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FERRIC HYDROXIDE-BASED MEDIA FOR REMOVAL OF TOXIC ARSENIC SPECIES. KINETIC, EQUILIBRIUM AND THERMODYNAMIC STUDIES

Adsorption studies were conducted to assess the feasibility of ferric hydroxide-based material for treatment of highly arsenic-contaminated effluents. The experiments were performed in a batch adsorption regime using a synthetic aqueous solution. The contact time between arsenic ions and the adsorbent, initial concentration of arsenic in treated solution, temperature of solution and adsorbent dose had a significant effect on the adsorption performance in the system. Both the mechanism of the process involved and the rate of As(III) and As(V) adsorption were analyzed based on pseudo-first- and pseudo-second order kinetic models. The adsorption data at constant temperature were described by the Langmuir and Freundlich isotherm equation, and the theoretical adsorption capacity of ferric hydroxide was determined to be 43.75 mg/g and 44.04 mg/g for arsenic(III) and (V), respectively. The estimated thermodynamic parameters, including changes in free energy, enthalpy and entropy, revealed that the adsorption is spontaneous and endothermic under applied experimental conditions.

1. INTRODUCTION

Toxic and harmful metal(loid)s are widespread, and their discharge through air and industrial effluents or leaching from the soil by acid rain into natural waters often causes the metals' degradation. Many chemical constituents introduced in excessive amounts into the aquatic ecosystem have a detrimental effect on humans and animals. The accumulation of metal(loid) species over time in living organisms can be damaging to them [1, 2].

One of common elements belonging to the metalloid group is arsenic, widely known for its high toxicity and carcinogenicity. Outbreaks of arsenic-related poisoning have been reported in many places around the world, most notably in Bangladesh, where

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because of decades of exposure to arsenic, millions of inhabitants suffer from severe health problems [3, 4].

The presence of arsenic of natural origin in aquatic environments depends on the local geology, hydrology and geochemical characteristics of the local aquifer materials [5]. In the environment, arsenic occurs in various oxidation states (-3, 0, +3, +5). However, in natural waters, arsenic is mostly observed in the inorganic oxyanion forms of trivalent arsenite (As(III)) or pentavalent arsenate (As(V)). As the speciation of arsenic strongly depends on pH and redox potential, in a reducing environment with pH values below pK_a 9.22, neutral H_3AsO_3 will predominate. However, under oxidizing conditions, $H_2AsO_4^-$ and $HAsO_4^{2-}$ are dominant at low and high pH values, respectively [6, 7].

Anthropogenic arsenic contamination in groundwater and surface water is a by-product of, among other things, power generation plants, mining activities, paper and chemical manufacturing, wood preservation, glass production, tanneries, petrochemical factories, and herbicide and pesticide manufacturing [8]. These industrial sectors produce large volumes of hazardous waste which, apart from arsenic, may contain elevated amounts of other dangerous compounds. Therefore, ensuring appropriate treatment of industrial waste before recycling or partial discharge is essential to guarantee the efficient protection of receiving natural waters and thus local communities.

The removal of various arsenic species from contaminated waters/wastewaters is possible due to the application of oxidation and precipitation methods, coagulation, ion exchange and sorption process or membrane separation. Each of these techniques have specific assets that lead to high treatment efficiency [9, 10].

Clearly, effective removal of arsenic as well as other harmful metal(loid)s may be reached by application of adsorption, widely recognized a simple and inexpensive treatment method. Development of high-performance and low-cost adsorbents during the last two decades has been remarkable. Studies of arsenic adsorption on metal oxide/hydroxide-based materials, namely, iron oxides/hydroxides such as granular ferric hydroxide, ferrihydrite, goethite, magnetite, and haematite, were comprehensively reviewed by Bail et al. [11], and Giles et al. [12].

Due to the natural affinity of arsenic for iron compounds, the implementation of iron-based adsorptive materials for treatment of arsenic-rich waters and wastewaters may be the best solution in many cases. Thus, in the present study, the removal of arsenic(III) and arsenic(V) by a granular ferric hydroxide media (GFH) has been investigated. The assessment of the effectiveness of iron-based adsorbent was performed based on kinetic, equilibrium and thermodynamic studies. The study was aimed at testing the application of adsorbent material for treatment arsenic-rich mine effluents in case of a catastrophic spill-out. The adsorption experiments with the use of synthetic solutions were performed in a batch adsorption system under simulated conditions and results are included in the present study. The influence of contact time, exceptionally high initial concentration of arsenic, solution temperature and adsorbent dose on adsorption performance was investigated.

2. MATERIALS AND METHODS

Adsorbent. A ferric hydroxide-based material (commercial name CFH12) used in the experiments was an adsorbent manufactured by Kemira Oyj, Finland. It was used as provided without any modification.

The morphology and chemical composition of GFH was analyzed using a scanning electron microscope (SEM, Joel) coupled with an energy dispersive X-ray (EDS) analyzer. The Brunauer–Emmer–Teller (BET) surface area and the porous characteristics were determined from the adsorption-desorption isotherms for liquid nitrogen at 77 K using Quantachrome Instrument. The X-ray diffractometer (XRD, D5005 Bruker/AXS) was also employed to analyse the ground, fresh adsorbent.

Synthetic solutions. Synthetic solutions were freshly prepared using Milli-Q water spiked with required amount of arsenic(III) or arsenic(V) solution. The stock solutions of As(III) and As(V) were prepared using NaAsO_2 and $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, respectively. pH of these synthetic solutions was adjusted to the required value by the addition of either HCl or NaOH, and a solution of NaCl was used as a background electrolyte.

Experimental methods. Adsorption experiments were performed in a batch regime at different initial arsenic concentration, contact time, solution temperature and mass of adsorbent. The adsorption equilibrium experiments were conducted for initial concentrations of As(III)/As(V) from 1 to 300 mg/dm^3 and adsorbent dose of 5 g/dm^3 . The samples were agitated in an incubator-shaker (IKA) at 295 K until equilibrium was reached. The initial pH of the solution was 7.0 and during the experiment it was monitored using a multi-meter (Hach-Lange). The adsorption equilibrium tests were also conducted at various temperatures (278, 285, 295 and 308 K). In this series of tests, the solution with initial concentrations of As(III)/As(V) in the range of 1–100 mg/dm^3 was constantly shaken with 5 g/dm^3 of GFH. To maintain desired temperature during the experiment, the incubator-shaker was connected with external circulation cooler (Labortechnik) filled with a glycol solution.

The kinetics studies were performed with adsorbent dose of 5 g/dm^3 , initial concentration of As(III)/As(V) of 1 and 20 mg/dm^3 and the initial pH of 7.0. The solutions with the adsorbent were continuously stirred for 5 h using a magnetic stirrer. Samples were collected at given time intervals and analyzed for the arsenic concentration using ICP-OES or ICP-MS technique.

To study arsenic adsorption at various material doses (1–10 g/dm^3), the experiments were conducted by agitating the samples in an incubator-shaker at 295 K. The initial pH of solution was adjusted to 7.0, and the initial As(III)/As(V) concentration was 20 mg/dm^3 .

3. RESULTS AND DISCUSSION

3.1. CHARACTERIZATION OF ADSORPTIVE MEDIA

The granular ferric hydroxide is a type of media with irregular grains of reddish-brown color and an average equivalent diameter d_{50} of 1.4 mm. It is a porous material with a specific surface area of 158 m²/g. The micropore and mesopore volume in GFH was of 0.0216 cm³/g and 0.0805 cm³/g, respectively. The adsorbent exhibited a wide range of pore sizes from 1.4 nm to 28.3 nm. The EDS analysis showed that in addition to iron, the GFH contains magnesium, aluminum, silica and sulfur (Fig. 1).

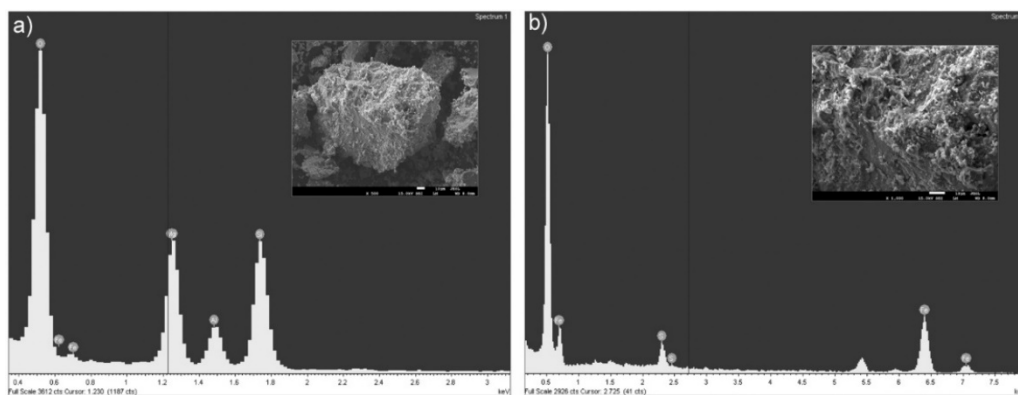


Fig. 1. SEM images at magnification 500× (a) and (b) 1000× and EDS spectra of the granular ferric hydroxide

The XRD analysis revealed the presence of goethite as a major mineral phase with iron in the form of Fe(III) oxyhydroxide. The detailed chemical composition, as well as characteristics of the porous morphology of GFH, was provided elsewhere [13].

3.2. KINETICS STUDIES

Adsorption kinetics describes the rate of adsorbate uptake at the solid–solution interface and provides valuable information regarding the rate-limiting reaction mechanisms. In this study, the experimental results demonstrating the adsorbed amount of arsenic against time were fitted into the most recognized models in, i.e.,

- the pseudo-first order model

$$q = q_{e-1} (1 - e^{-k_1 t}) \quad (1)$$

- the pseudo-second order model

$$q = \frac{k_2 q_{e-2}^2 t}{1 + k_2 q_{e-2} t} \tag{2}$$

where q and $q_{e-1, e-2}$ are the amounts of arsenic adsorbed at time t (q) and at equilibrium (mg/g), respectively, t is the contact time (min); k_1 is the equilibrium rate constant of the pseudo-first order adsorption (min^{-1}); and k_2 is the equilibrium rate constant of the pseudo-second order adsorption ($\text{g}/(\text{mg}\cdot\text{min})$). The model curves along with experimental data are shown in Fig. 2, while the kinetic parameters determined by employing the non-linear regression method are listed in Table 1.

Table 1

Parameters of kinetic models for the adsorption of As(III) and As(V) onto granular ferric hydroxide

Parameter	As(III)		As(V)	
	1	20	1	20
Experimental adsorption capacity				
q_{exp} , mg/g	0.170	1.883	0.238	4.156
Pseudo-first order kinetic model				
q_{e-1} , mg/g	0.113	1.847	0.217	4.147
k_1 , 1/min	0.313	0.011	0.283	0.014
R^2	0.480	0.969	0.856	0.986
Pseudo-second order kinetic model				
q_{e-2} , mg/g	0.126	2.373	0.230	5.160
k_2 , g/(mg·min)	2.188	0.005	1.605	0.003
R^2	0.625	0.978	0.938	0.991

Figure 2 shows that both As(III) and As(V) were successfully removed from the solution. The adsorption capacities along with the removal efficiencies increase upon increasing the contact time. As can be seen, at the beginning of the process, a rapid uptake occurs and is followed by a slower removal. The slower adsorption of arsenic species may arise from the decrease in the driving concentration difference between the bulk solution and the GFH surface. However, the rate of change in arsenic uptake with time was different for lower and higher initial concentrations of arsenic in solution. The percentage removal for 1 mg/dm³ of As(V) after 30 min contact was 85%, whereas the removal of As(III) reached 40%. The extension of the contact time to 5 h enables a slight improvement (1.3%) of arsenate removal, but in the case of arsenite, the increment was higher, and the recorded final removal efficiency reached 78% (q_{exp} 0.17 mg/g). The GFH performance in the more concentrated arsenic solutions (20 mg/dm³) resulted in maximum removal of As(III) and As(V), approximately 50% and 85%, respectively,

which corresponds to the adsorption of 1.88 mg/g and 4.16 mg/g. Effectiveness of granular ferric hydroxide in removing both forms of arsenic has also been confirmed by previous studies [14–16], where reported percentage removals of arsenite and arsenate species under various process conditions was even up to 100%.

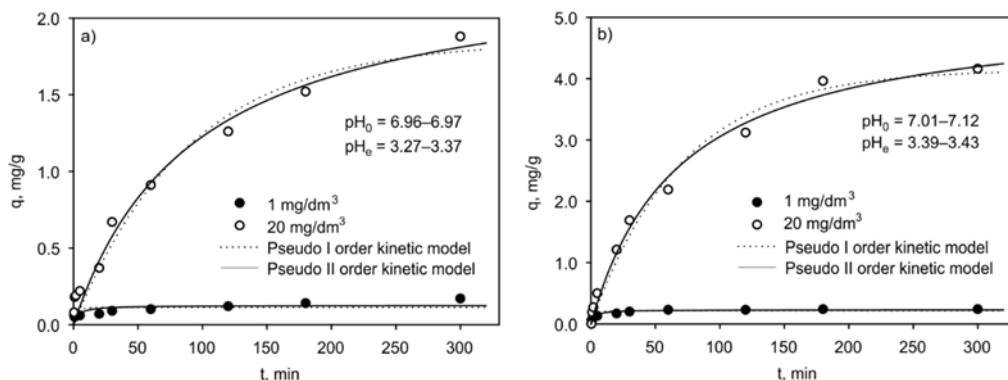


Fig. 2. Experimental kinetic data of As(III) (a) and As(V) (b) adsorption from the synthetic solutions fitted with kinetic models for various initial arsenic concentrations

The obtained experimental data were fitted to the pseudo-first order and pseudo-second order equations to describe the adsorption kinetics of arsenic oxyanions. The pseudo-first order kinetic model did not provide a satisfactory fit of data for initial arsenic(III)/(V) concentration of 1 mg/dm³ (Table 1). The model was more representative for simulating the adsorption process on the GFH at the higher initial concentration of arsenic (20 mg/dm³). From the correlation coefficient values, it is clear that overall the second order kinetic equation provides a better goodness of fit of adsorption data, assuming that the one of the rate-controlling factors in the investigated system may be chemical interaction. The adsorption capacity predicted by this model differed from that determined experimentally for solutions with 20 mg/dm³ of As(III) and As(V), while the good agreement was obtained for less concentrated solutions (Table 1).

The adsorption rate was inverse to the adsorption capacity (q_{exp} and q_{e-2}), as the faster adsorption resulted in a smaller amount of removed adsorbate. Furthermore, the values of the rate constant k_2 calculated for solution with As(III) were higher compared to those with As(V) and decreased as initial concentration of arsenite and arsenate species increased. Apparently, under applied process conditions ($\text{pH}_0 = 6.96 - 7.12$, $\text{pH}_e = 3.27 - 3.43$) neutrally charged H_3AsO_3 was more readily able to approach a negatively charged surface of GFH than As(V) oxyanions, which were present in solution in the form of HAsO_4^{2-} and H_2AsO_4^- .

The lower rate of arsenate adsorption than that of arsenite on metal (hydro)oxides surfaces was also observed by Qi and Pichler [17], who synthesized ferrihydrite and employed it as an adsorbent to study adsorption kinetics of arsenic oxyanions in single

and binary systems. Likewise, Ocinski et al. [18] reported the higher rate of arsenic adsorption by iron/manganese oxide-based sludge, as the initial concentration in aquatic solution decreased from 25 mg/dm³ to 6 mg/dm³. For 25 mg/dm³ of As(III), a higher value of the rate constant k_2 was accompanied by lower adsorption compared to As(V). The faster adsorption reaction at lower concentration of arsenite and arsenate on ferrihydrite was also recorded by other authors [19].

3.3. EQUILIBRIUM STUDIES

The adsorption isotherms for As(III) and As(V) were developed using the Langmuir (Eq. (3)) and Freundlich (Eq. (4)) isotherm models. The Langmuir isotherm equation assumes that there is no interaction between particular molecules of adsorbate, which leads to monolayer formation on the adsorbent surface. Thus, as saturation is reached, no further adsorption can occur, while the Freundlich isotherm model is an empirical expression and represents multilayer adsorption with a heterogeneous energetic distribution of active sites accompanied by interactions between adsorbed molecules.

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \tag{3}$$

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

where q_e and q_{\max} are the equilibrium and maximum adsorption capacities (mg/g), respectively, C_e is the equilibrium concentration of arsenic in the solution (mg/dm³), b is the Langmuir adsorption equilibrium constant (dm³/mg), K is the Freundlich constant (mg/(g·dm³)/mg)^{1/n} and $1/n$ dimensionless adsorption intensity constant. The experimental results fitted into Langmuir and Freundlich models are shown in Fig. 3. The isotherm parameters evaluated by non-linear regression are summarized in Table 2.

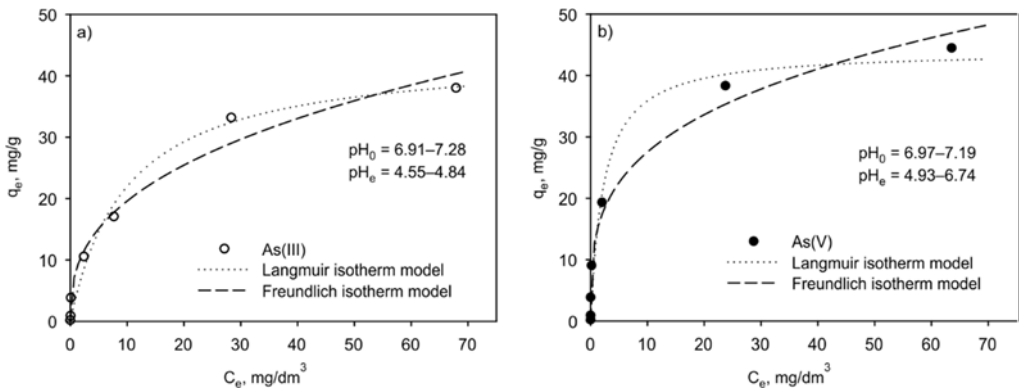


Fig. 3. Adsorption of As(III) (a) and As(V) (b) on granular ferric hydroxide at constant temperature fitted with Langmuir and Freundlich models

Table 2

Parameters of the isotherm models
for As(III) and As(V) onto granular ferric hydroxide

Parameter	As(III)	As(V)
Langmuir isotherm model		
q_m , mg/g	43.75	44.04
b , dm ³ /mg	0.101	0.439
R^2	0.986	0.974
Freundlich isotherm model		
K (mg/g)(dm ³ /mg) ^{1/n}	8.24	14.17
1/n	0.377	0.288
R^2	0.980	0.981

The correlation coefficients as a measure of goodness of fit of experimental data to the isotherm models show that both the Langmuir and Freundlich equations represent arsenic adsorption on GFH reasonably well (Table 2). In a studied adsorption system with As(III), the Langmuir model appears to be slightly better-fitting model than the Freundlich equation, while the reverse situation was observed in the case of As(V).

The theoretical maximum adsorption capacities determined from the Langmuir model for As(III) and As(V) are 43.75 mg/g and 44.04 mg/g, respectively, which was in a good agreement with experimental uptake (Fig. 3). In the case of Freundlich model, the comparable fit of equilibrium data was obtained for adsorbed As(III) ($R^2 = 0.980$) and As(V) ($R^2 = 0.981$). The Freundlich constant $1/n$ is a measure of adsorption intensity and ranged between 0 and 1, reflecting relatively strong adsorption and high affinity between adsorbate and adsorbent [20]. In this study, the calculated value of $1/n$ for As(III) and As(V) was lower than one, implying the occurrence of specific adsorption in the investigated system. The adsorption of fully protonated As(III) onto hydrous iron oxides is known to occur through a ligand exchange reaction. It has been reported that As(V) species may be adsorbed via both ligand exchange and Coulombic interactions [21], which is consistent with our findings. The occurrence of electrostatic interaction in uptake of As(V) onto GFH in reference to the surface charge of adsorbent has been discussed elsewhere [22].

3.4. EFFECT OF TEMPERATURE AND THERMODYNAMIC STUDIES

Temperature dependences of adsorption of As(III) and As(V) onto ferric hydroxide-based material are shown in Fig. 4. The higher solution temperature favoured adsorption of both forms of arsenic under the applied experimental conditions. However, the amount of adsorbed As(V) was higher than that of As(III) within the whole range of temperatures. As the temperature increased from 278 K to 308 K, the uptake capacity of arsenite and arsenate increased from 14.26 mg/g to 15.72 mg/g and from 17.29 mg/g

to 19.36 mg/g, respectively, indicating the endothermic nature of arsenic adsorption onto GFH. This observation is consistent with those reported previously [23, 24]. For example, Partey et al. [24] investigated the adsorption of arsenite and arsenate onto natural sorbents such as laterite iron concentrations and found that the adsorption capacity for both As(III) and As(V) increased with temperature, peaking at 333 K with higher uptake of As(III). Liu et al. [23] reported endothermic processes evidenced by increased adsorption of As(III) and As(V) onto magnetite nanoparticles upon increasing solution temperature from 283 K to 328 K.

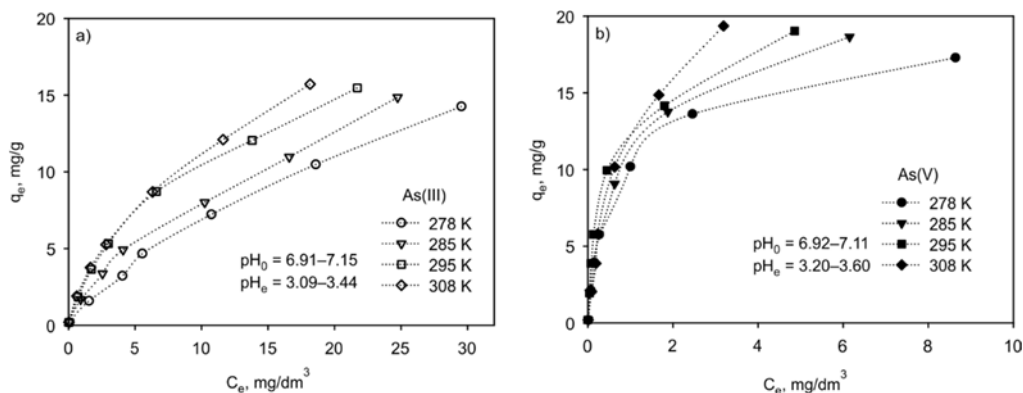


Fig. 4. Adsorption of As(III) (a) and As(V) (b) on granular ferric hydroxide at various temperatures

The present results show that removal of As(V) was more effective compared to that of As(III), especially at low equilibrium concentrations (Fig. 4). However, it was evident that despite the progressive saturation of GFH, the plateau region of maximum adsorption was not reached in the given process conditions. The adsorption capacity predicted by the Langmuir model was observed to be approximately twice the experimental values, indicating the lack of applicability of this model to the data over the studied arsenic concentration range. The obtained results were fitted into the Freundlich model, since the tested adsorbent exhibited infinite surface coverage, suggesting formation of a multilayer on the heterogeneous surface. The estimated Freundlich isotherm parameters along with correlation coefficients confirming a good mathematical fit are presented in Table 3.

Thermodynamic parameters including the changes of standard Gibbs free energy ΔG° (kJ/mol), standard enthalpy ΔH° (kJ/mol) and entropy ΔS° (kJ/(mol·K)) were also determined for the adsorption of arsenic oxyanions onto GFH at various temperatures.

$$\Delta G^\circ = -TR \ln K_e \quad (5)$$

$$\ln K_e = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (6)$$

$$K_e = K \rho_{w(T)} \left(\frac{1000}{\rho_{w(T)}} \right)^{1-1/n} \quad (7)$$

where R is the universal gas constant (8.314 J/(mol·K)), T – the absolute temperature (K), K_e – the dimensionless equilibrium constant [25], $\rho_{w(T)}$ – density of water (g/dm³), K – the Freundlich constant (mg/(g·dm³)/mg)^{1/n} (Eq. (4)).

Table 3

Freundlich isotherm model and thermodynamic parameters
for the adsorption of As(III) and As(V) at various temperatures

Temperature, K	278		285		295		308	
Species	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
Freundlich isotherm model								
K (mg/g·dm ³)/mg) ^{1/n}	1.33	8.79	1.82	9.78	2.85	11.23	2.83	11.09
$1/n$	0.704	0.345	0.650	0.381	0.552	0.350	0.593	0.508
R^2	0.998	0.954	0.998	0.976	0.996	0.979	0.999	0.980
Thermodynamic parameters								
$-\Delta G^\circ$, kJ/mol	16.63	20.99	17.79	21.77	19.51	22.87	20.34	23.84
ΔH° , kJ/mol	17.94	5.43						
ΔS° , kJ/(mol·K)	0.125	0.095						

The equilibrium constant (Eq. (7)) was expressed in terms of the Freundlich constants according to the approach proposed in [26, 27] and the assumption of the density of pure water ($\rho_{w(T)}$, g/dm³) at 278, 285, 295 and 308 K. The Gibbs free energy was calculated directly from Eq. (5). The change in standard enthalpy and entropy were estimated from the slope and intercept of the linear plot of $\ln K_e$ vs. $1/T$ (Eq. (6)) (not shown in this paper). The estimated thermodynamic parameters for the adsorption of As(III) and As(V) at various temperatures are given in Table 3.

The ΔG° values for As(III) decreased from –16.63 kJ/mol to –20.34 kJ/mol and for As(V) from –20.99 kJ/mol to –23.84 kJ/mol as the solution temperature increased. The calculated values of Gibbs free energy for the investigated system indicate spontaneous adsorption processes, associated with a negative change in free energy upon increasing temperature [26]. Adsorption becomes more thermodynamically favored at higher temperatures. The positive changes in standard enthalpy ΔH° for both arsenic forms confirmed the endothermic character of the examined adsorption process supported by the higher uptake of arsenic upon increasing temperature. However, ΔH° for arsenite adsorption (17.94 kJ/mol) is over three times higher than that of arsenate (5.43 kJ/mol) confirming that the adsorption of arsenite was likely to be attributed to formation of strong chemical bonds between As(III) and GFH, while weak electrostatic interactions contributed to the uptake of As(V). The value of the entropy change, ΔS° was positive, suggesting the

increased randomness of the organization of the adsorbate at the solid–liquid interface during the adsorption [27]. The degree of randomness of adsorbed arsenite was higher than that of arsenate, as the values of ΔS° were 0.125 (for As(III)) and 0.095 kJ/(mol·K), (for As(V)).

3.5. EFFECT OF MATERIAL DOSE

The removal of arsenic oxyanions from synthetic solution for various GFH doses is shown in Fig. 5.

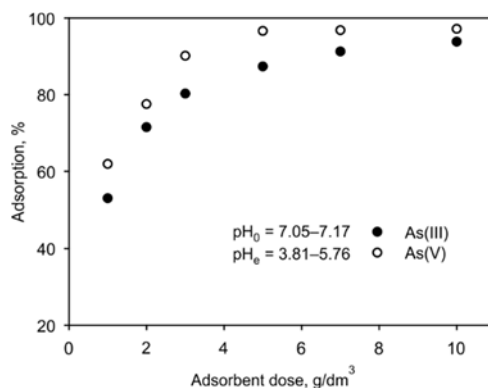


Fig. 5. Effect of the dose of the granular ferric hydroxide on the removal efficiency of As(III) and As(V) from the synthetic solution

Increase in the adsorbent dose resulted in the increase of percentage removal of arsenic species due to a higher number of available adsorption sites [28]. Under experimental conditions, a substantial difference was observed between adsorbed amounts of arsenic by particular doses of GFH. However, when the dose of adsorbent was higher than 5 g/dm³, the amount of remaining As(V) in the solution was almost constant, and further addition of GFH did not cause any significant changes in adsorption. This was probably due to a fixing of (pseudo)equilibrium between the arsenic ions bound to the adsorbent and those remaining in the solution. The percentage removal of As(III) was lower compared to that of As(V) and gradually increased from 52.9% to 93.8% as the mass of applied material increased from 1 g/dm³ to 10 g/dm³. Thus, to reduce the concentration of arsenic from 20 mg/dm³ to approximately 0.5 mg/dm³, a material dose of 5 g/dm³ was sufficient when As(V) was present in the solution. After addition of the maximal dose of GFH, it was possible to decrease the arsenite concentration only to 1.24 mg/dm³.

4. CONCLUSIONS

In the present work, the performed experiments confirmed that GFH adsorbent can be successfully applied for treatment of highly arsenic-contaminated waters and wastewaters. The feasibility of granular iron hydroxide GFH for removal of As(III) and As(V)

from aqueous solutions was assessed based on kinetic, equilibrium and thermodynamic data. The contact time between the arsenic ions and adsorbent had a strong effect on the adsorption efficiency. At the beginning of the process, rapid uptake occurred followed by a slower removal of arsenic species. However, the rate of As(III) and As(V) adsorption was higher for the less concentrated solution. It was demonstrated that for different initial concentrations of arsenic (1 mg/dm³ and 20 mg/dm³), the pseudo-second order kinetic model provided a better goodness of fit of experimental data. To investigate the adsorption capacity of GFH, the Langmuir and Freundlich isotherm equations were applied for modelling adsorption data. The theoretical maximum adsorption capacity estimated by means of the Langmuir model was comparable for both arsenic species. The adsorption of arsenite and arsenate was determined to increase upon increasing temperature being a spontaneous endothermic process. It was also confirmed that the treatment effect was highly dependent on the quantity of adsorbent with As(III) and As(V) removal over 90% for material doses of 7 and 5 g/dm³, respectively.

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