Adsorptive Removal of Pentavalent Arsenic from Aqueous Solutions by Granular Ferric Oxide

R. Zakhar,a,* J. Derco,a F. Čacho,b and O. Čižmárovác

aDepartment of Environmental Engineering, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovak Republic

bInstitute of Analytical Chemistry, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovak Republic

cThermo Fisher Scientific, Leškova 11, 811 04 Bratislava, Slovak Republic

Arsenic contamination of water resources, which is characterized by strong carcinogenic and toxic impacts, is a global problem. Therefore, the present study is focused on the isotherm and kinetic studies of pentavalent arsenic As(V) adsorption with initial concentration of 1 000 µg L−1 from aqueous solutions onto granular ferric oxide (GFO). Adsorption experiments were carried out by batch method, and the equilibrium and kinetic data were evaluated by the Langmuir, Freundlich, Dubinin-Radushkevich, Redlich-Peterson and Sips isotherm model, and pseudo-first and pseudo-second order kinetic model. The results obtained from this study imply that the adsorption of As(V) onto GFO was favourable, physical and multilayer process. The Sips and Redlich-Peterson isotherm and the pseudo-first order kinetic model gave the best fit to experimental data according to the values of correlation coefficient. The maximum theoretical adsorption capacity from Langmuir isotherm model was determined to be 1 900 µg g−1. In addition, the impact of different operating conditions such as As(V) initial concentration, adsorbent dose, agitation speed, pH, temperature, and presence of phosphates and silica on adsorption capacity of GFO was also investigated. As(V) was efficiently recovered from GFO by 0.1 M NaOH desorbing solution during the three adsorption-desorption cycles.

Keywords:
adsorption, arsenic, granular ferric oxide, isotherm models, kinetic models, regeneration

Introduction

The basic needs of mankind undoubtedly include access to quality and safe drinking water, which is a strategic raw material limiting the development of individual regions and entire geographical areas.1 There are still many places in the world that not only suffer from water shortages, but also from its contamination with harmful and toxic substances. At present, arsenic contamination of water resources, which is characterized by strong carcinogenic and teratogenic impacts, is coming to the fore.2

Arsenic was characterized as the 20th most occurring trace element in the earth’s crust, 14th in seawater, and 12th in the human body.3 It is released into water bodies by natural weathering reactions, biological activity, geochemical reactions, volcanic emissions, and anthropogenic activities, including mining activities, fossil fuel combustion, use of arsenic-based pesticides, herbicides and crop desiccants, and use of arsenic additives to livestock feed.4 From the water bodies it can be discharged in soils as well as sediments, and can be uptaken by plants. Plants such as rice, wheat, and oats can also absorb arsenic from the soil, which is irrigated with arsenic-contaminated water. Therefore, arsenic is often found in many crops. In addition, in some parts of the world arsenic-contaminated water is used for drinking purposes without treatment.5

In water, arsenic can be naturally found usually in two soluble arsenic forms such as As(III) (arsenite) and As(V) (arsenate).6 The distribution of these two soluble forms in natural water mainly depends on the redox potential (ORP) and the pH of the water. Under oxidizing conditions, the predominant form is pentavalent arsenic (arsenate), which is present in arsenic acid (H₃AsO₄), and oxyanionic
species such as $\text{H}_3\text{AsO}_4^-$, $\text{HAsO}_4^{2-}$, and $\text{AsO}_4^{3-}$. Organic arsenic compounds such as monomethyl arseneous acid (MMA(III)), monomethyl arsenic acid (MMA(V)), dimethyl arseneous acid (DMA(III)), and dimethyl arsenic acid (DMA(V)) can also be naturally present in water. Usually, these compounds occur in water at a concentration less than 1 $\mu$g L$^{-1}$ and due to this fact, they have no major significance in drinking water treatment.$^9,^{10}$

Arsenic contamination of water resources is a global problem, with reported studies in a large number of countries including Italy, Hungary, Serbia, Croatia, New Zealand, Bengal, Chile, Taiwan, Vietnam, Bangladesh, the United States, and Canada.$^{11,12}$ The concentration of arsenic in waters of the world varies considerably and can range from 0.5 to 5000 $\mu$g L$^{-1}$. Among the toxic and harmful pollutants, arsenic has high priority because it has been identified as a human carcinogen (Group 1), and can cause various chronic diseases. The toxicity and carcinogenicity of arsenic depends on its forms and oxidative states.$^{13}$ Many studies have indicated that arsenic ingestion can result in internal malignancies, including cancers of the kidney, bladder, liver, lungs, and other organs. It also has non-cancer effects that include cardiovascular, pulmonary, immunological, neurological, reproductive and endocrine (e.g. diabetes) disorders. In addition, arsenic has been shown to have genotoxicity. The health effects caused by acute arsenic poisoning are called arsenicosis, which has been also responsible for keratosis, skin changes and hyperkeratosis, skin lesions.$^{14-16}$ These aspects forced the World Health Organization (WHO) to reduce the maximum contaminant level of arsenic concentration in drinking water to 10 $\mu$g L$^{-1}$ from earlier limit of 50 $\mu$g L$^{-1}$ in 1993, which was also followed by the Unites States Environmental Protection Agency (US EPA) in 2001.$^{17}$

Different technologies have been used and proposed to remove arsenic from aqueous media. Therefore, many different technologies can be found around the world. Adsorption has been universally accepted as one of the most effective arsenic removal processes because of its easy operation and handling, low cost, low consumption of reagents, and it does not produce sludge and harmful by-products.$^{5,10,18,19}$ Adsorption is the process of removing dissolved solids from solutions by accumulating them on a suitable interface, respectively on the solid phase surface. The adsorbed molecules (adsorbate) can be bound to the surface of the solid (adsorbent) by van der Waals forces (physical adsorption) or by chemical bonds (chemisorption).$^{19-22}$ When the adsorbent material has been exhausted, it must be regenerated in order to be reused again. Successful desorption is considered to obtain regenerated media with approximately equal initial adsorption properties as before.$^{23}$ The possibility of adsorbent regeneration is not discussed in most arsenic adsorption studies. Depending on the used adsorbent, temperature and flow rate of regenerating agent, the strongly acidic (HCl, H$_2$SO$_4$, HNO$_3$, H$_3$PO$_4$) or strongly basic eluents (NaOH) and neutral electrolytes (NaCl) can be used for regeneration of exhausted media.$^{24,25}$

However, the desorption and regeneration process contributes to the accumulation of hazardous substances in concentrated form, which is related to the subsequent problem of safe disposal. Combustion is limited due to the volatility of arsenic-containing compounds. The recovery (recycling) of arsenic has low economic importance due to its limited use. For this reason, there is little commercial interest to invest in equipment and technology for the recovery of arsenic and its compounds. In addition, there are safety concerns associated with the storage of arsenic in concentrated form and probably terrible consequences associated with any accident in the place of storage. The dilution of arsenic waste with other waste streams and their subsequent dispersion in the environment can meet the regulatory limits, but definitely does not represent a technical solution for arsenic contamination. Currently, encapsulation of arsenic hazardous waste through solidification/stabilization techniques is considered to be the most attractive solution. During this process, contaminants may be chemically bound or encapsulated into a matrix. Cementitious solidification for land disposal of arsenic waste has been recognized by the US EPA and WHO as the best available technology.$^{26,27}$

The present study deals with the possibility of using granular ferric oxide (GFO) to remove pentavalent arsenic As(V) from aqueous solutions by batch adsorption experiments. The equilibrium data were analyzed so that we can understand the adsorption mechanism. Different equilibrium isotherm and kinetic models were applied to fit the experimental data. The impact of different operating conditions (As(V) initial concentration, adsorbent dose, agitation speed, pH, temperature, and presence of phosphates and silica) on the adsorption capacity of the GFO was also investigated. In addition, the possibility of regeneration and reuse of the GFO by different desorbing agents was studied. Results obtained from this study are presented and discussed.

**Material and methods**

**Reagents and solutions**

All used chemicals were of analytical laboratory grade, purchased from Merck Slovakia Ltd. All reagents and standards were prepared using demin-
eralized water. The As(V) stock solution was prepared by dissolving an accurately weighed amount of sodium arsenate heptahydrate (Na₂HAsO₄·7H₂O) in demineralized water to achieve a concentration of 1 g L⁻¹. The stock solutions were subsequently diluted to the required concentrations. To adjust the pH of stock solution, 0.1 M NaOH and 0.1 M HCl were used. After the adsorption, concentrated HCl solution (35 % w/w, ρ = 1.17 g cm⁻³) was added to the collected samples to store them. In the case of different concentrations of phosphates (PO₄³⁻) in the As(V) samples, a stock solution of 500 mg L⁻¹ PO₄³⁻ was used, which was prepared by dissolving an accurately weighed amount of dipotassium phosphate (K₂HPO₄) in demineralized water. In the case of different concentrations of silica (SiO₂) in the As(V) samples, the required silica concentration was obtained by adding the necessary amount of the solid substance, sodium metasilicate (Na₂SiO₃) directly to the As(V) samples. For As(V) desorption tests, 0.1 M solution of sodium hydroxide (NaOH), hydrochloric acid (HCl), acetic acid (CH₃COOH), sodium chloride (NaCl) and demineralized water were used as desorbing agents.

**Instruments and apparatus**

The shaking in batch experiments was conducted in a time- and RPM-controlled orbital shaker RSLAB-7PRO (Kvant Ltd., Slovakia). The pH was measured by a digital pH meter Jenway 3510 (Cole-Parmer, United Kingdom) with an accuracy of ± 0.003 unit. A high precision electrical balance ABS 220-4 (Kern & Sohn GmbH, Germany) was used for weighing. For experiments with different temperatures, a refrigerated/heating circulator F12-ED (Julabo, Germany) was used. The adsorption materials were dried in laboratory oven Venticell (MMM Medcenter GmbH, Germany). A PC-controlled automatic electrochemical laboratory analyzer EcaFlow Model 150 GLP (Istran Ltd., Slovakia) was used for quantitative determination of arsenic in solution.

**Analytical determination**

Determination of As(V) was done by flow-through chronopotentiometry using triple-electrode flow-through measuring cell (type 353c) with work electrode (type E-T/Au), platinum auxiliary electrode and argentochloride reference electrode. Each sample was analyzed ten times, and calibration was carried out before analysis with a freshly prepared arsenic standard.²⁸

**Preparation and characterization of adsorbent**

A granular ferric oxide (GFO) (Fig. 1) was obtained from Severn Trent (United Kingdom) and was used without further purification. It was only rinsed with demineralized water to remove dirt and then oven-dried at 105 °C for 24 h. Finally, the dried GFO was stored in desiccator for future use. The physicochemical properties of the GFO are shown in Table 1.

**Adsorption and kinetic studies**

Adsorption experiments were carried out by batch method at room temperature (20±2 °C). The 0.1 L of As(V) solution was taken in each Erlenmeyer flask of volume 0.2 L separately, which were placed in the orbital shaker, set at a speed of 150 rpm. The initial concentration of As(V) solution was kept at 1000 µg L⁻¹, while the dose of GFO adsorbent was 0.2 g. The time-dependent behaviour of As(V) adsorption was studied by varying the contact time between the adsorbate and adsorbent in the range 0–180 min (0, 3, 6, 15, 30, 60, 90, 120, 150 and 180 min). The pH of As(V) solution was adjusted to neutral with 0.1 M HCl or 0.1 M NaOH. At the end of each adsorption experiment, the solution and solid phase were separated by filtration with a standard filter paper. The filtrate was collected and subjected for As(V) determination following analytical method. The As(V) concentrations before and after adsorption were recorded, and then the adsorption capacity of GFO and the adsorption (removal) efficiency were calculated by the following equations:
where $q_e$ is the equilibrium adsorption capacity ($\mu g \cdot g^{-1}$) of GFO, $E_a$ is the adsorption (removal) efficiency (%), $c_0$ and $c_e$ are the initial and final concentration of As(V) in a determined time ($\mu g \cdot L^{-1}$), $V$ is the volume of As(V) solution (L), and $m$ is the mass of the adsorbent (g). The adsorption equilibrium time of GFO was also determined by this experiment. When the adsorption equilibrium contact time was found, the equilibrium sorption of As(V) onto GFO was carried out by batch method using 0.2 g of GFO and 0.1 L of As(V) solution with various concentrations in range $0$–$1000 \mu g \cdot L^{-1}$ ($0$, $100$, $200$, $400$, $600$, $800$ and $1000 \mu g \cdot L^{-1}$). For this experiment, 0.2 L Erlenmeyer flasks were used on orbital shaker, set at a speed of 150 rpm. The filtrate was collected and subjected to arsenic equilibrium concentration determination. For each As(V) equilibrium concentration, the equilibrium adsorption capacity was calculated according to the following equation:

$$q_e = \frac{(c_0 - c_e)V}{m}$$  

(3)

where $q_e$ is the equilibrium adsorption capacity ($\mu g \cdot g^{-1}$), $c_0$ and $c_e$ is the initial and equilibrium concentration of As(V) ($\mu g \cdot L^{-1}$), $V$ is the volume of As(V) solution (L), and $m$ is the mass of the adsorbent (g). Then the adsorption data were analyzed to see whether the isotherm obeyed the Langmuir, Freundlich, Redlich-Peterson, Sips or Dubinin-Radushkevich isotherm model equations (Table 3). Kinetic parameters were evaluated by pseudo-first and pseudo-second order kinetic model (Table 4).

### Impact of different operating conditions

The impact of different operating parameters, such as As(V) initial concentration, adsorbent dose, agitation speed, pH, temperature and presence of phosphates and silica, was studied by batch adsorption experiments. The duration of experiments was the adsorption equilibrium time. Thus, As(V) adsorption tests were performed for five different values of each parameter, which are summarized in Table 2. For all operating conditions, if the As(V) concentration was known, adsorption efficiency and capacity was calculated according to Equations 1 and 2.

### Desorption experiments

Repeated adsorption-desorption cycles were carried out to study the reversibility of the process and the possibility of GFO material regeneration and reuse in more than one adsorption process. In desorption experiments, 0.2 g of the GFO was firstly exposed to 1000 $\mu g \cdot L^{-1}$ of As(V) solution for the equilibrium time at neutral pH, room temperature (20±2 °C), and agitation speed of 150 rpm. The adsorbent was then separated from the As(V) solution by filtration. The obtained As(V)-loaded adsorbent was then brought in contact with 0.1 L of 0.1 M hydrochloric acid (HCl), 0.1 M acetic acid (CH$_3$COOH), 0.1 M sodium hydroxide (NaOH), 0.1 M sodium chloride (NaCl), and demineralized water for 2 h in orbital shaker at 150 rpm. Finally, the adsorbent was filtered with a standard filter paper and As(V) content in the filtrate was determined. The adsorption and desorption efficiencies were calculated according to the following equations:

$$E_a = \frac{(c_0 - c_e)}{c_0} \cdot 100 \%$$  

(4)

### Table 2 – Experimental setup for study of the impact of different operating conditions

| Changed operating parameter | Stable operating parameter |
|-----------------------------|---------------------------|
| As(V) initial concentration: 500, 1500, 2000 and 2500 $\mu g \cdot L^{-1}$ | Volume of solution 0.1 L, contact time 120 min, amount of adsorbent 0.2 g, neutral pH, temperature 20±2 °C, agitation speed 150 rpm |
| Adsorbent dose: 0.1, 0.2, 0.5, 0.8 and 1.0 g | As(V) initial concentration 1000 $\mu g \cdot L^{-1}$, volume of solution 0.1 L, contact time 120 min, neutral pH, temperature 20±2 °C, agitation speed 150 rpm |
| Agitation speed: 100, 150, 200, 250 and 300 rpm | As(V) initial concentration 1000 $\mu g \cdot L^{-1}$, volume of solution 0.1 L, contact time 120 min, amount of adsorbent 0.2 g, neutral pH, temperature 20±2 °C |
| pH: 2.5, 4.0, 7.0, 9.0 and 10.5 | As(V) initial concentration 1000 $\mu g \cdot L^{-1}$, volume of solution 0.1 L, contact time 120 min, amount of adsorbent 0.2 g, temperature 20±2 °C, agitation speed 150 rpm |
| Temperature: 10, 20, 30, 40 and 50 °C | As(V) initial concentration 1000 $\mu g \cdot L^{-1}$, volume of solution 0.1 L, contact time 120 min, amount of adsorbent 0.2 g, neutral pH, agitation speed 200 rpm |
| Presence of phosphates: 0, 1, 2, 3 and 4 mg $\cdot L^{-1}$ | As(V) initial concentration 1000 $\mu g \cdot L^{-1}$, volume of solution 0.1 L, contact time 120 min, amount of adsorbent 0.2 g, neutral pH, temperature 20±2 °C, agitation speed 150 rpm |
| Presence of silica: 0, 10, 20, 30 and 40 mg $\cdot L^{-1}$ | As(V) initial concentration 1000 $\mu g \cdot L^{-1}$, volume of solution 0.1 L, contact time 120 min, amount of adsorbent 0.2 g, neutral pH, temperature 20±2 °C, agitation speed 150 rpm |
\[ E_d = \frac{c_d}{c_i} \times 100\% \] (5)

where \( E_a \) is the adsorption efficiency (%), \( E_d \) is the desorption efficiency (%), \( c_i \) is the initial concentration of As(V) (μg L\(^{-1}\)), \( c_e \) is the equilibrium concentration of As(V) (μg L\(^{-1}\)), \( c_d \) is the As(V) concentration in the solution after desorption (μg L\(^{-1}\)), and \( c_s \) is the As(V) concentration present on the surface of the adsorbent material after the corresponding previous adsorption (μg L\(^{-1}\)).

**Experimental data processing**

For the experimental data analysis and fitting of the experimental values, nonlinear regression was used. Parameter values of adsorption isotherms, pseudo-first order and pseudo-second order kinetic models were determined by the grid search optimization procedure. The correlation coefficient between the experimental and calculated data was used for the evaluation of the quality of mathematical description of the experimental data:

\[ R_{xy} = 1 - \frac{(n-m)S_R^2}{(n-1)S_y^2} \] (6)

where \( R_{xy} \) is the correlation coefficient (–), \( n \) is the number of measurements, \( m \) is the number of parameters, \( S_R^2 \) is the residual sum of squares of experimental and calculated values, and \( S_y^2 \) is the dispersion of dependent variable values:

\[ S_R^2 = \frac{\sum (y_{i,e} - y_{i,c})^2}{n-m} \] (7)

\[ S_y^2 = \frac{n\sum y_{i,e}^2 - (\sum y_{i,e})^2}{n(n-1)} \] (8)

where \( y_{i,e} \) expresses experimentally measured dependent variable values, \( y_{i,c} \) expresses calculated dependent variable values, \( n \) is the number of measurements, and \( m \) is the number of parameters.

**Results and discussion**

**Modelling of the adsorption**

The impact of contact time on adsorption of As(V) on GFO with different time intervals (0–180 min) at initial arsenic concentration 1000 μg L\(^{-1}\) and 0.2 g of adsorbent dose is shown in Fig. 2.

As seen in Fig. 2, the adsorption capacity \( q_t \) and adsorption (removal) efficiency \( E_r \) of GFO rapidly increased in the first 15 minutes, and then continued to increase significantly up to 60 minutes. The fast adsorption rate at the beginning can be explained by the abundant availability of active sites on the adsorbent surface. Finally, the adsorption capacity increased at a lower rate up to 180 minutes and reached 493.0 μg g\(^{-1}\), meaning an adsorption (removal) efficiency equal to 98.60 %.

As the contact time increased, the value of the adsorption capacity and adsorption (removal) efficiency also increased and stabilized at a certain value. There was a balance between adsorbent and adsorbate. From Fig. 2, it was observed that the equilibrium for As(V) adsorption onto GFO was achieved in 120 minutes. Thereafter, the change in adsorption capacity and adsorption (removal) efficiency was negligible. In the equilibrium contact time, the adsorption capacity and adsorption (removal) efficiency of GFO were determined at 449.5 μg g\(^{-1}\) and 89.90 %.

In the present study, the Langmuir, Freundlich, Dubinin-Radushkevich, Redlich-Peterson and Sips nonlinear models were used to describe the equilibrium isotherm of As(V) adsorption onto GFO. The summarized isotherm models are shown in Table 3. Fig. 3 describes the modeled isotherm profiles for the adsorption of As(V). For each adsorption model, the correlation coefficient \( R_{xy} \) was calculated. Table 3 shows that the Sips and Redlich-Peterson iso-
therm gave the best fit to the experimental equilibrium data for As(V) adsorption according to the values of $R_L$. These two adsorption isotherms combine the Langmuir and Freundlich isotherm, as well as the heterogeneity of the adsorbent surface and a number of adsorption sites with the same adsorption potential. They describe adsorption on homogeneous and also heterogeneous surfaces. The Langmuir isotherm is valid for monolayer adsorption on the surface that contains a finite number of identical sites where adsorption of only one molecule is possible. This model assumes a uniform surface adsorption energy and no interactions between adsorbed molecules. From this isotherm the Langmuir maximum theoretical adsorption capacity $q_{\text{max}}$ can be investigated, which for GFO is equal to 1900.0 μg g⁻¹. The properties of this adsorption can be affirmed from viewpoint of equilibrium parameter $R_L$, which values were found to be greater than zero and less than one for all initial As(V) concentrations, indicating the favourable adsorption of As(V) by GFO. The Freundlich isotherm is used to describe adsorption characteristics for a heterogeneous surface. The value $1/n$ of Freundlich isotherm lies between zero and one, and it indicates also a favourable sorption process. The Dubinin-Radushkevich isotherm is generally applied to express the adsorption mechanism by Gaussian energy distribution on a heterogeneous surface. Based on the nonlinear plot obtained from Dubinin-Radushkevich model, the value of the adsorption energy $E_V$ was found to be 0.052 kJ mol⁻¹. This value is less than 8 kJ mol⁻¹, indicating that the physical adsorption was the process involved for adsorption of As(V) by GFO. It means that the adsorbed molecules of As(V) could form multilayer adsorption. Based on the results obtained from the isotherm models it follows that the adsorption of As(V) was most probably on heterogeneous surface, favourable, physical and multilayer process.30–34

Table 3 – Isotherm data for adsorption of As(V) onto GFO (As(V) concentration 0–1000 μg L⁻¹, volume of solution 0.1 L, contact time 120 min, amount of adsorbent 0.2 g, neutral pH, temperature 20±2 °C, agitation speed 150 rpm)

| Adsorption isotherm | Equation | Parameter (unit) | Value | $R_L$ (–) |
|--------------------|----------|------------------|-------|-----------|
| Langmuir (LI)      | $q_r = \frac{q_{\text{max}} K_r c_r}{1 + K_r c_r}$ | $q_{\text{max}}$ (μg g⁻¹) | 1900.00 | 0.9400 |
|                    |          | $K_r$ (L μg⁻¹) | 6.18×10⁻³ |         |
|                    |          | $R_L$ (–) | 0.10–1.00 | |
| Freundlich (FI)    | $q_r = K_r c_r^{1/n}$ | $K_r$ (μg(1−1/n) g⁻¹ Lⁿ) | 20.80 | 0.9300 |
|                    |          | $n$ (–) | 1.27 | |
| Dubinin-Radushkevich (D‐RI) | $\varepsilon = \frac{RT\ln(1 + \frac{1}{c_r})}{c_r}$ | $\beta$ (mol² kJ⁻¹) | 1.83×10⁻⁴ | 0.8576 |
|                    |          | $E_r$ (kJ mol⁻¹) | 0.05 | |
| Redlich-Peterson (R‐PI) | $q_r = \frac{K_{ar} c_r}{1 + ac_r b}$ | $K_{ar}$ (L g⁻¹) | 40.96 | 0.9556 |
|                    |          | $a$ (L μg⁻¹)b | 3.27 | |
|                    |          | $b$ (–) | 5.10×10⁻¹⁴ | |
| Sips (SI)          | $q_r = \frac{K_s a_r c_r}{1 + a c_r^{β_s}}$ | $K_s$ (μg(1−β_s) g⁻¹ Lβ_s) | 6.99 | 0.9602 |
|                    |          | $a_r$ (L μg⁻¹) | 1.13 | |
|                    |          | $β_s$ (–) | 9.10×10⁻¹⁶ | |
Kinetic studies

Analysis of the kinetic data in the adsorption process is important for describing the adsorption rate, which affects the total time required to form bonds between the adsorbent and the adsorbate. The kinetic parameters obtained from the nonlinear fittings of pseudo-first order (PFO) and pseudo-second order (PSO) models are shown in Table 4. The PFO and PSO plots of kinetic study are illustrated in Fig. 4. Table 4 suggests that the As(V) adsorption onto GFO followed the PFO model with correlation coefficient $R_{xy}$ equal to 0.9901, which assumes that the adsorption sites occupancy rate is proportional to the number of vacant sites. The equilibrium adsorption capacity $q_e$ calculated from the PFO kinetic model agree well with the experimental data value equal to 449.5 μg g$^{-1}$.

Table 4 – Comparison of PFO and PSO models parameters for As(V) adsorption onto GFO (As(V) initial concentration 1000 μg L$^{-1}$, volume of solution 0.1 L, contact time 180 min, amount of adsorbent 0.2 g, neutral pH, temperature 20±2 °C, agitation speed 150 rpm)

| Kinetic model | Equation | Parameter (unit) | Value | $R_{xy}$ (–) |
|---------------|----------|------------------|-------|--------------|
| PFO           | $q_t = q_e \left(1 - e^{-kt}\right)$ | $q_e$ (μg g$^{-1}$) | 500.50 | 0.9901 |
|               |          | $k_1$ (min$^{-1}$) | 1.65·10$^{-2}$ | |
| PSO           | $q_t = \frac{k_1 q_e t}{1 + k_2 q_e t}$ | $q_e$ (μg g$^{-1}$) | 520.00 | 0.9261 |
|               |          | $k_2$ (g μg$^{-1}$ min$^{-1}$) | 5.16·10$^{-5}$ | |

where $q_t$ is the adsorption capacity in time $t$, $q_e$ is the equilibrium adsorption capacity, $k_1$ is the pseudo-first order rate constant, and $k_2$ is the pseudo-second order rate constant.
Impact of different operating conditions

It is important to understand the impact of different operating conditions on As(V) adsorption by GFO media, since the treatment economics can be significantly affected. The impact of each operating parameter on As(V) adsorption by GFO is illustrated in Fig. 5. The impact of initial As(V) concentration was studied in range from 500 to 2500 μg L⁻¹. The adsorption (removal) efficiency $E_a$ increased (from 95.02 % to 71.38 %) with the increase in As(V) initial concentration. The lower efficiencies for higher concentrations can be explained by the saturation of active adsorption sites, which caused a decrease in the amount of available sites for further adsorption. On the other hand, naturally, the adsorption capacity $q_t$ of GFO increased with the increase in initial concentration of As(V).

The different doses of GFO used were 0.1, 0.2, 0.5, 0.8, and 1 g. The adsorption (removal) efficiency $E_a$ increased with the increasing adsorbent material doses until almost 100 %. It is logical that more material means more available free sites for adsorption. From the adsorbent dose of 0.5 g, there was no remarkable increase in the adsorption (removal) efficiency. The optimum dose was 0.5 g of GFO, reaching 98.63 % efficiency.

From the study of different agitation speeds, from 100 to 300 rpm, it was obtained that the adsorption (removal) efficiency $E_a$ increased with the agitation speed. This could have been due to the fact that the external mass transfer effect increased with the increase in agitation, resulting in better transport of solute from solution to the adsorbent active sites, and thus increasing the rate of adsorption. Maximum removal was observed at 250 rpm with adsorption (removal) efficiency of 98.73 %. However, at agitation speeds of 200, 250 and 300 rpm, the aqueous solutions were mixed so intensively that the turbulence caused more frequent abrasion of the adsorbent particles, and turbidity was observed in the aqueous solution.

In general, As(V) adsorption (removal) efficiency $E_a$ decreased with increasing pH. Then, it increased at pH 9.0, but with further increase in pH, it rapidly decreased. The maximum adsorption (removal) efficiency (99.00 %) was reached in acidic conditions, at pH 2.5. However, due to this pH, the adsorbent material was partially destroyed and part of the iron contained in the material was dissolved in the solution. Acidic condition is not recommended and optimum pH was found to be between 6.5 and 8.0, which is the most common pH range for ground or surface sources of drinking water.

The impact of temperature was investigated at different values like 10, 20, 30, 40 and 50 °C. From 10 to 30 °C the adsorption (removal) efficiency $E_a$ generally increased, reaching the highest level at 30 °C (97.55 %), and then at 50 °C the efficiency decreased to 73.08 %.

Generally, adsorption (removal) efficiency $E_a$ of the adsorbent decreased with increasing phosphates and silica concentration in the sample. It is known that phosphate ions are very adsorptive on the surface of ferric oxides (Fe₂O₃) present in GFO. Results indicate that arsenates and phosphates competed for the same surface sites. In the silica case, it is assumed that silica can increase the electrostatic repulsion of As(V), and can also reduce the number of available sites for the As(V) adsorption by coating the surface of GFO.

Desorption – regeneration of GFO

The reversibility of As(V) sorption onto GFO was studied using acidic (0.1 M HCl and 0.1 M CH₃COOH), basic (0.1 M NaOH), neutral (0.1 M NaCl) extracting solutions and demineralized water (Demi H₂O). Three cycles of adsorption and desorption were performed. The results are presented in Fig. 6. It is evident that the desorption efficiency $E_d$ depended on the nature of the desorbing solution. Both acid desorbing agents caused structural damage to the adsorbent material, which was destroyed and dissolved giving to the solution a yellow-orange colour and turbidity. In the case of 0.1 M HCl, the As(V) determination was not possible in the samples. The acid desorbing agents were not suitable for GFO regeneration. The basic solution of 0.1 M NaOH achieved the highest desorption efficiency along the three desorption processes, being 78.47 % for the first desorption, 74.19 % for the second, and 45.82 % for the third. Therefore, this solution was suitable for repeated regeneration of the tested GFO adsorbent. However, after the sec-
Fig. 5 – Impact of different operating conditions on As(V) adsorption by GFO
ond cycle, adsorption and desorption efficiency decreased, probably because of structural damage of the adsorbent material by the basic solution. Finally, under neutral conditions, using demineralized water and 0.1 M NaCl, the desorption efficiency was practically insignificant, but adsorption efficiency was kept high during the regeneration cycles. Maybe these two desorbing agents did not cause structural damage to GFO, and additionally the saturation of GFO was not achieved. Based on the results obtained from the experiments with demineralized water, it can be stated that the adsorption of As(V) onto the GFO was strong, and As(V) was not desorbed back into the demineralized water.

Conclusions

The present study shows that the GFO was successfully used as an adsorbent for the quantitative removal of As(V) from aqueous solutions. The applied mathematical models provided reasonable predictive performance of As(V) adsorption and worked satisfactorily. Based on the results obtained from the equilibrium and kinetic models, it follows that the adsorption of the As(V) onto GFO was favourable, physical and multilayer process. The study on equilibrium adsorption revealed that the Redlich-Peterson and Sips isotherm model ($R^2 > 0.95$) and pseudo-first order kinetic model ($R^2 > 0.99$) gave the best fit to experimental data. Under the equilibrium conditions, the maximum theoretical adsorption capacity of GFO predicted by the model was 1 900 μg g$^{-1}$. According to the results obtained from the impact of different operating conditions on As(V) removal from aqueous solutions, it follows that the adsorption (removal) efficiency decreased with the increase in As(V) initial concentration, and also with increased phosphates and silica concentration, the optimum dose of GFO was found to be 0.5 g, and the optimum pH was found between 6.5 and 8.0, the maximum As(V) removal was observed at agitation speed of 250 rpm and temperature of 30 °C. The basic solution of 0.1 M NaOH was suitable for repeated regeneration of the tested GFO, which caused the highest desorption efficiencies (78.47 %, 74.19 %, and 45.82 %) along the three adsorption-desorption cycles. Finally, it can be concluded that the application of static experiments is an effective method for modelling, optimization, and design of the adsorption process for As(V) removal from aqueous solutions.

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