminant removal processes are assumed to increase the overall sorbent performance in the continuous flow reactor.

4. Conclusions

Industrial by-products, blast furnace slag, waste filter sand, and modified blast furnace slag, exhibited substantial affinity towards inorganic arsenic species. Kinetic studies revealed that the slag materials were the most efficient in arsenic removal, attaining equilibrium sorption capacities in the range of 47.6–55.2 μg/g, while waste filter sand exhibited sorption capacities in the range of 25.4–29.8 μg/g for an initial arsenic concentration $C_o = 0.5$ mg/L. The complex nature of the sorption process in industrial by-products, including both chemisorption and physical sorption, was revealed by the equilibrium studies. Sorption capacities for As(V) compared to As(III) were significantly higher for blast furnace slag, while waste filter sand exhibited similar removal efficiencies for both arsenic species. The arsenic sorption process on the waste materials continued after monolayer saturation following the Freundlich isotherm model. Blast furnace slag exhibited the highest equilibrium sorption efficiency of 0.05 mg/g under the conditions that occur in real water treatment systems, while waste filter sand reached 0.02–0.03 mg/g. Compared to the equilibrium sorption efficiency of 0.05 mg/g obtained for the granular

TABLE 6: Maximum sorbent capacity at C_o = 0.5 mg/L in batch and continuous flow reactor.

Maximum sorbent capacity (μgAs/g)	BFS		IMOCS	
	As(III)	As(V)	As(III)	As(V)
Equilibrium capacity in batch reactor, q_e (μgAs/g)	47.6	51.7	25.4	29.8
Total sorbent capacity, K_E (μgAs/g), continuous flow reactor	87.4	66.3	139.9	108.8

ferric hydroxide, commercial arsenic sorbent, these results indicate that application of industrial by-products is feasible in real water treatment systems. Better sorption efficiencies are obtained in continuous flow reactor compared to batch reactor. The joint effect of sorption, coagulation, flocculation, sedimentation, and filtration that are developed during continuous flow in a fixed-bed reactor are assumed to benefit the efficiency of arsenic sorption in the continuous flow reactor.

Acknowledgments

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