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Cellular concrete-supported cost-effective adsorbents for aqueous arsenic and heavy metals abatement



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ABSTRACT

Aqueous arsenic and heavy metals in concentrations exceeding sanitary limits present an acute regional problem. Adsorption is an effective although costly method of pollutants removal. This makes the search for low-cost effective disposable adsorbents necessary. The adsorbents using vermiculite concrete and aerated autoclaved light concrete (aerocrete) modified with iron oxyhydroxide were synthesized and studied. The specimens of adsorbent materials showed the adsorption capacity more than two-fold exceeding the vermiculite-based adsorbents in respect to copper and lead cations, 53 and 195 mg g⁻¹, respectively, having the adsorption capacity for cadmium comparable to exfoliated vermiculite at 35.5 mg g⁻¹. Arsenic anions were adsorbed in amounts comparable to the ones of carbon composites-supported ferric oxyhydroxide adsorbents, up to 16 mg g⁻¹ of arsenate. The analysis of adsorption dependent on temperature showed its spontaneous low-energy ion-exchange character. Desorption of heavy metals and arsenic anions from used adsorbents meets the requirements of drinking water standards with the exception of cadmium, meeting the agricultural use standard of 0.01 mg L⁻¹. The new synthetic adsorbents were found to be cost-efficient, safe and reliable in removal of arsenic anions and heavy metals cations.

1. Introduction

The problem of pollution with toxic heavy metals caused by natural reasons and human industrial activities is attributable to many regional watersheds and ground waters used for water supply [1]. For example, approximately nine million people living in the Pearl River Delta are at risk of consumption of groundwater polluted with heavy metals and arsenic; the sediments of surface waters are also heavily polluted [2,3]. Among various physico-chemical methods used in heavy metals abatement [4], adsorption is often used at a polishing stage of water treatment [5]. The adsorbents of various nature are used including the natural and synthetic minerals, plant tissues and carbon-based adsorbents. Wide spectrum of adsorbents studied in potable water treatment indicates the method's relevance for its performance and, from the other hand, dissatisfaction with the commercially available adsorbents resulting in ongoing search for cost-effective solutions [6]. The search for low-cost disposable adsorbents derived from various waste materials of organic and inorganic nature has been undertaken for the last decades. The technical problems persisting the adsorbents in use include their relatively small contact surface, low adsorption capacity and

selectivity towards target pollutants, unsatisfactory mechanical strength and high hydrodynamic head loss, resulting in often non-satisfactory cost-to-quality ratio [5,7].

The cement-based low-cost adsorbents derived from the concrete wastes received attention lately. Ettringite $Ca_6Al_2(SO_4)_3(OH)_{12}$ ·26H₂O formed in the Portland cement hydration reaction in concrete slurries and wastes is an active adsorbent component of alkaline nature effective in adsorption of arsenate, borate, phosphate and fluoride anions [8–11].

Ferric oxides and hydroxides were under the scope in arsenic anions adsorption for the last decade, being mostly immobilized by ferric salts hydrolysis at the surfaces of adsorbents of organic and inorganic nature – activated carbons [12–14], wood- and straw-derived biochars [15], synthetic polymers [16] and clays [17], showing maximum Langmuir adsorption at a few tens of mg g⁻¹ level.

A synergic effect of cementitious support impregnated with iron hydroxides in phosphate adsorption was noticed when cement pellets were prepared as a cement mixture with the acid mine drainage (AMD) sludge showing a four-fold higher adsorption capacity due to Ca-precipitation of phosphate; hydrous ferric oxide exhibited only adsorption

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Received 31 May 2017; Received in revised form 14 July 2017; Accepted 26 July 2017 Available online 27 July 2017 2213-3437/ © 2017 Elsevier Ltd. All rights reserved. properties [18]. This property of concrete supports combined with iron hydroxides lead to an idea of the adsorbents' contact surface development.

Aerated autoclaved light concrete blocks with outstanding heat insulation properties are widely used in construction. The hydrogen gas bubbles formation in reaction of aluminium powder with calcium hydroxide and water create a developed, a few $m^2 g^{-1}$, contact surface with a potential of the rejects of the blocks being used as adsorbents and the adsorbent support. Such concrete itself showed satisfactory adsorption properties in removal of fluorides and phosphates from neutral and alkaline solutions [19,20]. The inclusion of iron and iron oxide dust to the cellular concrete mortar composition resulted in declaratively improved adsorption properties in respect of Ni and Zn cations, although the author presents incomplete quantitative data [21]. Introduction of iron oxides to the composition of the cellular concrete blocks, however, compromises the idea of utilized construction wastes: addition of rust to the blocks does not seem aesthetically appropriate for construction, i.e. the iron-containing cellular adsorbent is a specially manufactured material, not the utilized construction waste. Deposition of ferric hydroxide to the cellular concrete blocks analogous to the other adsorbents impregnation may present more practical alternative studied in the present work.

Another way of formation of lightweight aerated concrete is introduction of air-entraining aggregates such as exfoliated vermiculite to the concrete mortars. Vermiculite with its general formula $(OH)_4(Mg \cdot Ca)_x(Si_{8-x} \cdot Al_x)(Mg \cdot Fe)_6O_{20} \cdot 8H_2O$ with x = 1 to 1.4 [22] is extensively studied in adsorption as a substance with high cation exchange capacity. Cationic heavy metals were found to be better adsorbed from alkaline solutions, whereas anionic forms of vanadate and arsenate adsorb at vermiculite from acidic media [23-25]. Exfoliated vermiculite exhibits substantial Langmuir isotherm adsorption capacities reaching hundreds of mg g^{-1} in respect to the majority of heavy metals with exception of chromium [26], although certain discrepancies in the capacity order of magnitude are observed among various research reports [27]. The difference may be explained by the variations in vermiculite composition, the adsorbent preparation and the experimental conditions [28,29]. The pronounced adsorbent properties of vermiculite offer considering the vermiculite lightweight concrete rejects as an alternative low-cost adsorbent support.

None of the ferric-impregnated lightweight concretes was mentioned in extended reviews covering wide spectrum of adsorbents applicable to arsenic and heavy metals abatement [1,7], making the study in their preparation and testing a step towards the design of potentially cost-effective reliable adsorbent with extended contact surface. The objective of the present research is the development of novel adsorbents with improved capacity, stability and hydrodynamics using low-cost vermiculite concrete and aerated autoclaved light concrete (aerocrete) with their surface modified with ferric oxyhydroxide. The costs of vermiculite concrete and aerocrete vary within 5 to 10 EUR tonne⁻¹ making them potentially the most affordable adsorbent supports keeping in mind the usage of their rejects in adsorbent production. The target pollutants in the study, arsenic anions and cations of cadmium, copper and lead, were chosen for their abundant character and acute toxicity threatening public health.

2. Materials and methods

2.1. Materials

The molecular composition of aerocrete provided for the study by the manufacturer JSC GlavNovosibirskStroy (Novosibirsk, Russia) included, in accordance with the Interstate Standard [30], wt.%: $3CaO\cdotAl_2O_3-3$ to 6, $3CaO\cdotSiO_2-22$ to 30, $2CaO\cdotSiO_2-8$ to 12, Al_3O_3-2 to 3, SiO_2-60 to 65 with admixtures of Al, TiO_2 , MgO, K₂O, NaOH, CO₂ and H₂O. The composition of vermiculite comprising 20 wt.% of vermiculite concrete contains, wt.%: $SiO_2 - 38$ to 49, MgO — 20 to 24, $Al_2O_3 - 12$ to 18, $Fe_2O_3 - 5$ to 9, $K_2O - 5$ to 8, $TiO_2 - 1$ to 2, CaO - 0.7 to 1.5, with admixtures of MnO, FeO, Na_2O , Cr_2O_3 , CO_2 and H_2O [31].

Cellular concrete materials were crashed in agate mortar and screened at sieves with 1.5- and 2.5-mm openings. The fraction from 1.5 to 2.5 mm was used in the supported adsorbent preparation by soaking in the ferric chloride (RusKhlor Association, Russia) aqueous solution with subsequent addition of the 0.5-M aqueous solution of sodium hydroxide (JSC KhimProm, Russia) at 50 °C. The adsorbents were rinsed with distilled water until pH 6.5 to 7.2 and dried at 140 °C. The chemicals were of "chemically pure" grade adopted by Russian Federation identical to *Purissimum*, i.e. > 99% of the assay content.

2.2. Methods

2.2.1. Adsorption capacity and kinetics

2.2.1.1. Arsenic anions. Adsorption capacity was tested in stationary conditions: the adsorbent in amount of 0.2 g was added to the 50-mL samples of arsenite or arsenate solutions, containing from 10 to 100 mg L^{-1} of As. All the experiments were carried out in five batch replicates. Solutions containing arsenate AsO_4^{3-} were made of sodium dihydroarsenate NaH2AsO4 (JSC CosmoKhim, Russia). The arsenite solutions were prepared using the State Standard Specimen solution (JSC CosmoKhim, Russia) containing 100 mg L^{-1} of As in the form of AsO₃³⁻ and the distilled water. Samples were mixed with magnetic stirrers. The solutions were separated from the adsorbent particles using the desktop centrifuge Allegra 64R (Beckman Coulter, USA) at 20,000 rpm. The concentrations of arsenite in supernatant liquid were determined by the inverse voltammetry [32], and the ones of arsenate - by colorimetric analysis with ammonium molybdate [33]. In the voltammetry method, arsenite ions were preliminarily accumulated from the analysed solution as As (0) at the Au-C electrode for 10 min at the potential of E = -1.0 V with subsequent dissolution at linear growth of potential up to +0.6 V with the As peak registered at 0.05 ± 0.05 V at pH 3.5-4.5 [32]. Colorimetric analysis of arsenate was carried out with ammonia molybdate: 1 mL of solution containing 1 g of (NH₄)₂MoO₄ in 100 mL of 3.0 M H₂SO₄ was added to 10 mL of the analysed sample. Further, 0.5 mL of solution containing 0.15 g of hydrazine in 100 mL of bi-distilled water was added. The sample was heated in water bath for 15 min, cooled down to 20 °C and diluted to 25 mL. The optical density was measured at 750 nm [33]. The limits of detection and quantification with voltammetry for arsenite were 0.002 and 0.05 mg L^{-1} , respectively. The corresponding limits for arsenate determined by colorimetry were 0.005 and 0.025 mg L^{-1} .

The contact time sufficient for achieving the adsorption equilibrium was determined in kinetic experiments, when arsenate was adsorbed from the solution containing starting arsenic concentration of 20 mg L⁻¹, and the solution samples were withdrawn during the time of adsorption. The adsorption isotherms of arsenate and arsenite were obtained at temperatures 20, 40 and 60 °C for establishing the adsorption activation energy. To maintain the temperature, the thermostat TC-1/20 SPU (Smolensk Technology Designing Agency of Programmed Systems, Russia) was used. The effect of pH to the arsenic anions adsorption was not studied; all experiments were carried out in neutral media at pH from 6.5 to 7.2.

2.2.1.2. Metallic cations. The stock solutions of Cd^{2+} , Cu^{2+} and Pb^{2+} were prepared by dissolving appropriate amounts of analytical reagent grade $Cd(NO_3)_2$ ·4H₂O, $Cu(NO_3)_2$ ·3H₂O and $Pb(NO_3)_2$ (Aladdin Industrial Corporation, China) in bi-distilled water, respectively. In all adsorption batch equilibrium experiments, the adsorbent in amount of 0.07 g was added to 100 mL of the appropriate ion solution in 250 mL conical flasks placed to an orbital shaker (HZ-9310KA, Shanghai Hualin Industrial Ltd. Co., China) at 180 rpm. After the predetermined adsorption time, solution samples were filtered through the water phase pin type filters with the pore size of 0.45 μ m (ANPEL Laboratory

Technologies Inc., Shanghai, China). The aqueous metal ion concentrations were measured by using atomic absorption spectrophotometer (AAS) (AA-6300C, Shimadzu, Japan) with hollow cathode lamps AS-1 (Beijing General Research Institute for Nonferrous Metals, China) at the emission wavelengths 228.8, 324.8 and 283.3 nm for Cd²⁺, Cu²⁺ and Pb²⁺, respectively. The flame AAS (FAAS) used for higher concentrations has the limits of detection 0.001, 0.002 and 0.02 mg L^{-1} , and the limits of quantification 0.003, 0.006 and 0.06 mg L^{-1} for Cd²⁺, Cu²⁺ and Pb²⁺, respectively. The authors used also a more sensitive graphite furnace AAS (GFAAS) method [34-36], which has the limits of detection 0.00005, 0.0001 and 0.001 mg L^{-1} , and the limits of quantification 0.00015, 0.0003 and 0.003 mg L^{-1} for Cd²⁺, Cu²⁺ and Pb²⁺, respectively. Cations of Ni²⁺ and Zn^{2+} in the flow-through experiment were measured at 232.0 and 213.9 nm with the limits of detection and quantification of 0.001 and 0.003 mg L^{-1} , respectively.

The initial concentrations of Cd^{2+} , Cu^{2+} and Pb^{2+} were set as 10 mg L⁻¹ except for the experiments with the initial concentration of metal ions affecting the adsorption capacity of the adsorbents. The effect of pH on the adsorption capacity was studied by adjusting the pH from 2.0 to 5.0 using ST20 pH-meter (OHAUS, USA). Higher pH in heavy metals solutions were not tested avoiding hydroxides precipitation. The solutions were brought to the desired pH by adding sodium hydroxide or nitric acid solutions (Guangzhou Chemical Reagent Co., China). The adsorption kinetics was studied at pH 5.00 within the exposition time from 1 to 240 min. The maximum adsorption capacities were determined from Langmuir isotherms established with metal concentrations from 10 to 200 mg L⁻¹ at pH 5.00 for 2 h. To determine the adsorption activation energy, the experiments were conducted in the temperatures 15, 25 and 35 °C.

2.2.2. Desorption and elution experiments

The elution of the adsorbent components with water was determined in the tests, when 1.0 g samples of the adsorbents were placed to 100 mL of bi-distilled water and stirred with magnetic stirrers for 1 h.

The tests for arsenic anions desorption were carried out to determine the stability of the compounds formed at the adsorbent surface. For this, 0.2 g of the adsorbent samples were placed to 50 mL of arsenate or arsenite solution containing 100 mg L⁻¹ of As and mixed with magnetic stirrers. Then the dried at 105 °C 0.2 g adsorbent samples containing adsorbed arsenate or arsenite were stirred in 50 mL of bidistilled water for 24 h with subsequent analysis of the target anions in the solution. The analysis of the ions desorbed to the aqueous phase was carried out using the inductively coupled plasma atomic emission spectroscopy (ICP-AES) with iCAP 6300 Duo spectroscope (Thermo Electron Corporation, USA).

For the leaching tests of metallic ions, ten parallel samples each using 0.07 g of the adsorbent were placed to 100 mL of mixed metal ions solution portions at the initial concentrations of Cd^{2+} , Cu^{2+} and Pb^{2+} of 100 mg L⁻¹ and shaken at 180 rpm for 2 h at 25 °C. The filtered at a 0.45-µm membranes adsorbent was dried at 105 °C for 24 h. Three parallel samples of dried adsorbent in amount of 0.1 g each were added to 100 mL of distilled water at pH 5.5 and shaken at 100 rpm for 12 h at 25 °C. The metal ion concentrations were measured in filtered solutions using AAS (see above).

2.2.3. Characterisation of adsorbents

The Brunauer–Emmett–Teller (BET) method of nitrogen thermal desorption was used to determine the adsorbents' contact surface area and their porosity using the BET surface and porosity analyser Sorbtometer-M (JSC CataCon, Russia).

The content of iron in the adsorbents was determined in solutions resulted from the dissolution of 50 mg samples of adsorbents in 15 mL of 15-% hydrochloric acid (JSC CosmoKhim, Russia). The residual solids were separated using the centrifuge at 20,000 rpm with subsequent colorimetric measurement in the supernatant liquid with

sulphosalicylic acid (SigmaTech, Russia) according to the standard method with measurement of optical density at 400 nm using PD-303UV spectrophotometer (Apel, Japan) [33,37].

Thermal analysis of adsorbents was carried out using thermogravimetric analyser with differential scanning calorimetry (DSC) SDT Q600 V20.9 Build 20 (TA Instruments, USA).

For identification of the compounds at the adsorbent surface, the FT-IR spectra of FeAsO₄ and the adsorbents containing arsenate-ions were obtained within 400 to 4000 cm⁻¹ diapason using FT-IR spectroscope Nicolet 5700 (Thermo Electron Corporation, USA).

Morphology of adsorbents was observed using a scanning electron microscope TescanVega-3 (Tescan a. s., Czech Republic). Prior to scanning, a carbon film was sputtered on a thin layer of the adsorbent powder, applied on a conductive tape. Recording was carried out at the accelerating voltage of 20 kV.

2.2.4. Adsorption test with galvanic wastewater

The laboratory-scale flow-through reactor filled with the vermiculite concrete-supported ferric oxyhydroxide adsorbent was applied to adsorb Zn^{2+} , Cd^{2+} , Pb^{2+} , Cu^{2+} , and $Fe^{2+/3+}$ from the wastewater of galvanic production at JSC Scientific Production Centre "Polus", Tomsk, Russia. The acidic wastewater was preliminarily neutralized with lime to pH 8.2–8.3, which results in partial precipitation of heavy metals. The adsorbent 1.5–2.5 mm granules in amount of 83 g were placed to a column of 28 mm in diameter and 146 mm height, through which the wastewater was pumped at $15 L h^{-1}$ with the peristaltic pump MXHM 203E (Calpeda, Italy).

2.2.5. Surface charge of adsorbents

The surface charge of adsorbents was measured using the Zetasizer Nano ZSP electrophoretic instrument (Malvern Instruments Ltd., UK). The suspension of the adsorbent was prepared from its powder milled to the particle size < 0.1 mm in amount of 0.02 g suspended in 20 mL of distilled water and sonicated for 3–4 s. The 1.0 mL aliquot was used for the measurement. Three parallel measurements with sequential aliquots were carried out.

The surface charge was also verified using an indicator method with cationic methylene blue $[C_{16}H_{18}ClN_3S]H^+$ and the anionic eosin $[C_{20}H_6O_5Br_4]^{2-}$ dyes (CosmoKhim, Russia) suspending 0.2 g of the adsorbent powder in 50 mL of the dye solution containing from 0 to 1.6 mg L^{-1} of the dye. The optical density measured in 2 h in the centrifuged solution at 670 and 490 nm, respectively, showed a substantial adsorption of methylene blue and negligible one of eosin. Under the experimental conditions, the adsorption of methylene blue reached 0.80 and 0.62 mg g^{-1} at the vermiculite concrete- and aerocrete-supported adsorbents at the highest dye concentration.

2.3. Calculations

Calculations applied in the study are given by Frolov [38]. The removal rate and the adsorption capacity may be obtained from equilibrium binding data according to Eq. (1) and (2):

$$R = \frac{C_0 - C_e}{C_0} \times 100\%$$
(1)

$$Q = \frac{(C_0 - C_e)V}{W} \tag{2}$$

where *R* represents the removal rate, %; C_0 and C_e are the initial and equilibrium concentrations of adsorbate, respectively, mg L⁻¹; *Q* is the adsorption capacity, mg g⁻¹; *V* is the volume of the solution sample, L; *W* is the mass of used adsorbents, g.

The linear form of the pseudo-first-order rate description is given in Eq. (3):

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \tag{3}$$

where k_1 is the rate constant of the pseudo-first-order adsorption, min⁻¹; Q_e and Q_t are the adsorption capacities at the equilibrium and at the time *t*, respectively, mg g⁻¹. The rate constants k_1 , Q_e , and correlation coefficients R^2 are calculated using the slope and intercept of plots of $\ln(Q_e \cdot Q_t)$ versus *t*.

The pseudo-second-order rate expression is linearly expressed as Eq. (4):

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \tag{4}$$

where k_2 is the rate constant of the pseudo-second-order adsorption, g mg⁻¹ min⁻¹. The rate constants k_2 , Q_e , and correlation coefficients R^2 are calculated from the linear plots of t/Q_t versus t.

The linearized forms of Langmuir and Freundlich isotherms are expressed by Eq. (5) and (6), respectively:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{max}} + \frac{1}{Q_{max}b}$$
(5)

$$\ln Q_e = \frac{1}{n} \ln C_e + \ln K_F \tag{6}$$

where C_e is the equilibrium concentration of ions in the solution, mg L⁻¹, Q_e is the adsorption capacity at equilibrium, mg g⁻¹, Q_{max} is the maximum amount of adsorption, mg g⁻¹, *b* is the adsorption equilibrium constant, L mg⁻¹. K_F is the constant representing the adsorption capacity and *n* is the constant depicting the adsorption intensity.

The standard Gibbs free energy change ΔG° (kJ mol⁻¹), standard enthalpy change ΔH° (kJ mol⁻¹), and standard entropy change ΔS° (J mol⁻¹ K⁻¹) are calculated using the following equations:

$$K_0 = \frac{C_s}{C_e} \tag{7}$$

$$\Delta G^0 = -RT \ln K_0 \tag{8}$$

$$\ln K_0 = -\frac{\Delta H^0}{R} \times \frac{1}{T} + \frac{\Delta S^0}{R}$$
⁽⁹⁾

where *R* is the universal gas constant, 8.314×10^{-3} kJ mol⁻¹ K⁻¹; *T* is the absolute temperature, K; K_0 is the thermodynamic equilibrium constant; C_s and C_e are the concentration adsorbed on adsorbents and in solution at the adsorption equilibrium, respectively, mg L⁻¹.

3. Results and discussion

3.1. Physicochemical characteristics of the adsorbents

The results of surface analysis of cellular concretes and the ferric oxyhydroxide containing adsorbents are given in Table 1. One can see the attachment of ferric oxyhydroxide to the cellular concretes resulting in substantially increased contact surface determined by the porous

| Table 1 | | | | | |
|------------|-----|-----|-----------|----------|------------|
| Adsorbents | and | the | adsorbent | supports | parameters |

| Parameter | Adsorbent and support specimens | | | | |
|---|---------------------------------|---------------------------|------------------------------|---------------------------|--|
| | Aerocrete (AC) | AC-Ferric oxyhydroxide | Vermiculite concrete (VC) | VC-Ferric oxyhydroxide | |
| Iron content, mg g ^{-1} | 5.0 | 200.0 | 3.0 | 180.0 | |
| Contact surface area, m ² g ⁻¹ | 9.8 | 177.0 | 12.4 | 188.0 | |
| Pore volume, cm ³ g ⁻¹ | 0.004 | 0.059 | 0.005 | 0.081 | |

structure of attached oxyhydroxide. The order of magnitude increased volume of pores is explained by the attachment of porous oxyhydroxide to inner and outer surfaces of the macro-pores of the cellular concrete supports.

The SEM-images of the adsorbent supports and the ferric oxyhydroxide-modified adsorbents are given in Fig. 1. One can see the unmodified vermiculite concrete surface built of hexagonal grains with axial plane size of 100–350 nm (Fig. 1a). Modification of the surface results in its smoothing, the well-defined structure is lost. Instead, variably sized particles of 20–50 nm aggregated to 50–350 nm formations are seen at the surface (Fig. 1b). The aerocrete surface consists mainly of 200–500 nm grains and partially of the crystals of prolate form sized from 200 to 1200 nm as seen in Fig. 1c. The application of ferric oxyhydroxide results in the planarization of the surface covered with particles of 40–200 nm (Fig. 1d).

Manufacturing of the adsorbents foresees their drying after impregnation, rinsing and drainage, which, however, has to be conducted at a temperature low enough to avoid transformation of ferric oxyhydroxide to oxides showing substantially lower adsorption capacities [39]. The FT-IR-spectra of ferric-impregnated cellular concretes (not shown) contain the bands corresponding to FeOOH at 485 cm^{-1} and FeOOH•nH₂O at 700, 1030 and 1650 cm⁻¹ [37]. Thermogravimetric analysis of both adsorbents, ferric oxyhydroxide containing vermiculite concrete and aerocrete (thermogravimetric graphs are not shown), showed the first endothermic effect between 50 and 200 °C. This is determined by the loss of physically bonded water at the temperature from 50 to 150 °C, which may be considered as an interval safe for the adsorbents drying, and the chemically combined water above 150 °C. which also includes the dehydration of goethite FeOOH and its transformation to γ - and α -hematite Fe₂O₃. Such transformation is followed by a small exothermic effect observed in the present study from 225 to 230 to 300–335 °C, which is explained by the crystallization of hematite [37]. Other thermal effects indicated recrystallization of dehydrated calcium hydro-aluminates within the temperature interval from 456 to 570 °C, polymorph transformation of quartz from its β - to α - form at 570 °C, and dehydration of calcium hydro-silicates of tobermorite group (5CaO.5H₂O) at temperatures from 600 to 720 °C [37].

Both adsorbent specimens were tested for elution of ions in bi-distilled water as described in 2.2.2, see Table 2. The results were compared to the sanitary standards of drinking water applied in Russian Federation [40]. One can see that concentrations of all elements were below or equal to (chromium) the maximum permissible concentrations indicating the adsorbents' safety in respect of the secondary pollution.

The surface charge of the ferric oxyhydroxide-modified adsorbents comprised -15.7 and -14.2 mV for the vermiculite concrete- and aerocrete-supported adsorbents, respectively. The negative surface charge explains the difference in adsorption capacities and kinetics of arsenic anions and heavy metals cations. Together with the difference in adsorbents contact surface, the minor difference in the adsorption capacities of the adsorbents under the scope is also explained reasonably with the difference in the surface charge (see 3.3.4).

3.2. Impregnation of adsorbents with ferric oxyhydroxide and the effect of its quantity

The concentration of ferric chloride of 132 g L^{-1} in the soaking solution was established to be the optimum for the support surface coverage in the series of preliminary experiments (Fig. 2). Higher concentrations of ferric chloride resulted, apart from the moderate growth in iron content at the concrete support surface, in precipitation of the ferric oxyhydroxide flocks separate from the concrete supports thus deteriorating hydrodynamic properties of the adsorbent.

The amounts of adsorbed arsenate and arsenite were followed in their dependence on the ferric oxyhydroxide coverage (Fig. 3). The dependence of arsenite and arsenate adsorption capacity on the ferric oxyhydroxide surface concentration at both supports showed a



Fig. 1. SEM-images of a) vermiculite concrete (VC), b) VC-ferric oxyhydroxide, c) aerocrete (AC), d) AC-Ferric oxyhydroxide.

 Table 2

 Aqueous elution of elements from the adsorbents.

| Element | Concentration, mg L^{-1} | | | | |
|---------|----------------------------|---------------------------|------------------------|------------------------|--|
| | Bi-distilled water | VC-supported adsorbent | AC-supported adsorbent | Permissible maximum | |
| Al | < 0.01 | < 0.01 | < 0.01 | 0.5 | |
| Ca | 0.15 ± 0.01 | 8.2 ± 0.1 | 5.9 ± 0.1 | 100 | |
| Cr | < 0.001 | 0.05 ± 0.01 | 0.03 ± 0.01 | 0.05 | |
| Fe | 0.013 ± 0.01 | 0.09 ± 0.01 | $0.06~\pm~0.01$ | 0.3 | |
| K | < 0.05 | 0.16 ± 0.05 | $0.09~\pm~0.05$ | 12 | |
| Mg | < 0.05 | 1.9 ± 0.05 | 0.77 ± 0.05 | 50 | |
| Mn | < 0.001 | 0.002 ± 0.001 | < 0.001 | 0.1 | |
| Na | 0.55 ± 0.05 | 2.1 ± 0.05 | $0.90~\pm~0.05$ | 200 | |
| Si | $0.07~\pm~0.01$ | $0.19~\pm~0.01$ | $0.17~\pm~0.01$ | 10 | |

substantial growth until the iron content of about 150 mg g⁻¹. At the starting aqueous arsenic concentration of 20 mg L⁻¹, the maximum adsorption capacity reached about 11 mg g⁻¹ at the aerocrete-supported adsorbent, and about 12 mg g⁻¹ at the one supported with vermiculite concrete containing 150 mg g⁻¹ of iron. The minor difference in adsorption capacities of the adsorbents may be explained by the somewhat larger contact surface and the pores volume of the adsorbent supported by vermiculite concrete (Table 1). Above that iron content, no more than additional 1 mg g⁻¹ improvement of adsorption capacity was observed with the increasing iron content. The saturation of adsorption capacity at 150 mg g⁻¹ may be explained by complete occupation of the support surface with ferric oxyhydroxide with no particular increase in contact surface area at iron contents above that. Further studies were conducted with the adsorbents containing 180 and



• OVermiculite concrete ● Aerocrete

Fig. 2. Dependence of iron content at the adsorbent surface on the ferric chloride concentration in the soaking solution.

 200 mg g^{-1} of iron (see Table 1).

The dependence of adsorption capacity on the iron content in respect to heavy metals was verified in experimental tests with Pb^{2+} cation. The iron content close to 180 mg g⁻¹ at both, the vermiculite concrete- and the aerocrete-supported adsorbent showed the limits above which, similarly to the arsenic anions, the adsorbed amount of lead did not increase. This observation justifies the usage of the chosen adsorbents (Table 1) for further studies in respect to the heavy metals adsorption.



Fig. 3. Dependence of As adsorption on the content of Fe³⁺ in impregnated vermiculite concrete (left) and aerocrete (right) supported adsorbents: As starting concentration 20 mg L⁻¹, pH 6.5 to 7.2, adsorbent dose 0.2 g in 100 mL.

3.3. Adsorption kinetics and capacity

3.3.1. Adsorption kinetics

To determine the time sufficient for the adsorption equilibrium, the static experiments with arsenate were carried out as described in 2.2.1 with variable time of exposing. For the first 0.5 h of adsorption the surface concentration of arsenate reached about 80% of its maximum, whereas the time of reaching equilibrium concentration at 13.8 mg g⁻¹ equalled 2.5 h. Further adsorption experiments were carried out with this time. Similarly, the time sufficient for the adsorption of the heavy metal ions was found to be 2 h, which was used for the adsorption isotherms.

The kinetics of arsenate adsorption at the adsorbent supported with vermiculite concrete was tested as described in 2.2.1 and analysed using kinetic models of pseudo-first and pseudo-second order (see 2.3). Analogously, the adsorption kinetics for the heavy metals was analysed in respect to the pseudo-first and pseudo-second orders, and the results were brought together to Table 3. One can see a substantial difference in the adsorption rate constants for the metal cations and arsenate explained by the negative charge of the adsorbent surface (see 3.1).

The comparison of kinetic descriptions indicates better approximation of the model of pseudo-second order with its correlation exceeding 0.999. This brings to the assumption that the adsorption rate is determined not only by the rate of diffusion of adsorbate, but also by the rate of chemical reaction between the adsorbate and the adsorbent materials, making the chemical sorption through sharing the electrons between the adsorbent and metal ions the rate-limiting step [41,42]. The chemical sorption character was further proved in the IR reflection spectra (see 3.3.7). The equilibrium adsorption capacity derived from the pseudo-second order kinetic equation is also closer to the practical values than the pseudo-first order one.

3.3.2. Effect of pH on the heavy metals adsorption

The solution pH is a factor controlling the removal of ions from aqueous solutions affecting the surface charge of the adsorbent as well as the degree of ionization and speciation of the heavy metals in the solution [38,43–45]. In order to prevent the precipitation of heavy



Fig. 4. Effect of pH on the adsorption of Cd^{2+} , Cu^{2+} and Pb^{2+} onto the ferric oxyhydroxide impregnated vermiculite concrete adsorbent: initial cation concentration 10 mg L⁻¹, adsorbent dose 0.7 g L⁻¹, temperature 25 °C, contact time 2 h.

metal ions, the effect of pH on the removal of cations was studied in a pH range from 2.0 to 5.0. One can see the improved adsorption performance in respect to all three metals at pH closer to neutral (Fig. 4), similar to other adsorbents [41,46,47].

Poor adsorption at low pH is explained by protonation of adsorption sites and a net positive charge of the surface. The observed difference in removal rate of different metal ions at low pH could be explained by the difference in binding between the adsorbent functional groups and the metal ions dependent on the charges of the metal ions and the adsorbent surface, and the extent of metal ion hydrolysis [48]. At pH 5.0, however, the difference in adsorption capacity practically vanished. The pH of 5.0 was used in further studies.

Adsorption of arsenic anions was studied in neutral solutions only sufficient for the potable water needs, pH impact was not studied since exfoliated vermiculite and cement-based adsorbents' properties were studied previously, showing good adsorption of arsenate anions from aqueous solutions of wide range of pH [10,25].

Certain interest in adsorption of metallic cations is paid to the competitive adsorption of heavy metals under consideration to estimate

Table 3

Kinetic parameters for the adsorption of heavy metal cations and arsenic anions onto the vermiculite concrete in the single-element system.

| Ions | $Q_{e,exp}$, mg g ⁻¹ | Pseudo-first-order | Pseudo-first-order model | | Pseudo-second-order | model | |
|--------------------|----------------------------------|--------------------|--------------------------|--------|---|-------------------|-------|
| | | k_1, \min^{-1} | $Q_{e,cal}$ R^2 | | k_2 | $Q_{e,cal}$ | R^2 |
| | | | ${ m mg~g}^{-1}$ | | $\mathrm{g}\mathrm{mg}^{-1}\mathrm{min}^{-1}$ | ${\rm mg~g}^{-1}$ | |
| Cd ²⁺ | 12.90 | 0.0367 | 3.076 | 0.8617 | 0.0498 | 13.006 | 1.0 |
| Cu ²⁺ | 13.34 | 0.0519 | 1.005 | 0.7003 | 0.240 | 13.362 | 1.0 |
| Pb ²⁺ | 13.75 | 0.0397 | 0.667 | 0.9391 | 0.299 | 13.761 | 1.0 |
| AsO4 ³⁻ | 13.83 | 0.0239 | 10.06 | 0.9926 | 0.0029 | 15.75 | 1.0 |





Fig. 5. Effect of pH on the simultaneous adsorption of Cd^{2+} , Cu^{2+} and Pb^{2+} onto the ferric oxyhydroxide-impregnated vermiculite concrete adsorbent in the polymetallic solution: initial cation concentrations 10 mg L⁻¹, adsorbent dose 0.7 g L⁻¹, temperature 25 °C, contact time 2 h.

their mutual influence. The impact of pH was studied under conditions similar to the ones applied to the single-metal adsorption: the mixture of cations containing 10 mg L⁻¹ of each metal cation, Cd^{2+} , Cu^{2+} and Pb^{2+} , was brought to the equilibrium with the vermiculite concrete-supported adsorbent within 2 h at various pH, the results are shown in Fig. 5. One can see that, expectedly, adsorption, poor in strongly acidic solution, was improved with the growing pH. Lead cations won the competition, being completely removed at pH 5.0 unlike cadmium: the presence of competing lead and copper cations substantially interfered with cadmium adsorption.

3.3.3. Effect of temperature

The mechanism of adsorption is characterized through the changes in thermodynamic quantities, the Gibbs free energy ΔG^0 , enthalpy ΔH^0 and entropy ΔS^0 , as described in Eqs. (8) and (9) (see 2.3). To determine these quantities, the adsorption experiments at temperatures 15, 25 and 35 °C were carried out with solutions containing 10 mg L⁻¹ of metallic cations at the adsorbent concentration of 0.7 g L⁻¹ (see 2.2.1). The values of ΔH^0 and ΔS^0 were calculated from the slope and intercept of a linear plot of ln K_0 versus 1/T, respectively (Figure not shown).

Table 4 presents the thermodynamic parameters of heavy metal ions adsorption. Negative values of ΔG^0 indicate spontaneous adsorption with the degree of spontaneity increasing with temperature. The positive ΔH^0 confirm the endothermic nature of adsorption. The positive ΔS^0 reflects the high affinity of the adsorbents towards Cd^{2+} , Cu^{2+} and Pb^{2+} .

Adsorption of arsenate was characterized analogously (see 2.2.1) obtaining the adsorption activation energies ΔH^0 as small as 16.0 and 10.2 kJ mol⁻¹ for vermiculite concrete- and aerocrete-supported adsorbents, respectively. Relatively small value of adsorption activation energy and weak dependence of the reaction rate on temperature indicate prevailing character of the ion-exchange reactions [38], i.e. the reactions fall into the field of physical adsorption characterized by the activation energy within 10 to 40 kJ mol⁻¹. Physical adsorption is nonspecific, which may be observed in adsorption of both cations and anions in the present study. Formation of practically insoluble ferric arsenate, although not quantified under the experimental conditions, provides reliable detention of the anion (see 3.3.7).

3.3.4. Effect of initial metal ion concentration and adsorption isotherms

The initial adsorbate ion concentration plays an essential role in the adsorption mechanism [49]. For the adsorption isotherm studies, the metals concentrations ranging from 10 to 200 mg L⁻¹ were contacted with the adsorbent as described in 2.2.1. As shown in Fig. 6, the increasing concentrations of metal ions result in the increased adsorption capacity of Cd²⁺, Cu²⁺ and Pb²⁺ reaching the equilibrium. The results showed that the loading capacities were in the order of

Table 4

Values of thermodynamic parameters for the adsorption of metallic cations and arsenic anions on the cellular concrete-supported ferric oxyhydroxide adsorbents.

| Adsorbate | ΔH^0 , | ΔS^0 , J | <i>Т</i> , К | Ko | ΔG^0 , | R^2 |
|--------------------------------|----------------------|-------------------|--------------|-----------|----------------------|-------|
| | kJ mol ⁻¹ | $mol^{-1} K^{-1}$ | | | kJ mol ⁻¹ | |
| Vermiculit | e concrete-sup | ported ferric oxy | hydroxide | adsorbent | | |
| Cd^{2+} | 37.51 | 157.32 | 288.15 | 26.63 | -7.86 | 0.995 |
| | | | 298.15 | 42.96 | -9.32 | |
| | | | 308.15 | 73.56 | -11.01 | |
| Cu ²⁺ | 17.55 | 99.60 | 288.15 | 106.72 | -11.19 | 0.973 |
| | | | 298.15 | 129.95 | -12.07 | |
| | | | 308.15 | 171.75 | -13.18 | |
| Pb ²⁺ | 25.64 | 132.92 | 288.15 | 201.05 | -12.71 | 0.984 |
| | | | 298.15 | 272.60 | -13.90 | |
| | | | 308.15 | 403.11 | -15.37 | |
| AsO3 ³⁻ | 14.30 | 60.26 | 293.15 | 3.98 | -3.36 | 0.996 |
| | | | 313.15 | 5.62 | -4.49 | |
| | | | 333.15 | 7.94 | -5.73 | |
| AsO4 ³⁻ | 16.60 | 69.94 | 293.15 | 5.13 | -3.99 | 0.999 |
| | | | 313.15 | 6.69 | -4.95 | |
| | | | 333.15 | 9.34 | -6.19 | |
| Aerocrete- | supported ferri | c oxyhydroxide a | adsorbent | | | |
| Cd^{2+} | 39.79 | 164.50 | 288.15 | 24.52 | -7.67 | 0.995 |
| | | | 298.15 | 40.08 | -9.15 | |
| | | | 308.15 | 72.16 | -10.96 | |
| Cu ²⁺ | 18.70 | 102.88 | 288.15 | 98.98 | -11.01 | 0.969 |
| | | | 298.15 | 118.95 | -11.85 | |
| | | | 308.15 | 164.55 | -13.07 | |
| Pb ²⁺ | 26.90 | 136.96 | 288.15 | 192.45 | -12.60 | 0.996 |
| | | | 298.15 | 269.24 | -13.87 | |
| | | | 308.15 | 399.18 | -15.35 | |
| AsO3 ³⁻ | 8.10 | 40.62 | 293.15 | 4.67 | -3.75 | 0.994 |
| | | | 313.15 | 5.89 | -4.60 | |
| | | | 333.15 | 6.91 | -5.35 | |
| AsO ₄ ³⁻ | 10.20 | 49.83 | 293.15 | 6.17 | -4.43 | 0.996 |
| • | | | 313.15 | 7.50 | -5.25 | |
| | | | 333.15 | 8.91 | -6.06 | |
| | | | | | | |



Fig. 6. Dependence of the adsorption of Cd^{2+} , Cu^{2+} and Pb^{2+} at the vermiculite concrete-supported adsorbent on the initial metal ion concentration: ferric oxyhydroxide content in the adsorbent 200 mg g⁻¹, pH 5.0, adsorbent dose 0.7 g L⁻¹, 25 °C, contact time 2 h.

 $Pb^{2+} > Cu^{2+} > Cd^{2+}$ within the studied range of initial metal ion concentrations. A higher initial metal ion concentration, providing a greater driving force overcoming the mass transfer resistance as a concentration gradient [50], enhances the adsorbed amount of metal ions.

Further, the adsorption data were obtained in terms of dependence 'equilibrium aqueous concentration – adsorption capacity' and analysed by means of linearized Langmuir and Freundlich isotherms (see 2.3). The results are summarized in Table 5. One can see that the Langmuir isotherm model with the correlation coefficient $R^2 > 0.99$ fits better to the experimental data compared to the Freundlich isotherm model. Derived from the Langmuir isotherm model, the maximum adsorption

Table 5

Isotherm parameters for the heavy metal cations and arsenic anions adsorption on the cellular concrete-supported adsorbents.

| Metal ion | $Q_{e,exp},$ | Langmuir model | | | Freundlich model | | |
|--------------------------------|-----------------|---------------------------------------|-----------------------|----------------|------------------|-------|----------------|
| | mg g | $Q_{\rm max}$, mg g ⁻¹ | b, L mg ⁻¹ | R ² | K _F | n | R ² |
| Vermiculit | e concrete-supp | orted adsorbe | nt | | | | |
| Cd^{2+} | 35.5 | 36.0 | 0.45 | 0.999 | 16.4 | 5.86 | 0.972 |
| Cu ²⁺ | 52.7 | 53.2 | 0.30 | 0.996 | 25.4 | 6.67 | 0.905 |
| Pb ²⁺ | 195.7 | 197.6 | 1.45 | 1.000 | 71.8 | 2.90 | 0.785 |
| AsO3 ³⁻ | 9.3 | 9.5 | 5.06 | 1.000 | 6.6 | 7.11 | 0.807 |
| AsO4 ³⁻ | 16.2 | 17.8 | 0.32 | 0.999 | 5.2 | 2.80 | 0.922 |
| Aerocrete- | supported adsor | bent | | | | | |
| Cd^{2+} | 28.4 | 28.7 | 0.48 | 0.998 | 14.1 | 6.12 | 0.969 |
| Cu ²⁺ | 42.0 | 42.4 | 0.39 | 0.996 | 23.0 | 7.00 | 0.900 |
| Pb ²⁺ | 155.3 | 157.0 | 1.70 | 0.999 | 65.4 | 3.08 | 0.870 |
| AsO3 ³⁻ | 7.2 | 7.3 | 9.70 | 1.000 | 6.0 | 13.09 | 0.887 |
| AsO ₄ ³⁻ | 11.5 | 12.0 | 0.76 | 1.000 | 6.2 | 5.09 | 0.916 |

capacities of Cd^{2+} , Cu^{2+} and Pb^{2+} at the vermiculite concrete-supported adsorbent were 36.0, 53.2 and 197.6 mg g⁻¹, respectively, which were closer to the experimental ones. The similar picture, although with smaller adsorption capacities, was observed with the aerocrete-supported adsorbent. The Langmuir model considers the adsorbent surface containing a single-type binding site adsorbing a single ion per binding site comprising a monolayer coverage [51,52].

The data on the heavy metals competitive adsorption, when the cations were present in aqueous solutions in equal initial concentrations, are given in Fig. 7. The Langmuir and Freundlich isotherm analysis of equilibrium adsorption capacities is shown in Table 6. One can see substantially decreased absolute adsorption capacity values compared to the single-metal solutions having the prevailing adsorption of lead cations followed by copper, and cadmium showing the smallest adsorption capacity. The isotherms appear to be better described with the Langmuir model with the correlation coefficient $R^2 > 0.99$ compared to the Freundlich model. The maximum adsorption capacities of Cd^{2+} , Cu^{2+} and Pb^{2+} at the vermiculite concrete-supported adsorbent were 7.9, 33.4 and 66.8 mg g⁻¹, respectively, being fairly close to the experimentally observed ones. Vermiculite concrete-supported adsorbent showed higher adsorption capacity than the aerocrete-supported one.

The analysis of the factors influencing the adsorption rate and strength of heavy metals cations in previous publications shows that ionic radii and, thus, their hydrated radii present the reason of selectivity together with the nature of the adsorbent, i.e. the character of the adsorption centres. The largest ionic radius of Pb^{2+} at its smallest



Fig. 7. Dependence of the adsorption of Cd^{2+} , Cu^{2+} and Pb^{2+} at the vermiculite concrete-supported adsorbent on the initial metal ion concentration in the polymetallic solution: ferric oxyhydroxide content in the adsorbent 200 mg g⁻¹, pH 5.0, adsorbent dose 0.7 g L⁻¹, 25 °C, contact time 2 h.

Table 6

Isotherm parameters for the competitive adsorption of Cd^{2+} , Cu^{2+} and Pb^{2+} onto the cellular concrete-supported adsorbents in the equal initial concentrations polymetallic solution.

| Metal ions $Q_{e,exp}$, | | Langmuir model | | | Freundlich model | | |
|--------------------------|------------------|---|------|----------------|------------------|-------|----------------|
| | nig g | $\begin{array}{l} Q_{\max}, & b, \ L \ mg \\ mg \ g^{-1} \end{array}$ | | R ² | K _F | n | R ² |
| Vermiculite | e concrete-suppo | orted adsorbe | nt | | | | |
| Cd^{2+} | 7.9 | 7.9 | 0.63 | 1.000 | 6.6 | 28.51 | 0.971 |
| Cu ²⁺ | 33.1 | 33.4 | 0.30 | 0.997 | 17.7 | 7.64 | 0.928 |
| Pb ²⁺ | 66.5 | 66.8 | 0.87 | 1.000 | 26.2 | 4.61 | 0.937 |
| Aerocrete-s | upported adsort | oent | | | | | |
| Cd^{2+} | 6.3 | 6.4 | 0.69 | 0.999 | 5.1 | 29.44 | 0.964 |
| Cu ²⁺ | 26.1 | 26.3 | 0.31 | 0.996 | 13.4 | 8.03 | 0.941 |
| Pb ²⁺ | 53.6 | 53.9 | 0.94 | 0.999 | 22.0 | 5.14 | 0.940 |

hydrated radius in the row Pb < Cu < Cd, results in its highest adsorption equilibrium constant at goethite [53]. The selectivity is not that pronounced as in the present research for the difference in the adsorbent character. Higher selectivity towards Pb²⁺ compared to Cd²⁺ adsorption was observed with the Na-montmorillonite and kaolinite clays similar in composition to the cellular concretes used in the present research as the adsorbent support. The selectivity and greater retention of Pb²⁺ over Cd²⁺ at both clays was justified by Inyang et al. [54] indicating that smaller hydrated radius of Pb²⁺ lead to a closer fit to the clay surface than cadmium ions. The sequence similar to the present research in adsorption capacity of Pb²⁺ > Cu²⁺ > Cd²⁺ as well as in quantitative ratio was observed with nitric acid activated carbon nanotubes [55].

One can see from Table 6 the maximum amounts of heavy metals cations adsorbed from the multi-cation solution yielding to the ones observed for the individual cation solutions (Table 5): the difference depends on the cation and shows the discrepancy caused by the competition. The adsorption capacity in multi-metallic solutions shown by Pb^{2+} , Cu^{2+} and Cd^{2+} was smaller than the one observed in the singlemetallic solutions for both adsorbents for 2.9, 1.6 and 4.5 times, respectively, showing high disproportion in decrease. Cadmium cation with the lowest adsorption capacity and the weakest detention predictably showed the lowest potential in competitive adsorption. Conserving in sequence the the adsorption capacity $Pb^{2+} > Cu^{2+} > Cd^{2+}$, the relative difference in the adsorption changed substantially. However, the sum molar adsorption capacity remained virtually the same, showing the molar fraction of adsorbed cations relative to the ferric oxyhydroxide molecules in the competitive adsorption comprising 28.3%, whereas individual cations adsorbed molar ratios comprised 29.2%, 25.8% and 9.0% for Pb2+, Cu2+ and Cd^{2+} , respectively.

One can see that the application of the single component isotherms to the multicomponent system is possible only qualitatively, presuming the descending order of the components' adsorption capacity. Quantitative application, however, is problematic due to the difference in competing behaviour. For example, copper ions were influenced by the competing components to a lesser extent compared to the lead and cadmium cations. Cadmium cation suffered the strongest displacement under the competing adsorption conditions.

3.3.5. Adsorption isotherms of arsenate and arsenite

Adsorption isotherms of arsenate and arsenite anions for both adsorbents are shown in Fig. 8: one can see a noticeably higher adsorption rates of arsenate and the greater capacities of vermiculite concretesupported adsorbent. The parameters of both Langmuir and Freundlich isotherms treated in their linearized forms are given in Table 4 together with heavy metal cations. The conclusion in respect to the adsorption mechanism of arsenate and arsenite is in agreement with the observations made for the adsorption of heavy metals – the adsorption better



Fig. 8. Adsorption isotherms for cellular concrete-supported ferric oxyhydroxide adsorbents in respect to aqueous arsenate and arsenite at 25 °C: ferric oxyhydroxide content in the adsorbents180 and 200 mg g⁻¹ in vermiculite concrete- and aerocrete-supported adsorbents, respectively, adsorbent dose 4.0 g L⁻¹, pH 6.5–7.2, adsorption time 2.5 h.

described with the Langmuir model follows the monolayer adsorption (see 3.3.2). The maximum adsorption capacities of arsenic anions according to the Langmuir isotherms are substantially lower than the corresponding numbers for the heavy metal cations and do not exceed 19.08 and 9.51 mg As g^{-1} for AsO₄³⁻ and AsO₃³⁻ at the vermiculite concrete-supported adsorbent, showing even smaller numbers for ferric oxyhydroxide-modified aerocrete adsorbent.

The adsorption of arsenate exceeding the one of arsenite was previously observed on the nano-sized fibrous aluminium oxide [56] and on the ferric hydroxide impregnated active carbon [12]. The observation was explained by much smaller dissociation degree of arsenous acid ($pK_1 = 9.2$) compared to the arsenic one ($pK_1 = 2.2$) [57], which makes arsenite being mostly non-dissociated in neutral aqueous media and, thus, adsorbed mostly by non-ionic hydrogen bonds, whereas arsenate is mostly adsorbed as negatively charged anion. The difference in adsorption capacity of two arsenic species points to the preliminary oxidation of arsenite to arsenate potentially beneficial for arsenic removal. Such benefit is also observed in competing adsorption of both species. The binary arsenate-arsenite adsorption was described in respect to the adsorption at goethite: the minor influence of arsenite to the arsenate adsorption and the major impact of the arsenate presence to the adsorption of arsenite at neutral pH range was reported [58]. This follows the trend observed with the competitive adsorption of heavy metals - the weakest adsorbate experiences the strongest negative impact of competition.

Adsorption capacities of arsenic anions substantially smaller than the ones observed in respect to the heavy metals are explained with the negative surface charge of the adsorbents, making the ion-exchange (see 3.3.3) for the positively charged heavy metals cations easier than for the negatively charged anions.

3.3.6. Adsorption capacity analysis

The comparison of adsorption capacities of adsorbents similar to the ones considered in this study is given in Table 7. The similarity consists of either cement-supported adsorbents, or ferric oxyhydroxide attached adsorbents with various supports. The analysis may not be considered as quantitatively correct for different and often approximately known densities of adsorbents, when the adsorption capacity is given per unit of the adsorbent mass: the calculation relative to the adsorbent contact surface is often problematic for the lack of data on the latter.

One can see that the aerocrete- and vermiculite concrete-supported ferric oxyhydroxide adsorbents showed moderate adsorption capacity in respect of arsenate and arsenite, when compared to iron-containing activated carbon adsorbents (Tables 3 and 6), which may be explained most of all by the different densities of the supports. The adsorption capacities in respect of metals, however, were shown in a good correspondence with the ones observed with vermiculite and its compositions regardless only 20% wt. of vermiculite content in the studied vermiculite concrete-supported adsorbent, demonstrating the role of ferric oxyhydroxide applied in the study. Higher adsorption capacities shown by the cement-containing sludge are compromised by a weak detention of arsenate resulting in arsenic leaching in concentrations from 0.3 to 1.2 mg L^{-1} [10] an order of magnitude exceeding the maximum permissible concentration for drinking water [40] Table 7.

3.3.7. Desorption

The desorption experiments conducted as described in 2.2.2, showed the amount of desorbed arsenate not exceeding 0.01% of adsorbed quantity thus making the arsenic concentration not exceeding 0.05 or 0.01 mg L^{-1} , the maximum permissible limit for drinking water for Russia and China, respectively [40,63]. The concentrations of heavy metals under consideration comprised 0.01 and 0.08 mg L^{-1} for cadmium and copper, respectively. Lead showed desorption below the limit of its detection with the used instrument, i.e. 0.001 mg L^{-1} , which is far below the drinking water limit of 0.03 mg L^{-1} adopted in Russia [40] and 0.01 mg L^{-1} in China [67]. One can see that the heavy metals under consideration in their leaching do not logically follow their adsorption pattern: the best adsorbed lead is practically not emitted by the adsorbent, although the weakly adsorbed cadmium is lost in amounts smaller than better adsorbed copper. For copper with its drinking water safety limit of 1.0 mg L^{-1} , the leaching from the saturated vermiculite concrete-supported adsorbent, however, does not represent a hazard. Cadmium was desorbed to the slightly acidic water (pH 5.5) in concentration exceeding the limit for drinking water of 0.001 mg L^{-1} [67]. The standard of China for the surface waters used for agricultural purposes of 0.01 mg L^{-1} [68] is, however, satisfied, as well as the standard for integrated wastewater discharge of 0.1 mg L^{-1} [69].

A good retention of arsenate is explained by the chemisorption reaction between arsenate anion and ferric cation at the adsorbent surface, in which ferric arsenate is formed. For this, the IR-spectra of scattered reflection were obtained (Fig. 9). One can see the characteristic peaks at the aerocrete-supported adsorbent surface induced by ferric arsenate at 460–480 and 860 cm⁻¹ [70,71]. Ferric arsenate is known to be poorly soluble having the solubility product as low as 1×10^{-21} [72].

3.4. Adsorption test with the galvanic wastewater

An adsorption test with the wastewater of galvanic production was undertaken using a flow-through column as described in 2.2.4. The wastewater with a trace content of heavy metals left dissolved after the lime application was filtered through a layer of vermiculite concretesupported adsorbent. Concentrations of metals in the filtrate showed good removal of metals after treatment of 250 L of the wastewater (Table 8). One can see that at the adsorbed amounts below the adsorption capacity (Table 3) the removal rate is sufficiently high to provide the wastewater discharge to a water body of fishery purpose at the required sanitary level stricter than the one of drinking water [73]. The pH of filtrate remained unaltered at pH 8.2–8.3.

4. Conclusions

The specimens of aerocrete- and vermiculite concrete-supported ferric oxyhydroxide adsorbent materials obtained and characterized in experimental research show the adsorption capacity exceeding the activated carbon- and vermiculite-based adsorbents in respect to heavy metal cations. Arsenic anions are adsorbed in amounts comparable to the ones of activated carbon-supported adsorbents. The obtained adsorbents exhibit the following advantages:

Table 7

-

Adsorption capacities of concrete-supported and iron oxyhydroxide impregnated adsorbents.

| Adsorbed axionsUSecondS | Adsorbent type | Adsorbent | Pollutant | Maximum adsorption capacity, mg $\rm g^{-1}$ | Source of data |
|--|--------------------------|--|------------------|--|----------------|
| Cement-based adsorbents Concrete sludge Borate 50.0 [6] Waste cement pre-heated 34.7 10.0 Concrete sludge pre-heated 197.0 20.0 Concrete sludge pre-heated 197.0 20.0 Concrete sludge pre-heated 2.83.12.9 20.0 Concrete sludge pre-heated 2.83.12.7 20.0 Concrete sludge pre-heated 2.83.0 [5] Concrete sludge pre-heated 2.83.0 [5] Concrete sludge pre-heated 2.73.10 [1] Concrete sludge pre-heated 7.0 [1] Concrete sludge pre-heated Arsenate 3.50 [2] Dry residue of acid mine drainage 7.0 [2] [2] Dry residue of acid mine drainage 7.0 [2] [2] Pre-ir-condified peanut straw biochar Arsenate 38.39.2 [3] Ferri-condified resonus brochar Arsenate 60.4 [3] Polycaryonitrile-based fibrous sorbents Arsenate 60.4 [3] Activated carbon composites Arsenate 2.34 [6] Verniculite adsorbents Exfoliated verniculite Ca ² -4 3.5 [2] Verniculite adsorbents Exfoliated verniculite Ca ² -4 3.5 | Adsorbed anions | | | | |
| Mate cement pre-heated 28.3 [19] Wate cement pre-heated 347 347 Concrete sludge pre-heated 15.0 201 Aerocret Floride 288-12.9 201 Concret sludge norbars Phosphate 31-50 159 Concret sludge Phosphate 31-50 159 Iron-modified adsorbents Cement-based mortars Phosphate 31-50 180 Iron-modified adsorbents Cement-based mortars Phosphate 31-50 180 Iron-modified adsorbents Cement-based mortars Phosphate 32-51.3 180 Iron-impregnated activated carbon Arsenate 38.7 180 180 Iron-impregnated activated carbon Xarenate 37.7 181 191 Fervic-modified pennutstraw biochar Xarenate 37.4 161 161 Fervic-modified pennutstraw biochar Xarenate 37.4 161 161 Fervic-traved carbon composites Arsenate 37.4 161 161 161 Fervic-tr | Cement-based adsorbents | Concrete sludge | Borate | 50.0 | [8] |
| Mate cement pre-heated 1670 Concrete sludge pre-heated 1750 Aerocrete Phosphate 88-12.9 201 Aerocrete-based mottras Phosphate 12.73.0.0 [1] Concret sludge pre-heated Phosphate 83.0.1 [5] Concret sludge activated activated activated activated Phosphate 8.30.1 [1] Iron-impregnated activated activated activate Areance 8.8-93.2 [1] Herric-modified peanut straw biochar Areance 8.8-93.2 [1] Activated carbon Areance 8.8-93.2 [1] Areinet carbon Areance 8.8-93.2 [1] Activate carbon composites Areance 8.4 [2] Activate carbon composites Areance 8.4 [3] Areance 2.34 [3] [3] [3] | | Waste cement | Arsenate | 28.3 | [10] |
| Concrete sludge pre-heated 175.0 Accorete Fluoride 288-12.9 (20) Accorete Phosphate 31-50.1 [5] Concrete sludge pre-heated Phosphate 31-50.3 [6] Iron-modified adsorbents Gement-bourd pellets of acid mine drainage Phosphate 33.0 [18] Iron-impregnated activated carbon Arsenate 33.6 [12] [16] Iron-impregnated activated carbon Arsenate 33.7 [16] [16] Perrie-modified peanut straw biochar Arsenate 3.7 [16] [16] Feroi-modified rice straw biochar Arsenate 3.34 [16] [16] Feo/-Activated carbon | | Waste cement pre-heated | | 34.7 | |
| Concret sludge pre-heated150AerocretaPhorphate28-12.9AerocretaPhorphate28-12.9AerocretaPhorphate28-12.9Concreta sludgePhorphate1-50Concreta sludgePhorphate31-50Concreta sludgePhorphate31-50Concreta sludgePhorphate31-50Concreta sludgePhorphate31-50Concreta sludgePhorphate31-50Concreta sludgeArenate31-50Price-Hound Pelleta cald nine drainage7011Price-Hound PelletaArenate33-7012Price-Hound PelletaArenate33-7013Price-Hound PelletaArenate33-7013Price-Hound PelletaArenate33-7013Price-Hound PelletaArenate31-5013Price-Hound PelletaArenate31-5013Price-Hound PelletaArenate31-5013Price-Hound PelletaArenate13-5013Price-Hound PelletaArenate13-5013Price-Hound PelletaPrice-Hound Pelleta1313Price-Hound PelletaPrice-Hound Pelleta1313Price-Hound PelletaPrice-Hound Pelleta1313Price-Hound PelletaPrice-Hound Pelleta1313Price-Hound PelletaPrice-Hound Pelleta1313Price-Hound PelletaPrice-Hound Pelleta1313Price-Hound PelletaPrice-Houn | | Concrete sludge | | 167.0 | |
| AcrocreteFluoride288–12.9(20)Cement-based mortarsPhosphate12.7-31.0(11)Coment-based mortarsPhosphate31-50(59)Coment-bound pellets of acid mine drainagePhosphate83.0(18)Dry residue of acid mine drainagePhosphate83.6-51.3(12)Dry residue of acid mine drainageArsenate83.6-51.3(12)Ferric-modified peanut straw biocharArsenate83.8-39.2(15)Ferric-modified rice straw biocharArsenate60.4(13)Fe/C/Activated carbonArsenate60.4(13)Fe/C/Activated carbonArsenate2.34(16)FO/Activated carbonArsenate8.9(16)FO/Activated carbonArsenate1.9(17)FO/Activated carbonArsenate2.34(16)FO/Activated carbonCd ² +37.3(61)FO/Activated carbonCd ² +37.3(61)Formactivated carbon compositesNi ² +25.3(28)Adsorbed heavy metalsExfoliated verniculiteCd ² +5.9(21)Verniculite adsorbentsFa ² +3.24(23)(21)Foliated verniculiteCd ² +5.5(23)(21)Atural verniculiteCd ² +5.5(23)(21)Foliated verniculiteCd ² +5.5(23)(21)Foliated verniculiteCd ² +5.5(63)(21)Foliated verniculiteFa ² +3.7(61)(61 | | Concrete sludge pre-heated | | 175.0 | |
| Cement-based mortarsPhosphate12.7-31.0[1]Concrete sludgePhosphate31-50[5]Concrete sludgePhosphate31-50[8]Dry residue of acid mine drainage707070Urresidue of acid mine drainage707070Urresidue of acid mine drainage88-630.27070Fori-comingenated activated carbonAscenate38.6-51.33070Ferri-condified restraw biocharAscenate30.7[1]70Ferri-condified restraw biocharAscenate60.4[1]70Ferri-condified restraw biocharAscenate60.4[1]70Ferri-condified restraw biocharAscenate23.4[6]60Ferri-condified restraw biocharAscenate23.4[6]60Ferri-condified restraw biocharAscenate23.4[6][6]Ferri-condified restraw biocharAscenate8.9[6][6]Ferri-condified restraw biocharAscenate8.9[6][6]Activated carbon compositesAscenate8.9[6][6]Astore transcriptioneCal ² 6.4[6][6][6]Astore transcriptione1010[6][6][6]Astore transcriptione1010[6][6][6]Astore transcriptione1010[6][6][6]Astore transcriptione1010[6][6][6]Astore transcriptione< | | Aerocrete | Fluoride | 2.88-12.9 | [20] |
| Iron-modified adsorbentsConcrete sludgePhosphate31-50[59]Iron-more caid mine drainage7.07.0Iron-impregnated activated carbonArsenate345-51.3[12]Iron-impregnated activated carbonArsenate38.39.215]Ferric-modified peanut straw biocharArsenate3.37[15]Ferric-modified rice straw biocharArsenate2.016]Ferric-modified rice straw biocharArsenate7.416]Ferric-modified rice straw biocharArsenate2.34[6]Polyacrylouritile-based fibrous sorbentsArsenate2.34[6]Polyacrylouritile-based fibrous sorbentsArsenate2.34[6]Polyacrylouritile-based fibrous sorbentsArsenate2.34[6]Activated carbon compositesArsenate2.34[6]Activated carbon compositesCla ² +3.73[6]Activate darbon compositesCla ² +2.34[6]Activate darbon compositesNi ² +2.34[2]Activate darbon compositesNi ² +3.73[2]Atural vermiculiteNi ² +3.74[2]Atural vermiculiteNi ² +5.9[2]Atural vermiculiteCla ² +5.2[2]Atural vermiculiteCla ² +5.2[2]Atural vermiculiteCla ² +5.2[2]Atural vermiculiteCla ² +3.7[6]Atural vermiculiteCla ² +5.2[6]Atural vermiculite <td></td> <td>Cement-based mortars</td> <td>Phosphate</td> <td>12.7-31.0</td> <td>[11]</td> | | Cement-based mortars | Phosphate | 12.7-31.0 | [11] |
| Iron-modified adsorbents Cement-bound pellets of acid mine drainage Phosphate 8.0 [18] Dry residue of acid mine drainage 7.0 7.0 Iron-impregnated activated carbon Arsenite 3.8,6-51.3 [12] Arsenite 3.8,6-39.2 7.0 7.0 Ferric-modified restraw biochar Arsenate 3.7 [13] Ferric-modified restraw biochar 7.0 7.0 7.0 Activated carbon Arsenate 3.7 [13] Ferric-modified restraw biochar 7.0 7.0 7.0 Activated carbon Arsenate 0.4 [13] Ferric-modified restraw biochar 7.0 7.0 7.0 Activated carbon Arsenate 0.4 [13] Ferric-modified restraw biochar Arsenate 0.34 [16] Iron-activated carbon composites Arsenate 3.7 6.1 Iron-activated carbon composites Arsenate 18.9 6.1 Adsorbed heavy metals Kefolated vermiculite Materia 7.3 [16] Katorbed vermiculite Vermiculite 10 ² 10.3 [16] Arzenat Iron-activated carbon composite 10 ² 10.3 [16] Arzenat Iron-acti | | Concrete sludge | Phosphate | 31–50 | [59] |
| Pry residue of acid mine drainage 71.0 Iron-impregated activated carbon Arsenite 38.6-51.3 [12] Arsenite 38.8-39.2 [15] Ferric-modified peant straw biochar 70.0 [15] Ferric-modified rice straw biochar 70.0 [15] Ferric-modified rice straw biochar 70.0 [16] Ferric-modified restraw biochar 71.0 [16] Adsorbed heavy metal [16] [16] [16] Adsorbed restraw biochar [16] [16] [16] Adsorbed restraw biochar [16] [16] | Iron-modified adsorbents | Cement-bound pellets of acid mine drainage | Phosphate | 83.0 | [18] |
| Iron-impregnated activated carbonArsenate43.6–51.3[12]ArseniteArsenite38–39.215]Ferric-modified peanut straw biochar37.7[15]Ferric-modified rice straw biochar70.016]Activated carbonArsenate60.4[16]Polyacrylonitrile-based fibrous sorbentsArsenate2.34[16]Digacrylonitrile-based fibrous sorbentsArsenate2.34[16]Adsorbed heavy metalsKefoliated vermiculiteCd ²⁺⁴ 3.7.3[6]Adsorbed heavy metalsKefoliated vermiculiteCd ²⁺⁴ 3.7.3[6]Adsorbed heavy metalsKefoliated vermiculiteNi ²⁺ 2.64[2]Adsorbed heavy metalsKefoliated vermiculiteCd ²⁺⁴ 3.7.3[6]Adsorbed heavy metalsKefoliated vermiculiteNi ²⁺ 2.64[2]Adsorbed heavy metalsKefoliated vermiculiteCd ²⁺⁴ 3.7.4[2]Adsorbed heavy metalsKefoliated vermiculiteNi ²⁺ 2.64[2]Adsorbed heavy metalCd ²⁺⁴ 5.5[2][2]Adsorbed heavy metalNi ²⁺ 5.5[2][2]Adsorbed heavy metalCd ²⁺⁴ 5.5[2][2]Adsorbed heavy metalCd ²⁺⁴ 5.5[3][3]Adsorbed heavy metalCd ²⁺⁴ 5.5[3][4]Adsorbed heavy metalCd ²⁺⁴ 5.5[3][4]Adsorbed heavy metalCd ²⁺⁴ 5.5[6][3]Adsorbed heavy met | | Dry residue of acid mine drainage | | 71.0 | |
| ArseniteArsenite $38.8-39.2$ Ferric-modified rice straw biocharArsenate 33.7 [5]Ferric-modified rice straw biochar 27.0 $$ | | Iron-impregnated activated carbon | Arsenate | 43.6-51.3 | [12] |
| Ferric-modified peanut straw biocharArsenate33.7[15]Ferric-modified rice straw biochar27.07.0Activated carbon7.47.4FeO/Activated carbon7.46.0Ion-activated carbon compositesArsenate2.34Orbardited carbon compositesArsenate2.34Vermiculite adsorbettsKafolated vermiculite6.1Vermiculite adsorbettsCd ²⁺ 37.3Kafolated vermiculiteCd ²⁺ 6.1Vermiculite adsorbettsKafolated vermiculite6.1Vermiculite adsorbettsKafolated vermiculite20.3Vermiculite adsorbettsKafolated vermiculite2.34Vermiculite adsorbettsKafolated vermiculite2.34Vermiculite adsorbettsKafolated vermiculite2.3Vermiculite adsorbettsKafolated vermiculite2.3Vermiculite adsorbettsKafolated vermiculite2.3Vermiculite adsorbettsS.32.3Vermiculite adsorbettsS.52.3Vermiculite adsorbettsCd ²⁺ 5.52.3Vermiculite adsorbettsCd ²⁺ 3.22.3Vermiculite adsorbettsCd ²⁺ 3.22.3Vermiculite adsorbettsS.52.32.3Vermiculite adsorbettsS.52.32.3Vermiculite adsorbettsS.52.32.3Vermiculite adsorbettsS.52.33.3Vermiculite adsorbettsS.52.33.3Vermiculite adsorbettsS.5 | | | Arsenite | 38.8–39.2 | |
| Ferric-modified rice straw biochar27.0Activate carbonSenate60.4[13]FeO/Activate carbon74.416]Polyacrylonitrile-based fibrous sorbentsArsenate3.34[16]Iron-activated carbon compositesArsenate18.9[60]Adsorbed heavy metalsCd ²⁺ 3.7.3[61]Vermiculite adsorbentsPh ²⁺ 9.64.1[70]Activate carbon compositesN ²⁺ 20.6[80]Autral vermiculiteN ²⁺ 23.4[81]Autral vermiculiteN ²⁺ 3.4[81]Autral vermiculiteN ²⁺ 3.4[81]Autral vermiculiteO ²⁺ 3.4[81]Autral vermiculiteCd ²⁺ 5.5[23]Autral vermiculiteCd ²⁺ 5.5[31]Autral vermiculiteCd ²⁺ 5.5[63]Exfoliated vermiculiteCa ²⁺ 3.6[41]Autral vermiculiteCa ²⁺ 3.6[61]Autral vermiculiteN ²⁺ 3.6[61]Autral vermiculiteN ²⁺ 3.6[63]Exfoliated vermiculiteN ²⁺ 3.7[63]Exfoliated vermiculiteN ²⁺ 3.7[61]Exfoliated vermiculiteN ²⁺ 3.6[63]Exfoliated vermiculiteN ²⁺ 3.6[63]Exfoliated vermiculiteN ²⁺ 3.6[63]Exfoliated vermiculiteN ²⁺ 3.6[65]Exfoliate vermiculiteN ²⁺ 3.6[65] | | Ferric-modified peanut straw biochar | Arsenate | 33.7 | [15] |
| Activated carbonArsenate60.4[13]Fe/Activated carbon74.416]Polyacrylonitrile-based fibrous sorbentsArsenate2.34[16]Ion-activated carbon compositesArsenate18.9[61]Adsorbed heavy metalsExfoliated verniculite Cd^{2+} 37.3[61]Verniculite adsorbentsExfoliated verniculite Cd^{2+} 0.6[61] L^{2+} 20.6[72][72][72] L^{2+} 23.4[73][62] L^{2+} 23.4[73][62] L^{2+} 19.3[62][73] L^{2+} 19.3[62][73] L^{2+} 25.5[33][34] L^{2+} 39.2[34][34] L^{2+} 39.2[34][34] L^{2+} 25.5[63]Exfoliated verniculite L^{2+} 35.5[63]Exfoliated verniculite L^{2+} 31.7[64] L^{2+} 32.6[63][63] L^{2+} 35.5[63][63] L^{2+} 15.5[63][63] L^{2+} 15.5[63][63] L^{2+} 15.5[63][63] L^{2+} 15.5[63][63] L^{2+} 15.5[63][63] L^{2+} 15.5[63][65] L^{2+} 15.5[63][65] L^{2+} 15.5[65][65] L^{2+} 15.5[65][65] $L^{$ | | Ferric-modified rice straw biochar | | 27.0 | |
| FeO/Activated carbon74.4Polyacrylonitrile-based fibrous sorbents Polyacrylonitrile-based fibrous sorbents activated carbon compositesArsenate2.34[16]Adsorbed heavy metalsKarenate8.8[60][60]Adsorbed heavy metalsExfoliated vermiculite Cd^{2+} 37.3[61]Vermiculite adsorbentsExfoliated vermiculite Cd^{2+} 37.3[61] Pb^{2+} 64.1[62][62][62] Pa^{2+} 26.3[23][62] Pa^{2+} 19.3[62][62] Pa^{2+} 19.3[62][62] Pa^{2+} 19.3[62][23] Pa^{2+} 19.3[24][24] Pa^{2+} 39.2[24][24] Pa^{2+} 25.5[63][24] Pa^{2+} 25.5[63][64] Pa^{2+} 25.5[63][64] Pa^{2+} 25.5[63][64] Pa^{2+} 10.5[65][65] Pa^{2+} <td></td> <td>Activated carbon</td> <td>Arsenate</td> <td>60.4</td> <td>[13]</td> | | Activated carbon | Arsenate | 60.4 | [13] |
| Polyacrylonitrile-based fibrous sorbents Iron-activated carbon compositesArsenate2.34[16]Adsorbed heavy metalsVermiculite adsorbentsExfoliated vermiculite Cd^{2+} 37.3[61]Pb ²⁺ 064.1 Cu^{2+} 20.6[28]Exfoliated vermiculite Cu^{2+} 23.4[28]Natural vermiculiteNi ²⁺ 23.4[62]Exfoliated vermiculite Cd^{2+} 3.4[62]Vermiculite clay mineral Cd^{2+} 5.5[23]Vermiculite clay mineral Cd^{2+} 5.6.2[24] Cq^{2+} 39.2[24][25] Cq^{3+} 25.0[63][63]Exfoliated vermiculite Ni^{2+} 3.7.7[63]Exfoliated vermiculite Ni^{2+} 3.6.1[63]Exfoliated vermiculite Ca^{2+} 3.6.1[63]Exfoliated vermiculite Ca^{2+} 3.7.7[63]Exfoliated vermiculite Ca^{2+} 3.7.7[63]Exfoliated vermiculite Ca^{2+} 3.7.7[63]Exfoliated vermiculite Ca^{2+} 3.7.7[64]Exfoliated vermiculite Ca^{2+} 3.7.7[64]Exfoliated vermiculite Ca^{2+} 3.7.7[65]Exfoliated vermiculite Ca^{2+} 3.6.3[65]Exfoliated vermiculite Ca^{2+} 3.6.3[65]Exfoliated vermiculite Ca^{2+} 3.6.3[65]Exfoliated vermiculite Ca^{2+} 3.6.3[65]< | | FeO/Activated carbon | | 74.4 | |
| Iron-activated carbon compositesArsenate18.9[60]Adsorbed heavy metalsExfoliated vermiculiteCd ² +37.3[61]Vermiculite adsorbentsExfoliated vermiculitePb ² +64.1[61]Pb ² +64.1Cu ² +20.6[28]Exfoliated vermiculiteNi ² +23.4[62][62]Natural vermiculiteNi ² +19.3[62][62]Exfoliated vermiculiteCd ² +5.9[23][61]Vermiculite clay mineralCd ² +5.6[23][24]Vermiculite clay mineralCd ² +5.0[24][26]Ca ³ +25.0[63][61][61]Exfoliated vermiculiteNi ² +3.17[63][63]Exfoliated vermiculiteZa ² +3.17[64][65]Exfoliated vermiculiteZa ² +86.3[65][65] | | Polyacrylonitrile-based fibrous sorbents | Arsenate | 2.34 | [16] |
| Adsorbed heavy metals Exfoliated vermiculite Cd^{2+} 37.3 [61] Pb^{2+} 64.1 Cu^{2+} 20.6 Lu^{2+} 20.6 20.6 Lu^{2+} 23.4 23.4 Natural vermiculite Lu^{2+} 23.4 Luc^{2+} 23.4 62.2 Luc^{2+} 23.4 62.2 Luc^{2+} 25.9 62.2 Luc^{2+} 5.9 23.2 Luc^{2+} 56.2 (24.2) Luc^{2+} 56.2 (24.2) Luc^{2+} 39.2 (Cr^{3+}) 25.0 Luc^{2+} 25.0 (63.2) (63.2) Luc^{2+} 25.0 (63.2) (65.2) $Luc^$ | | Iron-activated carbon composites | Arsenate | 18.9 | [60] |
| Address Exfoliated vermiculite Cd^{2+} 37.3 $[61]$ Vermiculite adsorbents Exfoliated vermiculite Pb^{2+} 64.1 Cu^{2+} 20.6 Exfoliated vermiculite Nt^{2+} 25.3 $[28]$ $Natural vermiculite$ Nt^{2+} 23.4 $[62]$ Exfoliated vermiculite $S.9$ $[62]$ $[62]$ Exfoliated vermiculite $S.9$ $[23]$ $[24]$ Vermiculite clay mineral Cd^{2+} 5.5 $[23]$ Vermiculite clay mineral Cd^{2+} 5.9 $[24]$ $Ntaral vermiculite Cd^{2+} 5.9 [24] Ntaral vermiculite Cd^{2+} 5.9 [24] Ntaral vermiculite clay mineral Ntara vertaral vertaral vertaral vertaral vertaral vertaral vertaral vertaral vertaral vertara$ | Adsorbed beauty metals | | | | |
| $ \begin{array}{cccccccccccccccccccccccccccccccccccc$ | Vermiculite adsorbents | Exploited vermiculite | Cd^{2+} | 27.2 | [61] |
| Cu^{2+} 20. Cu^{2+} 25.3[28] Zn^{2+} 23.4Natural vermiculiteNi ²⁺ 19.3Exfoliated vermiculite5.9Natural vermiculite Cd^{2+} 5.5Natural vermiculite Cd^{2+} 56.2Vermiculite clay mineral Cd^{2+} 39.2 Cr^{3+} 25.5[63]Exfoliated vermiculite Ni^{2+} 31.7Exfoliated vermiculite Zn^{2+} 31.7Exfoliated vermiculite Xn^{2+} 31.7Exfoliated vermiculite Zn^{2+} 31.7Exfoliated vermiculite Xn^{2+} 31.7Exfoliated vermiculite Zn^{2+} 31.7Exfoliated vermiculite Zn^{2+} 31.7Exfoliated vermiculite Zn^{2+} 31.7Exfoliated vermiculite Zn^{2+} 36.3Exfoliated vermiculite Zn^{2+} 36.3Exfoliated vermiculite Zn^{2+} 31.7Exfoliated vermiculite Zn^{2+} 31.7Exfoliated vermiculite Zn^{2+} 36.3Exfoliated vermiculite< | verificulte adsorbents | Exionated vermicunte | Db ²⁺ | 64.1 | [01] |
| Exfoliated vermiculite hi^{2+} 25.3 [28] Zn^{2+} 23.4 [62] Natural vermiculite hi^{2+} 19.3 [62] Exfoliated vermiculite 5.9 [23] Natural vermiculite Cd^{2+} 5.5 [23] Vermiculite clay mineral Cd^{2+} 56.2 [24] Zn^{2+} 39.2 [62] [62] Cr^{3+} 25.0 [63] [63] Exfoliated vermiculite Xn^{2+} 31.7 [64] Exfoliated vermiculite Zn^{2+} 31.7 [64] Zeolite-vermiculite granular composite hi^{2+} 16.5 [65] Exfoliated vermiculite Zn^{2+} 86.3 [66] | | | Cu ²⁺ | 20.6 | |
| Zn^{2+} 23.4 Natural vermiculite Ni^{2+} 19.3 [62] Exfoliated vermiculite 5.9 [23] Natural vermiculite Cd^{2+} 5.5 [23] Vermiculite clay mineral Cd^{2+} 56.2 [24] Zn^{2+} 39.2 [62] [63] Cr^{3+} 25.5 [63] Exfoliated vermiculite Zn^{2+} 31.7 [64] Zeolite-vermiculite granular composite Ni ²⁺ 16.5 [65] Exfoliated vermiculite Zn^{2+} 86.3 [66] | | Explicited vermiculite | Ni ²⁺ | 25.3 | [28] |
| Lin 25.4 Natural vermiculite Ni^{2+} 9.9 Exfoliated vermiculite 5.9 Natural vermiculite clay mineral Cd^{2+} 5.5 Vermiculite clay mineral Cd^{2+} 56.2 Cr^{3+} 39.2 Cr^{3+} 25.5 Exfoliated vermiculite Xn^{2+} 25.5 Exfoliated vermiculite Xn^{2+} 31.7 Exfoliated vermiculite granular composite Ni^{2+} 16.5 $[65]$ Exfoliated vermiculite Zn^{2+} 86.3 $[66]$ | | Exionated vermeunte | $7n^{2+}$ | 23.3 | [20] |
| Exfoliated vermiculite N1 19.5 [02] Exfoliated vermiculite 5.9 [23] Natural vermiculite Cd^{2+} 5.5 [23] Vermiculite clay mineral Cd^{2+} 56.2 [24] Zn^{2+} 39.2 [63] [63] Exfoliated vermiculite Ni^{2+} 25.0 [63] Exfoliated vermiculite Zn^{2+} 31.7 [64] Zeolite-vermiculite granular composite Ni^{2+} 16.5 [65] Exfoliated vermiculite Zn^{2+} 86.3 [66] | | Natural vermiculite | Ni ²⁺ | 10.2 | [69] |
| Natural verniculité Cd^{2+} 5.5 [23] Verniculite clay mineral Cd^{2+} 56.2 [24] Zn^{2+} 39.2 [26] [27] Cr^{3+} 25.0 [63] [63] Exfoliated verniculite Ni^{2+} 25.0 [63] Exfoliated verniculite Xn^{2+} 31.7 [64] Zeolite-verniculite granular composite Ni^{2+} 16.5 [65] Exfoliated verniculite Zn^{2+} 86.3 [66] | | Explicited vermiculite | 141 | 59 | [02] |
| Vermiculite clay mineral Cd^2 5.6.2 [24] Zn^{2+} 39.2 Cr^{3+} 25.0 Exfoliated vermiculite Ni^{2+} 25.5 [63] Exfoliated vermiculite Zn^{2+} 31.7 [64] Zeolite-vermiculite granular composite Ni^{2+} 16.5 [65] Exfoliated vermiculite Zn^{2+} 86.3 [66] | | Natural vermiculite | Cd^{2+} | 5.5 | [23] |
| Zn^{2+} 39.2 [24] Zn^{2+} 39.2 Cr^{3+} 25.0 Exfoliated vermiculite Ni^{2+} 25.5 [63] Exfoliated vermiculite Zn^{2+} 31.7 [64] Zeolite-vermiculite granular composite Ni^{2+} 16.5 [65] Exfoliated vermiculite Zn^{2+} 86.3 [66] | | Vermiculite clay mineral | Cd ²⁺ | 56.2 | [23] |
| Lin 51.2 Ct^{3+} 25.0 Exfoliated vermiculite Ni^{2+} 25.5 Exfoliated vermiculite Zn^{2+} 31.7 Zeolite-vermiculite granular composite Ni^{2+} 16.5 Exfoliated vermiculite Zn^{2+} 86.3 | | vermicunte elay mineral | $7n^{2+}$ | 30.2 | [24] |
| Exfoliated vermiculite Ni ²⁺ 25.5 [63] Exfoliated vermiculite Zn ²⁺ 31.7 [64] Zeolite-vermiculite granular composite Ni ²⁺ 16.5 [65] Exfoliated vermiculite Zn ²⁺ 86.3 [66] | | | Cr^{3+} | 25.0 | |
| Extolated verniculte 141 25.5 $[65]$ Exfoliated verniculte granular composite Xn^{2+} 31.7 $[64]$ Zeolite-verniculite granular composite Ni^{2+} 16.5 $[65]$ Exfoliated verniculite Zn^{2+} 86.3 $[66]$ | | Exploited vermiculite | Ni ²⁺ | 25.5 | [62] |
| Extended verniculte Zin^{2+} 31.7 $[04]$ Zeolite-verniculte granular compositeNi ²⁺ 16.5[65]Exfoliated verniculte Zn^{2+} 86.3[66] | | Explorated vermiculite | $7n^{2+}$ | 20.0 | [64] |
| ExplorateIn10.5[63]Exfoliated verniculite Zn^{2+} 86.3[66] | | Zeolite-vermiculite granular composite | Ni ²⁺ | 16.5 | [65] |
| | | Exfoliated vermiculite | Zn ²⁺ | 86.3 | [66] |



Fig. 9. IR-spectra of scattered reflection of the aerocrete-supported ferric oxyhydroxide adsorbent and ferric arsenate: characteristic peaks at 460–480 and 860 cm⁻¹.

- the adsorbents are produced using rejects of construction materials with the highest cost-efficiency available for disposable materials;
- the production of the adsorbent materials is simple requiring lowcost chemicals and producing no hazardous wastes;
- the developed contact surface at the big grain size of high concrete strength makes the hydrodynamics of the adsorbent bed presumably favourable;
- the adsorbents reliably detain adsorbed pollutants making the spent materials safe for landfilling: the leaching of arsenic, copper and lead meets the requirements of drinking water standards, the leaching of cadmium fits to the agricultural water use standard.

The properties of the cellular concrete-based adsorbent materials make them promising in heavy metals and arsenic abatement with safe long-term storage of spent adsorbents.

Table 8

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Adsorption performance in the galvanic production wastewater treatment: vermiculite concrete-supported adsorbent, treated wastewater volume 250 L.

| Metallic ion | Concentration prior to adsorption, mg ${\rm L}^{-1}$ | Concentration in the filtrate, mg L^{-1} | Removal rate, % | Integrated adsorbed amount, mg g^{-1} | Discharge standard, mg L ⁻¹ [73] |
|--|--|--|--|--|--|
| $\begin{array}{c} Zn^{2+} \\ Ni^{2+} \\ Cd^{2+} \\ Pb^{2+} \\ Cu^{2+} \\ Fe^{2+/3+} \end{array}$ | 0.188 0.03 0.05 0.017 0.051 2.723 | 0.0024 ND ^a ND ND 0.0001 0.057 | 98.7 > 99.7 > 99.9 > 94.1 99.8 97.9 | 0.560 0.090 0.150 0.050 0.155 8.030 | 0.01 0.01 0.005 0.006 0.001 0.1 |
| Total adsorb | ed amount, mg g $^{-1}$ | | | 9.035 | |

^a Not detected.

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