Effect of Matrix Solution on As(V) Adsorption onto Iron-containing Materials

pH and kinetic studies

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In the present paper is investigated the effect of the presence of some competing anionic (NO_3^-, PO_4^{3-}, Cl^- and Co_3^{2-}) and cationic (Mg^{2+} and Mn^{n+}) species on the adsorption of arsenic (V) on two iron containing materials: a waste material and a synthetic material. The waste material was an iron containing sludge (IS) resulting from hot-dip galvanization. The synthetic material was Fe_2O_3 obtained through annealing of $Fe(COO)_2 \cdot 2H_2O$ at 550 °C. For the studies, a synthetic solution containing 100 μg As(V)/L was used. The adsorption of As(V) over the initial pH range 2-11 for IS and 2-8 for Fe_2O_3 was not strongly dependent on pH. The influence of ionic species was investigated in single and in multicomponent competing ion solutions at two concentrations: 10 mg/L and 100 mg/L, respectively. Adsorption experiments were also carried out on a real groundwater containing the studied ions. The adsorption experiments were performed at different contact times (1, 2, 3, 4, 8 and 24 h). The presence of any ionic species has a negative effect on As(V) adsorption onto Fe_2O_3. Only PO_4^{3-} showed a negative effect on the adsorption of As(V) onto IS. The other studied ions, in single and in multicomponent solutions had a positive effect on the adsorption of As(V) onto IS. Fe_2O_3 proved to be more efficient than IS for the adsorption of As(V) from solutions containing only this species (adsorption capacities of 97 μg/g and 45 μg/g, respectively). The presence of other species was benefic for the adsorption of As(V) onto IS from solutions containing all ions and the real underground water. The values of the adsorption capacity reached in these cases were very close for both adsorbent materials (~85 μg/g for the real water and ~80 μg/g for the all ions synthetic solution). These results indicate that IS would be a suitable adsorbent for the removal of As(V) ions from natural waters. The adsorption process followed a pseudo-second-order kinetics and the theoretically predicted equilibrium adsorption capacities were close to the experimentally determined values.

Keywords: arsenic, adsorption, iron sludge, anion, cation, kinetics

The effects of pollution of natural systems with arsenic are serious and dangerous to human life. Especially contamination of drinking water sources with arsenic is a matter of worldwide concern. The symptoms of chronic poisoning in human beings are numerous: skin cancer, liver, lung, kidney and bladder cancer, as well as conjunctivitis, hyperkeratosis and, in severe cases, gangrene in the limbs and malignant neoplasm [1-3].

For this reason, World Health Organization (WHO) set the maximum permissible limit in drinking water at 10μg/L [4]. Due to the high toxicity of arsenic, remediation of arsenic contaminated soils and groundwater is necessary to protect the environment and the public health [5].

A variety of treatment processes has been studied for arsenic removal from water. One of the most used methods is the adsorption. The most efficient adsorbent materials are those with iron content considering the affinity of arsenic towards iron [6-10].

Since underground water and surface water usually contains some soluble solutes, the effect of these species on the removal of As(V) through adsorption should be studied. Many researchers reported that competing solutes affect the removal of As(V) by adsorbents.

The literature data indicate that arsenic adsorption is strongly decreased by the presence of phosphate; due to their structural resemblances, they compete for the binding sites of the adsorbent [5, 11-15].

Some studies found that the presence of NO_3^-, Cl^- and SO_4^{2-} has negligible effects on As(V) uptake, these ions forming outer-sphere complexes that do not interfere with the inner-sphere complex formed by As(V) at the adsorbent surface [11-13]. As a potential competitor or extractor of arsenic, CO_3^{2-} has a negligible to moderate effect [16, 17], a moderate to notable effect [13, 18] or equivocal results were obtained [19]. Some studies revealed the cooperative effect of metal cations such as Ca^{2+}, Mg^{2+} and Fe^{3+} on adsorption of arsenic, which could be attributed to the favorable electrostatic effects, as the adsorption of metal cations increases the amount of positive charge on the adsorbent surface [5, 7, 20].

The difference and sometimes even the contradiction between the results reported by different researchers may be due to different experimental conditions (pH value, anion concentration, adsorbent, solid:liquid ratio).

The present paper reports studies on the effect of the presence of some competing anionic (NO_3^-, PO_4^{3-}, Cl^- and CO_3^{2-}) and cationic (Mg^{2+} and Mn^{n+}) species on the adsorption of arsenic (V) on two iron containing materials: an iron containing sludge (IS) resulting from hot-dip galvanization and synthetic Fe_2O_3.

Experimental part

The adsorption of As(V) was studied in batch experiments using two iron containing materials: a

synthetic material and a by-product resulting from another technology. The synthetic material used as adsorbent was Fe_2O_3 obtained through annealing of analytical grade $Fe(COO)_2 \cdot 2H_2O$ at 550°C. The by-product is an iron sludge (IS) resulting during the neutralization with lime of wastewaters from hot dip galvanization. IS was grinded and sieved. The fraction with particles size between 0.1 and 0.2 mm was used after drying at 105°C.

The influence of pH on the adsorption performance of the IS and Fe_2O_3 was studied by batch equilibration technique [1, 9, 10, 21]. A known amount of IS (0.1 g) was suspended in 100 mL of a 100 µg/L As(V) solution. The value of the initial pH of the As(V) solution (pH_i) was varied between 2 and 12, being adjusted to the desired value using 0.1 M/2 M NaOH or 0.1 M/2 M HNO_3, thereby keeping the volume variation of the solution to a value as low as possible. The pH values of the solutions were measured by means of a CRISON MultiMeter MM41 fitted with a glass electrode, which was calibrated using various buffer solutions. The suspensions were left to equilibrate for 24 h at laboratory temperature (23 ± 1 °C), then were filtered and the final pH values of the solutions (pH_f) determined.

The adsorption experiments were carried out using a 100 mg As(V)/L synthetic solutions without or with ionic species (NO_3^-, PO_4^{3-}, Cl^-, CO_3^{2-}, Mg^{2+} and Mn^{n+}). The influence of each ionic species was studied at two concentrations: 10 mg/L and 100 mg/L respectively, in single component solutions (containing only one anionic species at the time). It was also studied the influence of all mixed anionic species and respectively all species (anionic and cationic) at two total concentrations: 10 mg/L and 100 mg/L. Concentration range of ionic species was chosen to fit the concentrations usually found in groundwater. Adsorption experiments were also carried out on a real groundwater with the following composition: As – 70 µg/L; Mn^{n+} - 0.17 mg/L; PO_4^{3-} - 5 mg/L; NO_3^- - 40 mg/L; Cl^- - 15 mg/L; CO_3^{2-} - 50 mg/L. During the batch adsorption experiments, the pH of the suspensions was left to drift freely.

All reagents used to prepare the synthetic solutions were in analytical reagent grade. Samples of 0.1 g adsorbent material were treated with 100 mL solution and left at laboratory temperature (23 ± 1°C) at different contact times (1, 2, 3, 4, 8 and 24 h). After contact time elapsed, the suspensions were filtered and the residual concentration of arsenic in the filtrate was determined through atomic absorption spectrometry with hydride generation, using a VARIAN SPECTR AA110 spectro-photometer with hydride system VGA 77.

Results and discussions

The experimental data for the composition of IS resulting from chemical analysis are: Fe – 31.6%, Zn – 1.91%, Pb – 0.03%, Ca – 15.6% and Cl – 24.3% [9, 22]. The major component of this material is iron, which makes it suitable for arsenic removal from water, due to the high affinity of arsenic towards iron [6-10]. The difference up to 100% is represented by hydrogen and oxygen, because metallic ions are present in the material mainly as oxides, hydroxides and chlorides.

The adsorption capacity (adsorption performance) is expressed as the amount of As(V) adsorbed per gram of adsorbent q_t (µg/g) at a moment t and is calculated using the following equation [8, 9, 21, 22]:

$$q_t = (C_o - C_t) \frac{V}{m} \qquad (1)$$

where:

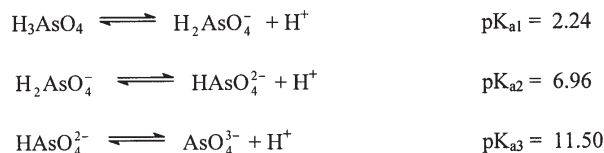C_o is the initial concentration of arsenic in solution,

µg/L;

C_e – residual concentration of arsenic in solution at a moment t, µg/L;

V - volume of solution, L;

m - amount of adsorbent, g.

Influence of pH

To understand the characteristics of the surface charge generated on IS and Fe_2O_3 in aqueous media, the point of zero charge, pH_{pzc}, of these materials was determined by batch equilibration technique. In the case of IS this value was $pH_{pzc} = 6.2$ for initial solutions having pH values in the range 4-10 [9]. For Fe_2O_3 the value was $pH_{pzc} = 6.1$ in the initial pH range 6-9.5 [21] The fact that both materials have nearly neutral point of zero charge suggests that both negatively and positively charged ions could be adsorbed [23].

The experimental results of effect of pH on sorption performance are shown in figure 1a where As(V) equilibrium uptake (q_e) and equilibrium solution pH (pH_f) are plotted against the initial solution pH (pH_i). As is evident from figure 1a, the adsorption of As(V) over the pH_i range 2-11 for IS and 2-8 for Fe_2O_3 is not strongly dependent on pH, which is highly advantageous for practical operation [20].

The pH dependence of As(V) adsorption is influenced by the distribution of metal species in the solution phase, which, on the other hand, depends on the pH of the medium. Pentavalent arsenic exists in the form of H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-}, depending on the solution pH. The distribution of these species as a function of solution pH is presented in figure 2. The values of relative proportions of the species (α_i) were calculated based on the three dissociation equilibriums of arsenic acid and their respective acidity constants [24]:

$$H_3AsO_4 \rightleftharpoons H_2AsO_4^- + H^+ \qquad pK_{a1} = 2.24$$

$$H_2AsO_4^- \rightleftharpoons HAsO_4^{2-} + H^+ \qquad pK_{a2} = 6.96$$

$$HAsO_4^{2-} \rightleftharpoons AsO_4^{3-} + H^+ \qquad pK_{a3} = 11.50$$

The pH dependence of As adsorption is usually explained in terms of ionization of both adsorbates and adsorbents [25]. In the pH_f range 2.30 – 6.80, the predominant species $H_2AsO_4^-$ is primarily responsible for adsorption and maximum As(V) removal was reached for both sorbents (fig. 1b) [1]. This pH range is below the pH_{pzc} of both materials (IS – 6.2; Fe_2O_3 – 6.1); sorbed protons on the functional groups of the surface cause an overall positive surface charge [26], and adsorption of anionic As(V) is enhanced by Coulombic attractions (non-specific adsorption) (eq. 2) [25]. Surface protonation and the number of positively charged sites decreases as the pH increases and therefore arsenic uptake should decrease [17, 26], but such effect was not observed in this study. The probable cause is that as pH increases and approaches the almost neutral pH_{pzc}, the second type of mechanism (eq. 3) becomes predominant.

Although at pH_f values higher than pH_{pzc} the surfaces exhibit a net negative charge due to the dissociation of proton of the hydroxide group [8], a significant adsorption still takes place. The adsorption of As(V) species is favoured electrostatically up to the pH_{pzc} of the adsorbents but beyond this point specific adsorption (ligand exchange) plays an important role [27].

When the pH is above 7, the negatively charged $HAsNO_4^{2-}$ becomes predominant, whereas the oxide surface also
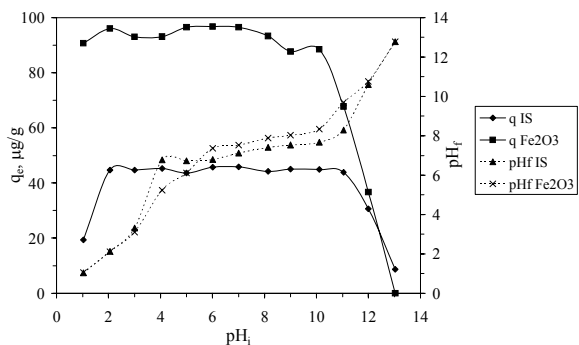
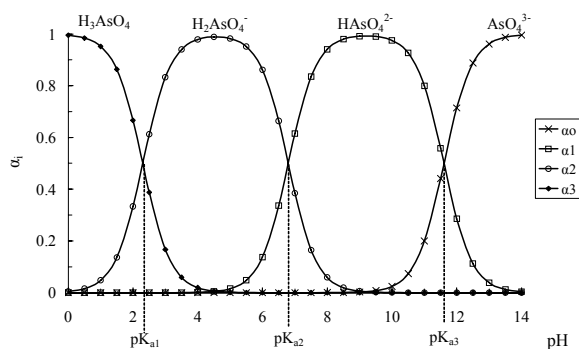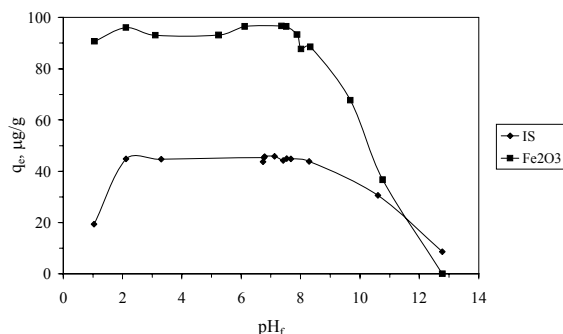Fig. 1. Influence of pH on As(V) adsorption onto IS and Fe_2O_3

Fig. 2. Distribution of As(V) species as a function of solution pH

becomes negatively charged; thus, electrostatic repulsion results in decreased adsorption [1, 8, 17]. Beyond pH 9.5 AsO_4^{3-} is formed (above 11.60 becomes predominant) and arsenic uptake decreases abruptly. Besides the electrostatic repulsion, the decrease of adsorption performance under basic conditions may also be caused by the fact that the hydroxyl groups become more plentiful on the surface of the adsorbents with the increase of pH, thereby limiting adsorption [1].

At pH values lower than 2.3, although H_3AsO_4 predominates over $H_2AsO_4^-$, $H_2AsO_4^-$ can be preferentially sorbed [26]. As(V) predominant species H_3AsO_4 is neutral and exhibits no electrostatic interactions with adsorbents surface, and $H_2AsO_4^-$ concentration is lower in this pH range. As a result, the arsenic uptake decreased. In the case of IS, the decrease in the extent of adsorption may be also attributed to the partial dissolution of the material and a consequent decrease in the number of adsorption sites [27, 28].
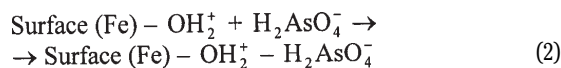
It was also observed that the initial pH of the suspensions was shifted during adsorption (fig. 1a). However, there is no regular trend in the change of pH. In the lower pH range of 2–7, the pH of the solutions shifted toward higher pH (i.e., basic) after adsorption for both adsorbents. Above pH 7, the shifts are toward the acidic region. One may notice that both $pH_f - pH_i$ plots show a plateau for pH_i values in the range 4-10 for IS and 6-10 for Fe_2O_3. The presence of such

a plateau indicates that the materials are ampholytes and behaved as acid–base buffers [1, 9, 21]. The plateau corresponds to the pH range where buffering of the materials surface occurs.
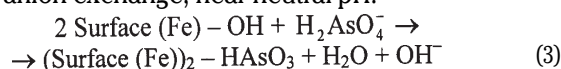
The shape of $pH_f - pH_i$ curves is similar to the $pH_f - pH_f$ plots obtained in view of pH_{pzc} determination for both materials, in the presence of NaCl as background electrolyte and without As(V) [9, 21]. In the presence of As(V), the pH value of the plateau shifted to higher values: from pH_{pzc} = 6.2 to pH_f ~7.2 for IS and from pH_{pzc} = 6.1 to pH_f ~7.8 for Fe_2O_3. This shift in pH may be attributed to the sorption reactions of As(V) which releases OH groups from sorbent (eq. 3), as a result of ligand exchange [1, 15].

The results demonstrate the operation of two types of mechanisms: (1) non-specific adsorption – surface complexion due to electrostatic attractive interaction (eq. 2), and (2) specific adsorption in a two-step process resulting in the formation of an inner-sphere bidentate surface complex (eq. 3) [1, 3]:

- surface complexion, $pH < pH_{pzc}$:

$$\text{Surface (Fe)} - OH_2^+ + H_2AsO_4^- \rightarrow$$
$$\rightarrow \text{Surface (Fe)} - OH_2^+ - H_2AsO_4^- \qquad (2)$$

- anion exchange, near neutral pH:

$$2\,\text{Surface (Fe)} - OH + H_2AsO_4^- \rightarrow$$
$$\rightarrow (\text{Surface (Fe)})_2 - HAsO_3 + H_2O + OH^- \qquad (3)$$

Influence of contact time and competing ions

The influence of contact time on the adsorption capacity towards As(V) of the two studied adsorbent materials is shown in figures 3 and 4. Initially sorption takes place more quickly (in the first four hours) and then it continued slowly up to the maximum sorption. The equilibrium was reached for most of the systems after 8 h, and thereafter the amount of adsorbed As(V) did not change significantly with the increase of contact time. For some systems, especially for ion concentration of 10 mg/L, the adsorption capacity still increased at 24 h contact time showing that the equilibrium was not reached. Curves are single, smooth and continuous, leading to saturation, and suggests the possible
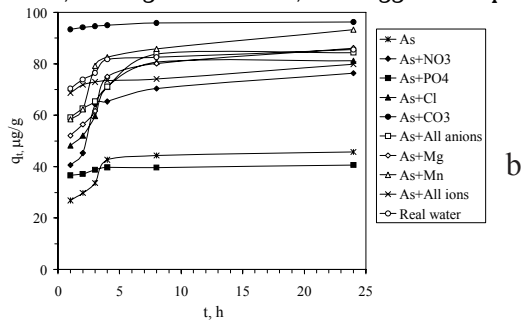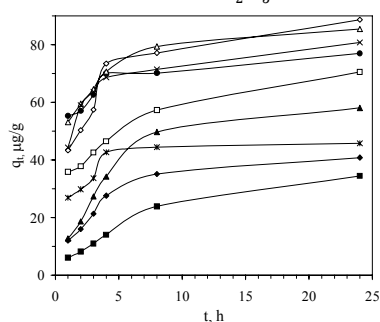

Fig. 3. Influence of contact time on As(V) adsorption capacity of IS
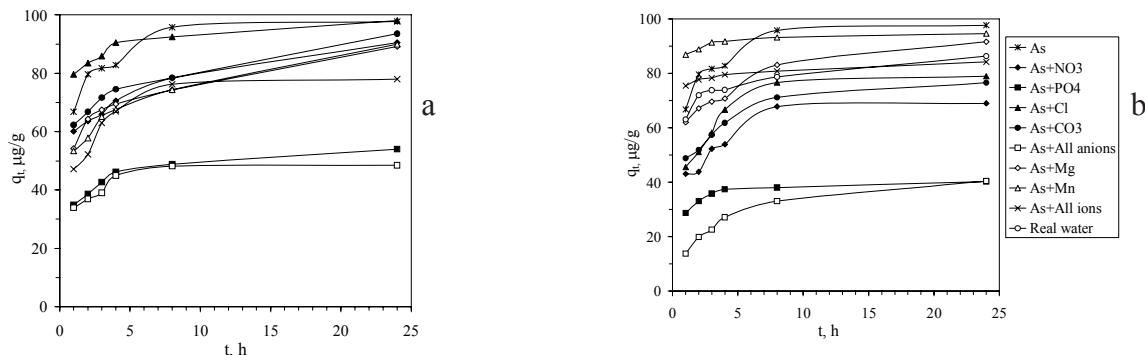(a) – ion concentration 10 mg/L; (b) – ion concentration 100 mg/L

Fig. 4. Influence of contact time on As(V) adsorption capacity of Fe_2O_3
(a) – ion concentration 10 mg/L; (b) – ion concentration 100 mg/L

monolayer coverage of As(V) on the IS and Fe_2O_3 surface [29].

The mechanism of solute transfer to the solid includes diffusion through the boundary layer or fluid film around the adsorbent particle and diffusion through the pores to the internal adsorption sites. At the onset of the process, the concentration gradient between the layer or film and the solid surface is large, and hence the transfer of solute onto the solid surface is faster. The fast diffusion on to the external surface is followed by slow diffusion into the intra particle matrix. In this stage, solute takes more time to transfer from the solid surface to internal adsorption sites through the pores. Finally, the equilibrium is attained [29].

Figure 3a shows that the individual presence of some of the studied species (Cl^-, CO_3^{2-}, Mg^{2+} and Mn^{n+}) in a concentration of 10 mg/L has a positive effect on the As(V) adsorption onto IS, the adsorption capacities reached after 24 h being higher than the value obtained for As(V) alone. The same effect is present when the solution contains the mixture of all studied anions or the mixture of all studied ions. For these systems, the pseudo-second order kinetic model predicted even higher values of the adsorption capacities (table 3), because after 24 h contact time the equilibrium was not reached. In the case of solutions containing NO_3^- and PO_4^{3-} respectively, although at 24 h contact time the experimental adsorption capacities were lower than the value reached for As(V), the pseudo-second order kinetic model predicted higher values and closer to the value obtained for As(V) alone.

At an ionic species concentration of 100 mg/L, after 24 h contact time the equilibrium was reached for most systems (fig. 3b). The experimental adsorption capacities were higher than for the 10 mg/L concentration in the systems containing Cl^-, CO_3^{2-}, NO_3^-, Mn^{n+} and the mixture of all anions. For systems containing Mg^{2+} and the mixture of all ions, the values were almost the same as for 10 mg/L. For 100 mg/L PO_4^{3-} was reached a lower adsorption capacity (40.7 μg/L) than the value predicted by the pseudo-second order kinetic model in the case of 10 mg/L solution (47.0 μg/L) and lower than that for the As(V) alone (45.8 μg/L). The experimental results show that in the case of IS used as adsorbent material, all studied ions had a positive influence on As(V) uptake increasing the adsorption capacity, with the exception of PO_4^{3-} which lowered the adsorption capacity, but only for the higher concentration (100 mg/L). This observation is consistent with literature data, which indicate that arsenic adsorption is strongly decreased by the presence of phosphate, because of the competition for the binding sites of the adsorbent material between arsenic and phosphate. These ions compete because of the structural resemblances – they are tetrahedral anions that form inner-sphere complexes via a ligand-exchange mechanism with the

functional groups at the surfaces of iron containing materials such as iron oxides and hydrous iron oxides [5, 11-15].

In the case of IS, the decrease of the adsorption capacity was not strong, probably due to the fact that IS has a complex composition and PO_4^{3-} may interact with some of the IS components. Ionic species, CO_3^{2-}, Mg^{2+} and Mn^{n+} had the most positive influence on As(V) uptake by the IS. The cooperative effect of metal cations such as Ca^{2+}, Mg^{2+} and Fe^{3+} on adsorption of As(V) and As(III) was previously observed by other researchers and could be attributed to the favorable electrostatic effects, as the adsorption of metal cations increases the amount of positive charge on the adsorbent surface [5, 7, 20]. Previously published studies found that as a potential competitor of arsenic, CO_3^{2-} has a negligible to moderate effect [16, 17], a moderate to notable effect [18] or equivocal results were obtained [19]. In our study, we found that the individual presence of CO_3^{2-} had a positive effect on As(V) uptake by IS, especially for higher concentration (100 mg/L), when the highest adsorption capacity was reached (96.3 μg/L).

As(V) uptake onto IS from the real underground water (~85μg/g) was close to that reached for the both synthetic solutions (~80μg/g), and was much higher than the value obtained for the solution containing As(V) alone (~45 μg/g) (fig. 3a).

Figure 4a,b shows that for both studied concentrations, the presence of any ionic species (either in single or multicomponent solution) has a negative effect on As(V) adsorption onto Fe_2O_3. For some of the species, after 24 h contact time the equilibrium was not reached, especially for the lower concentration. At higher contact time an increase in As(V) uptake in the presence of these species may be expected and the values to become closer to that obtained for arsenic alone (~ 97 μg/g).

The most negative impact on As(V) uptake was found for the presence of and for the solutions containing all anions. In the case of Fe_2O_3 as opposite to IS, the results are consistent with literature data, which indicate that arsenic adsorption is strongly decreased by the presence of phosphate.

The effect of cationic species on As(V) adsorption onto Fe_2O_3 is less evident. Their influence compensates the negative effect of PO_4^{3-} and for the solutions containing all ions and for the real water were reached good adsorption capacities (~84 μg/g for 100 mg/L solution and ~86 μg/g, respectively).

Comparing the efficiencies of the adsorbent materials used in this study, although Fe_2O_3 proved to be more efficient than IS for the adsorption of As(V) from solutions containing only this species, the presence of other species was benefic for the adsorption of As(V) onto IS from solutions containing all ions and real underground water. The values of the
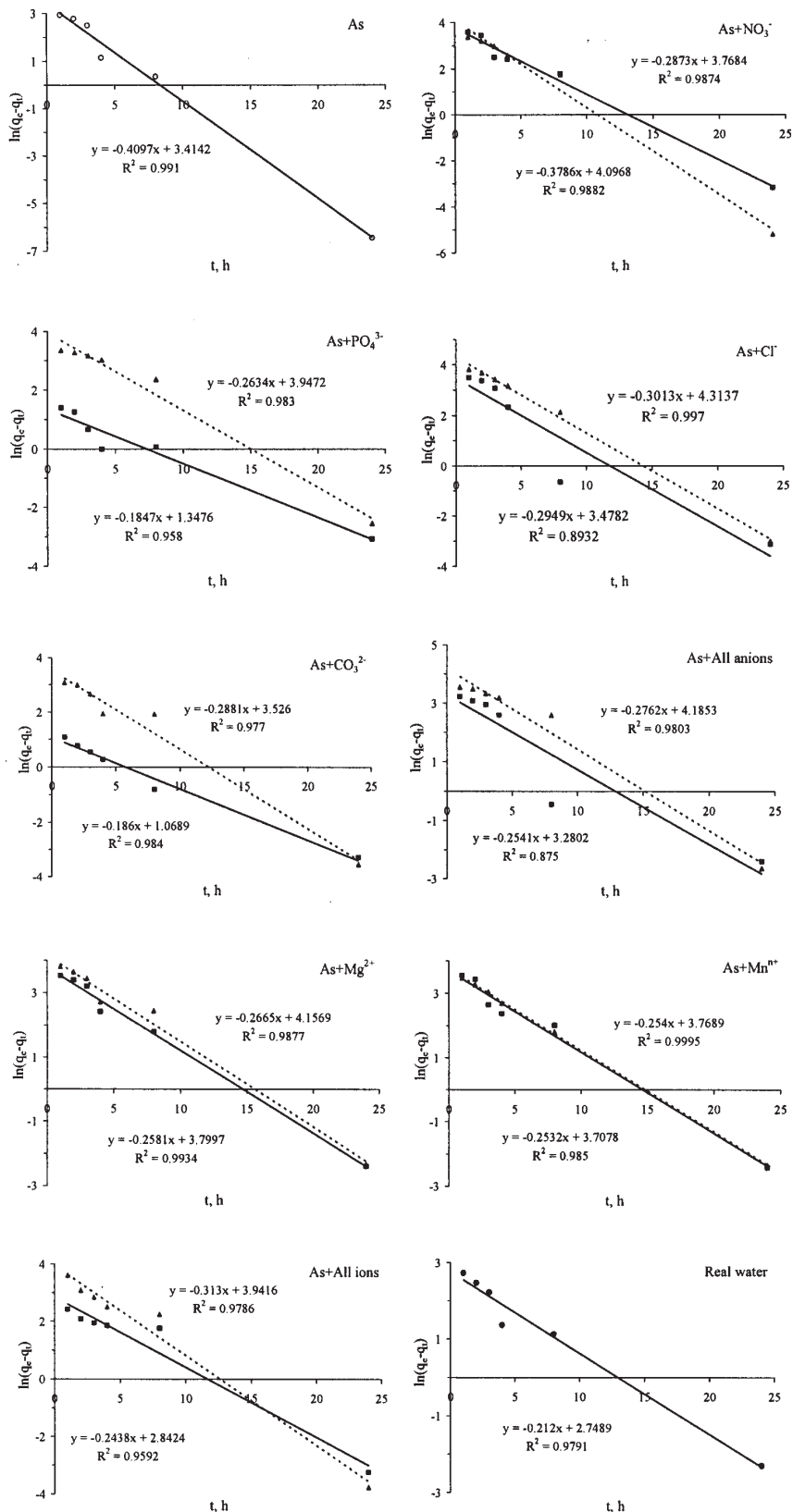
Fig. 5. Pseudo-first-order kinetic plots for
As(V) adsorption onto IS
(- ▲ -) 10 mg/L; (-■-) 100 mg/L

adsorption capacities reached in these cases were very close for both adsorbent materials.

Kinetic studies

Various models can describe the transient behaviour of a batch adsorption process. Most of these have been reported as pseudo-first-order and some as pseudo-second-order kinetic processes. In order to express the kinetics of arsenic adsorption on the two studied adsorbent materials the data were analyzed using both models.

The pseudo-first-order kinetic model based on the solid capacity and proposed by Lagergren can be used to determine the rate constant for the adsorption process and the integrated form is expressed by the following equation [1, 9, 10]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (4)$$

where q_t and q_e represent the amounts of the arsenic adsorbed on the iron oxide at time t and at equilibrium time, respectively, $\mu g/g$; k_1 is the specific adsorption rate constant, h^{-1}.

The linear form of the pseudo-second-order rate expression of Ho and McKay, based on the solid phase sorption, is given by [1, 9, 10, 30]:
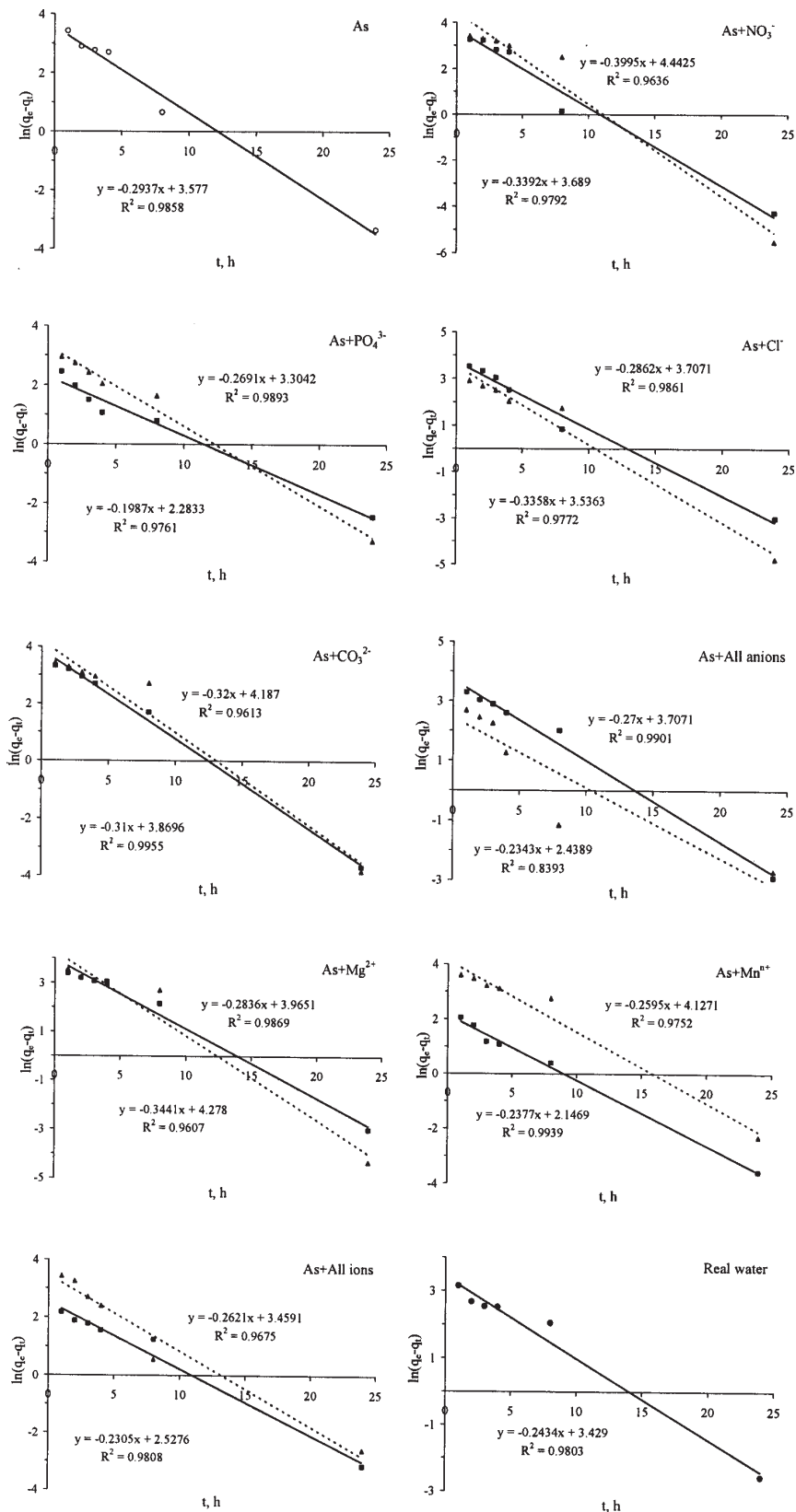
Fig. 6. Pseudo-first-order kinetic plots for As(V) adsorption onto Fe_2O_3 (- ▲ -) 10 mg/L; (-■-) 100 mg/L

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \qquad (5)$$

where $h = k_{s2} \cdot q_e^2$; k_2 is the pseudo-second-order constant, $h^{-1}(\mu g/g)^{-1}$; q_t and q_e have the meanings mentioned before.

To assess the extent to which the kinetic equations fit the experimental data, two different error functions were examined.

The normalized standard deviation, Δq (%), was estimated using the equation [9, 31, 32]:

$$\Delta q(\%) = 100 \sqrt{\frac{1}{p-1} \sum_{i=1}^{p} \left(\frac{q_{exp} - q_{calc}}{q_{exp}} \right)_i^2} \qquad (6)$$

where q_{exp} is the experimentally determined adsorption capacity ($\mu g/g$), q_{calc} is the adsorption capacity calculated according to the model equation ($\mu g/g$) and p is the number of experimental data points.

The average relative error E (%), which minimizes the fractional error distribution across the entire concentration range, was estimated via the equation [9, 33, 34]:

Table 1
KINETIC PARAMETERS FOR As(V) SORPTION ONTO IS, PSEUDO-FIRST-ORDER KINETIC MODEL

Sample	Ion concentration 10 mg/L						Ion concentration 100 mg/L					
	q_e, exp., µg/g	q_e, kinetic plot, µg/g	k_1, h^{-1}	R^2	Δq, %	E, %	q_e, exp., µg/g	q_e, kinetic plot, µg/g	k_1, h^{-1}	R^2	Δq, %	E, %
As	45.8	30.4	0.4097	0.9910	47.1	22.2						
As+ NO$_3^-$	40.8	60.1	0.3786	0.9882	81.0	65.6	76.4	43.3	0.2873	0.9874	38.7	62.2
As+ PO$_4^{3-}$	34.4	51.8	0.2634	0.9830	135	183	40.7	3.85	0.1847	0.9580	104	108
As+ Cl$^-$	58.1	74.7	0.3013	0.9970	60.6	36.7	81.2	32.4	0.2949	0.8932	76.2	58.1
As+ CO$_3^{2-}$	77.0	34.0	0.2881	0.9770	74.9	56.2	96.3	2.91	0.1860	0.9840	108	116
As+All anions	70.5	65.7	0.2762	0.9803	28.4	8.01	84.3	26.6	0.2541	0.8750	85.8	73.7
As+Mg^{2+}	88.6	63.9	0.2665	0.9877	47.8	22.8	86.1	44.7	0.2581	0.9934	68.6	47.1
As+Mn^{n+}	85.4	43.3	0.2540	0.9995	70.4	49.5	93.2	40.8	0.2532	0.9850	76.4	58.3
As+All ions	80.8	51.5	0.3130	0.9786	55.5	30.9	79.9	17.2	0.2438	0.9592	94.6	89.5
Real water	85.5	15.6	0.2120	0.9791	97.7	95.4						

Table 2
KINETIC PARAMETERS FOR As(V) SORPTION ONTO Fe$_2$O$_3$, PSEUDO-FIRST-ORDER KINETIC MODEL

Sample	Ion concentration 10 mg/L						Ion concentration 100 mg/L					
	q_e, exp., µg/g	q_e, kinetic plot, µg/g	k_1, h^{-1}	R^2	Δq, %	E, %	q_e, exp., µg/g	q_e, kinetic plot, µg/g	k_1, h^{-1}	R^2	Δq, %	E, %
As	97.7	35.8	0.2937	0.9858	80.9	65.4						
As+ NO$_3^-$	90.5	85.0	0.3995	0.9636	27.3	7.45	69.0	40.0	0.3392	0.9792	58.0	33.7
As+ PO$_4^{3-}$	54.0	27.2	0.2691	0.9893	70.2	49.2	40.2	9.81	0.1987	0.9761	93.8	88.1
As+ Cl$^-$	98.1	34.3	0.3358	0.9772	81.6	66.6	79.0	40.7	0.2862	0.9861	66.9	44.7
As+ CO$_3^{2-}$	93.6	65.8	0.3200	0.9613	50.0	25.0	76.6	47.9	0.3100	0.9955	56.7	32.2
As+All anions	48.4	11.5	0.2343	0.8393	92.8	86.1	40.4	40.7	0.2700	0.9901	15.4	2.37
As+Mg^{2+}	89.2	72.1	0.3441	0.9607	39.1	15.3	91.7	52.7	0.2836	0.9869	63.1	39.8
As+Mn^{n+}	90.0	62.0	0.2595	0.9752	53.5	28.6	94.7	8.56	0.2377	0.9939	104	107
As+All ions	77.9	31.8	0.2621	0.9675	77.9	60.7	84.2	12.5	0.2305	0.9808	99.7	99.3
Real water	86.3	30.8	0.2434	0.9803	83.8	70.3						

$$E(\%) = \frac{100}{p-1} \cdot \sum_{i=1}^{p} \left(\frac{q_{calc} - q_{exp}}{q_{exp}} \right)^2_i , \qquad (7)$$

Figures 5 and 6 present the plots of $\ln(q_e-q_t)$ versus t for As(V) adsorption onto IS and Fe$_2$O$_3$ respectively, for all studied solutions. The slopes and intercepts of the plots are used to estimate the pseudo-first-order rate constant (k_1) and the equilibrium adsorption capacity (q_e), respectively. Tables 1 and 2 summarize the values of the kinetic parameters, together with the regression coefficients (R^2) and the estimated errors obtained from the pseudo-first-order kinetic plots for both studied adsorbent materials.

In the case of the pseudo-second-order kinetic model, a plot of t/q_t versus t should yield a straight line. From the intercept and slope (figs. 7 and 8) are calculated the second-order rate constant (k_2) and the equilibrium adsorption capacity (q_e). The values of the kinetic parameters, together with the regression coefficients (R^2) and the estimated errors obtained for both studied adsorbent materials from the pseudo-second-order kinetic plots are summarized in tables 3 and 4, respectively.

The values of the correlation coefficient R^2 were higher and closer to 1 and the estimated errors were smaller in the case of the pseudo-second-order kinetic model. For the pseudo-first-order model there was a difference between the q_e values experimentally obtained and the values calculated from the kinetic plots. In the case of the

Table 3
KINETIC PARAMETERS FOR AS(V) SORPTION ONTO IS, PSEUDO-SECOND-ORDER KINETIC MODEL

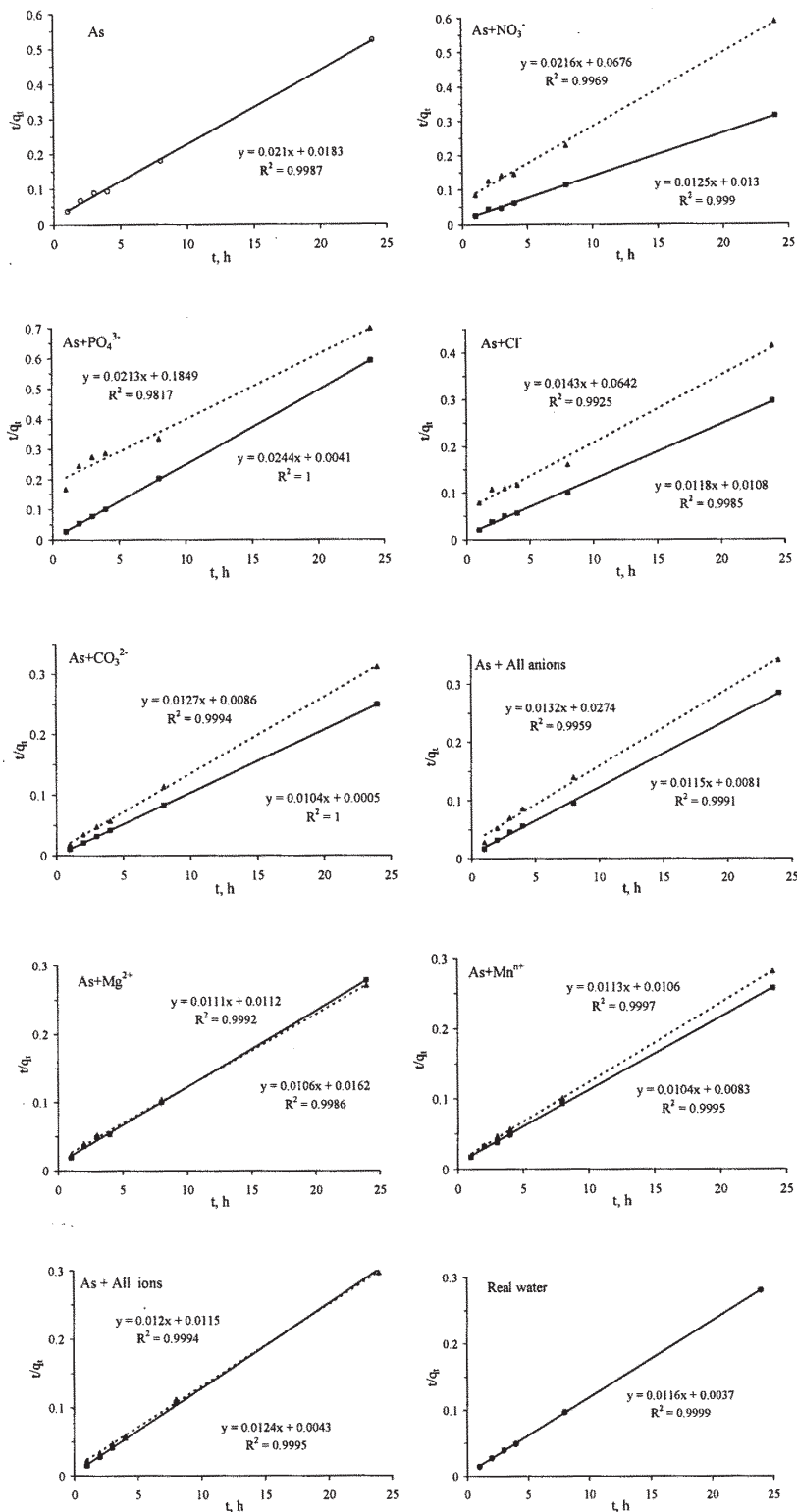| Sample	Ion concentration 10 mg/L						Ion concentration 100 mg/L					
	q_e, exp., µg/g	q_e, kinetic plot, µg/g	k_2, h^{-1} (µg/g)$^{-1}$	R^2	Δq, %	E, %	q_e, exp., µg/g	q_e, kinetic plot, µg/g	k_2, h^{-1} (µg/g)$^{-1}$	R^2	Δq, %	E, %
As	45.8	47.6	0.02402	0.9987	8.10	0.66						
As+ NO$_3^-$	40.8	46.4	0.006870	0.9969	7.82	0.61	76.4	79.7	0.01216	0.9990	8.25	0.68
As+ PO$_4^{3-}$	34.4	47.0	0.002453	0.9817	10.9	1.20	40.7	40.9	0.1458	0.99996	2.20	0.05
As+ Cl$^-$	58.1	69.7	0.003204	0.9925	8.61	0.74	81.2	84.7	0.01294	0.9985	8.07	0.65
As+ CO$_3^{2-}$	77.0	78.9	0.01874	0.9994	7.32	0.54	96.3	96.4	0.2068	0.99999	0.75	0.006
As+All anions	70.5	75.9	0.006337	0.9959	14.8	2.18	84.3	87.0	0.01630	0.9991	7.70	0.59
As+Mg^{2+}	88.6	94.0	0.006980	0.9986	8.54	0.73	86.1	89.7	0.01111	0.9992	8.14	0.66
As+Mn^{n+}	85.4	88.6	0.01199	0.9997	6.67	0.44	93.2	96.2	0.01311	0.9995	6.39	0.41
As+All ions	80.8	83.7	0.01238	0.9994	3.39	0.11	79.9	80.6	0.03601	0.9995	6.33	0.40
Real water	85.5	86.6	0.03655	0.9999	3.28	0.11						

Fig. 7. Pseudo-second-order kinetic plots for
As(V) adsorption onto IS
(-▲-) 10 mg/L; (-■-) 100 mg/L

Table 4
KINETIC PARAMETERS FOR As(V) SORPTION ONTO Fe_2O_3, PSEUDO-SECOND-ORDER KINETIC MODEL

Sample	Ion concentration 10 mg/L						Ion concentration 100 mg/L					
	q_e, exp., $\mu g/g$	q_e, kinetic plot, $\mu g/g$	k_2, h^{-1} $(\mu g/g)^{-1}$	R^2	Δq, %	E, %	q_e, exp., $\mu g/g$	q_e, kinetic plot, $\mu g/g$	k_2, h^{-1} $(\mu g/g)^{-1}$	R^2	Δq, %	E, %
As	97.7	100	0.01700	0.9996	3.99	0.16						
As+ NO_3^-	90.5	94.0	0.009610	0.9982	12.3	1.51	69.0	72.1	0.01378	0.9985	9.46	0.89
As+ PO_4^{3-}	54.0	55.7	0.02119	0.9996	6.34	0.40	40.2	40.9	0.05372	0.9999	1.47	0.02
As+ Cl^-	98.1	99.5	0.02434	0.9998	5.38	0.29	79.0	82.5	0.01229	0.9992	6.42	0.41
As+ CO_3^{2-}	93.6	96.7	0.009755	0.9973	12.0	1.44	76.6	79.6	0.01274	0.9995	8.46	0.72
As+All anions	48.4	49.7	0.03701	0.9994	5.30	0.28	40.4	44.7	0.008596	0.9992	5.39	0.29
As+ Mg^{2+}	89.2	92.5	0.009439	0.9973	10.8	1.16	91.7	95.0	0.01087	0.9989	10.9	1.19
As+ Mn^{n+}	90.0	94.2	0.007805	0.9972	12.2	1.48	94.7	95.1	0.08004	0.99999	1.50	0.02
As+All ions	77.9	80.8	0.01524	0.9994	5.42	0.29	84.2	84.9	0.05010	0.9999	4.24	0.18
Real water	86.3	88.1	0.01875	0.9994	6.84	0.47						
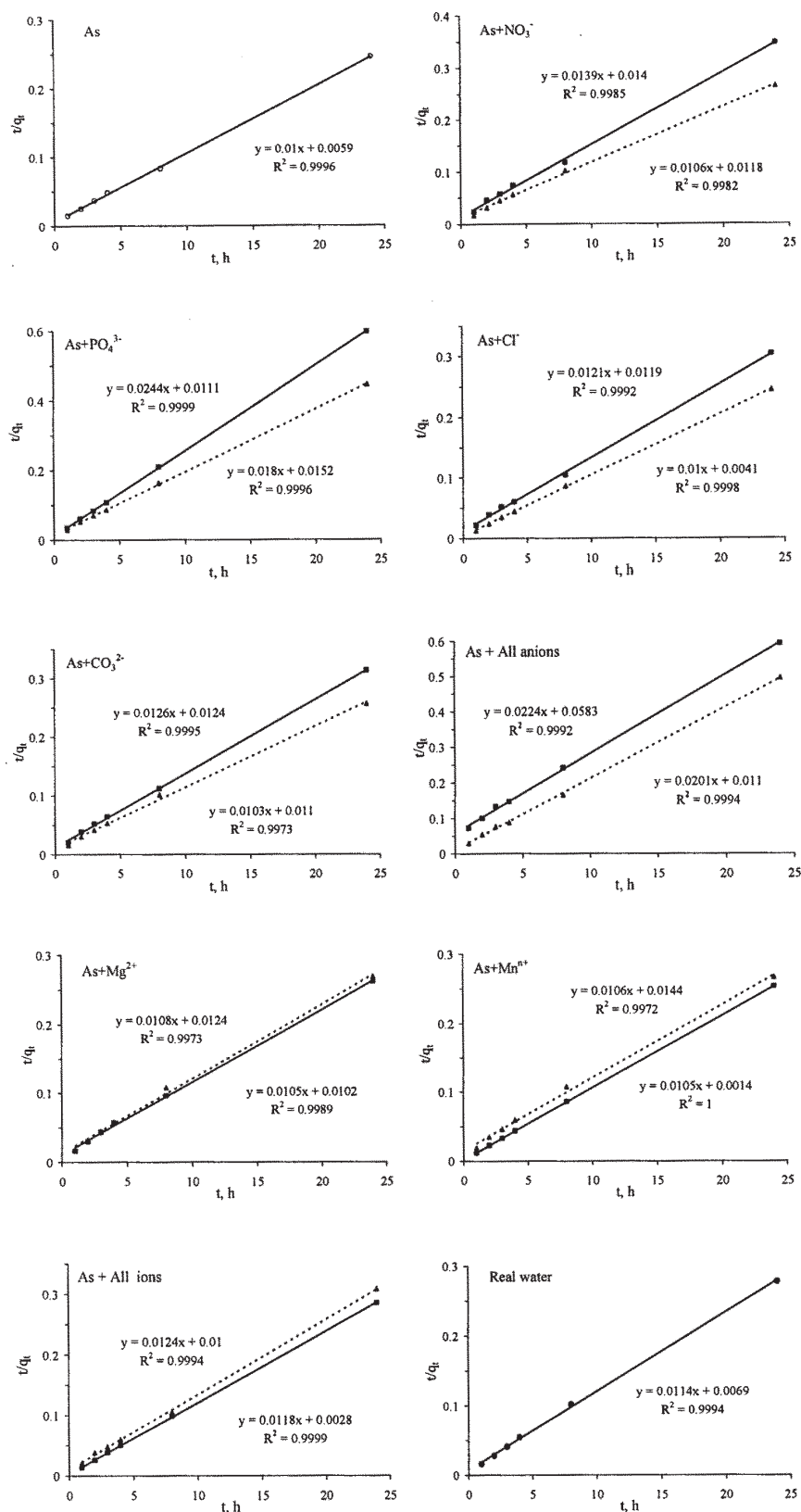
Fig. 8. Pseudo-second-order kinetic plots for
As(V) adsorption onto Fe_2O_3
$(-\blacktriangle-)$ 10 mg/L; $(-\blacksquare-)$ 100 mg/

pseudo-second order model, the theoretically predicted equilibrium adsorption capacities are close to the experimentally determined values. This indicates that the kinetics of As (V) removal through adsorption onto both adsorbent materials is well explained and approximated by the pseudo-second-order kinetic model. This kinetic model is used to describe chemisorption involving valency forces through the sharing or exchange of electrons between the adsorbent and adsorbate as covalent forces, and ion exchange.

Conclusions

In the present paper is investigated the effect of the presence of some competing anionic (NO_3^-, PO_4^{3-}, Cl^- and CO_3^{2-}) and cationic (Mg^{2+}, Mn^{n+}) species on the adsorption of arsenic (V) on two iron containing materials: a waste material and a synthetic material. The waste material was an iron containing sludge (IS) resulting from hot-dip galvanization. The synthetic material was Fe_2O_3 obtained through annealing of $Fe(COO)_2 \cdot 2H_2O$ at $550°C$. For the studies, a synthetic solution containing 100 μg As(V)/L was used.

The effect of pH on As(V) adsorption performance was studied in the 2-12 pH range. The adsorption of As(V) over the initial pH range 2-11 for IS and 2-8 for Fe_2O_3 was not strongly dependent on pH, which is highly advantageous for practical operation. The results demonstrated that in adsorption of As(V) onto both IS and Fe_2O_3 operate two types of mechanisms: (1) non-specific adsorption – surface complexion due to electrostatic attractive interaction, and (2) specific adsorption in a two-step process resulting in the formation of an inner-sphere bidentate surface complex.

The influence of ionic species was investigated in single and in multicomponent competing ion solutions at two concentrations: 10 mg/L and 100 mg/L, respectively. Adsorption experiments were also carried out on a real groundwater containing the studied ions. The adsorption experiments were performed at different contact times (1, 2, 3, 4, 8 and 24 h).

The experimental results showed that the presence of any ionic species (either in single or multicomponent solution) has a negative effect on As(V) adsorption onto Fe_2O_3. The most negative effect was observed for PO_4^{3-} solutions and solutions containing all studied anions, due to competition of As(V) and PO_4^{3-} for binding sites.

Only PO_4^{3-} showed a negative effect on the adsorption of As(V) onto IS, but this effect was much diminished compared with the adsorption onto Fe_2O_3, due to the interaction of PO_4^{3-} with some components of the IS. The other studied ions, in single and in multicomponent solutions had a positive effect on the adsorption of As(V) onto IS.

Comparing the efficiencies of the adsorbent materials used in this study, although Fe_2O_3 proved to be more efficient than IS for the adsorption of As(V) from solutions containing only this species (adsorption capacities of 97 μg/g and 45 μg/g, respectively), the presence of other species was benefic for the adsorption of As(V) onto IS from solutions containing all ions and the real underground water. The values of the adsorption capacity reached in these cases were very close for both adsorbent materials (~85 μg/g for the real water and ~80 μg/g for the all ions synthetic solution).These results indicate that although IS is a waste, it has the same efficiency as the synthetic, more expensive Fe_2O_3, and would be a suitable adsorbent for the removal of As(V) ions from underground waters.

The experimental data were fitted to the pseudo-first-order and pseudo-second-order kinetic models. It was found that the adsorption process followed a pseudo-second-order kinetics and the theoretically predicted equilibrium adsorption capacities were close to the experimentally determined values.

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