Carbonate effects and pH-dependence of uranium sorption onto bacteriogenic iron oxides: Kinetic and equilibrium studies

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Abstract

The removal of U(VI) from groundwaters by adsorption onto bacteriogenic iron oxides (BIOS) has been investigated under batch mode. The adsorbent dosage, the uranium concentration, the concentration of carbonate and the use of a real groundwater spiked with uranium comprised the examined parameters. In addition, the effect of pH was examined in two different water matrixes, i.e., in distilled water and in real groundwater. Equilibrium studies were carried out to determine the maximum adsorption capacity of BIOS and the data correlated well with the Langmuir and Freundlich models. The presence of carbonate affected adversely the adsorption of U(VI) onto BIOS. The maximum adsorption capacity of BIOS was $9.25 \, mg \, g^{-1}$ at 0.1 mM carbonate concentration and decreased to $6.93 \, mg \, g^{-1}$ at 0.5 mM carbonate concentration, whereas at carbonate concentration of 2 mM practically no adsorption occurred. The data were further analyzed using the pseudo-second order kinetic equation, which fitted best the experimental results. The initial adsorption rate (h) was found to increase with decreasing the concentration of carbonate in all cases. When experiments were accomplished in the absence of carbonate, the pH values did not have an effect on the adsorption of U(VI). However, the extent of U(VI) adsorption was strongly pH-dependent when the experiments were carried out in the real groundwater. The maximum adsorption capacity increased sharply as the pH decreased and optimum removal was obtained in the pH range 3.2–4.0, thus bacteriogenic iron oxides can found application in the removal of U(VI) by adsorption from low pH or low carbonate waters.
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1. Introduction

Uranium is a significant contaminant of water and soil at sites of uranium mining, milling and at environmental locations where uranium has accumulated through natural geologic or hydrologic processes. In particular, uranium contamination of ground waters is a matter of great concern because of the high toxicity of dissolved uranium and its worldwide occurrence in ground waters. Nephritis is the primary chemically induced effect of uranium in humans, while it is also considered as carcinogenic, causing bone cancer. Uranium was detected in groundwaters in several areas across the world such as in Norway, Finland, Germany, Greece, USA, Canada and Australia [1].

The recommended maximum admissible concentration (MAC) for uranium in drinking water from the World Health Organisation is currently $15 \, \mu g \, L^{-1}$ [1].

In oxic waters uranium is present in its hexavalent form. The hexavalent uranium is mainly present as the uranyl ion (UO_2^{2+}) or with its hydroxy complexes, but in the presence of other anions such as carbonate, phosphate and sulfate, uranyl forms complexes and therefore its speciation is greatly affected by the groundwater composition [2]. Several methods have been examined for the removal of uranium such as the use of cation exchange, anion exchange, granular ferric hydroxide, ultrafiltration, activated carbon and the use of titanium dioxide. Only titanium dioxide and anion exchange were able in removing uranium (i.e., from 10–$20 \, \mu g \, L^{-1}$ initial uranium concentration to below $1 \, \mu g \, L^{-1}$) [3].

The use of biological iron oxidation for the removal of uranium was also unable in removing uranium (data not presented). In particular, in an attempt to remove uranium simultaneously with arsenic by the application of biological oxidation

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of dissolved iron from groundwaters and thus by sorption onto the produced biogenic iron oxides, no removal of U(VI) was achieved, even at very low initial uranium concentrations, i.e., 10–$20\,\mu g\,L^{-1}$ and relatively high Fe(II) concentrations (i.e., $2.8\,mg\,L^{-1}$).

However, it is well established that the mobility of uranium in subsurface environments is generally controlled by the interactions with solid surfaces and in particular with iron oxides. The adsorption of U(VI) on different iron oxides, such as ferrihydrite, hematite and goethite has been well documented [4–7]. Nevertheless, most of these studies used synthetic iron oxides and therefore, the reported results are not completely representative of the subsurface environment. Iron oxides in the subsurface, are usually poorly ordered, containing amounts of silicate and organic mater as well as partly degraded bacterial cells. These materials, which are called bacteriogenic iron oxides, comprise effectively a sorbent phase for dissolved metals [8]. They have been found to remove efficiently arsenic from groundwaters during the biological oxidation of Fe(II) [9]. In other studies it was reported that U(VI) was retained on the surface of BIOS collected from the subsurface [10] and furthermore, it was found that uranium was retained as U(VI) on bacteriogenic iron oxides, produced during anaerobic bioxidation of Fe(II) [11].

Therefore, in the present study, U(VI) sorption was investigated under batch mode, to determine the parameters affecting the sorption of uranium onto bacteriogenic iron oxides and to establish the conditions, under which U(VI) can be removed by the use of BIOS. To the best of our knowledge, the carbonate effects on the U(VI) sorption by BIOS and the pH dependence of this procedure have not been previously investigated, particularly in dilute uranium solutions, i.e., from concentrations as low as $2.1 \times 10^{-7}\,M$.

To achieve the goals of our study, the following parameters were examined: sorption time, solution pH, the initial U(VI) concentration, the adsorbent dosage, the groundwater composition and the carbonate concentration. Real groundwater was spiked with uranium, in order to simulate better uranium-contaminated groundwaters. Further experiments have been performed using distilled water spiked with carbonate to evaluate separately the effect of most commonly anion found in groundwater on the U(VI) sorption kinetics. The experimental data were correlated to the pseudo second order sorption kinetic model and the corresponding kinetic parameters were determined. The software program MINEQL$^+$ [12] was used to elucidate the speciation of uranium in the examined groundwater.

2. Materials and methods

2.1. Materials

All chemicals used were reagent-grade and all solutions were prepared with distilled water. All glassware was acid-washed and rinsed with distilled water. Experiments were carried out either with distilled water (DW) or with the Marienfelde, Berlin, groundwater (GW). The composition of the groundwater used in this study is given in Table 1. U(VI) stock solution of 100 mg/L was prepared by uranyl nitrate hexahydrate.

Table 1
Composition of Marienfelde groundwater, used in the U(VI) removal experiments

Ion composition	Concentration (mg L^{-1})
Na$^+$	44
K$^+$	2.4
NH$_4^+$	0
Ca^{2+}	205
Mg^{2+}	18
Fe(tot)	0
Mn^{2+}	0
Sr^{2+}	0.3
Cl$^-$	100
SO$_4^{2-}$	245
NO$_3^-$	0.8
PO$_4^{3-}$	0
HCO$_3^-$	325

2.2. Bacteriogenic iron oxides (BIOS)

The BIOS were obtained from a drinking water treatment unit, operating at the Research Site Marienfelde of the Federal Environmental Agency in Berlin, Germany. The unit is used to remove iron and manganese from groundwater. The treatment is based on the biological oxidation of iron and manganese, by the indigenous bacteria *Gallionella ferruginea* and *Leptothrix ochracea*. These bacteria accelerate the oxidation of iron and manganese, which is then hydrolyzed and the insoluble products are removed from water by filtration [i.e., 13,14]. During the backwashing of the filters, the excessive quantity of iron oxides was removed; part of backwashing sludge was collected, dried and washed. The residual product comprised the so-called bacteriogenic iron oxides (BIOS). BIOS consisted mainly of iron (37% in dry weight basis) and the XRD pattern indicated an entirely amorphous material. Under the scanning electron microscope, it was evident that iron oxides were incorporated in the bacterial structure of *G. ferruginea* and *L. ochracea* [14]. These results were consistent with previous investigations, and indicated that iron in the BIOS was only in the form of amorphous ferrihydrite [7].

2.3. Batch adsorption studies

Aliquots of uranium stock solution were spiked either in the groundwater or in distilled water to reach the desired final U(VI) concentration. The pH was adjusted and afterwards the aliquots were transferred to 250 mL conical flasks for the batch experiments, which were performed at ambient laboratory temperature ($20 \pm 1\,^\circ C$). Immediately before the beginning of the experiments, the quantity of BIOS was introduced in the aliquots and the batch tests were afterwards performed in a shaker. After the end of the experiments the aliquots were immediately filtered though 0.45 μm filters, the final pH of the filtrate was measured and afterwards the filtrate was stored with 2% HNO$_3$ and analyzed with ICP-MS (detection limit = 0.1 μg L^{-1}). The experiments were performed in open-air system to simulate conditions prevailing in pump and treat groundwater treatment methods.

To examine the effect of sorbent quantity, series of experiments was performed by varying the sorbent dosage, whereas afterwards by keeping the sorbent dosage constant, the effect of pH, carbonate concentration and of other parameters was examined. The pH was adjusted by addition of HCL or NaOH and the variation of carbonate concentration was performed by diluting different amounts of $NaHCO_3$ in distilled water. The effect of groundwater composition was examined by mixing groundwater with distilled water in different ratios and thus changing the concentrations of major groundwater components such as carbonate, calcium, magnesium, sulfate, chloride. All experimental series were performed at least twice and standard deviations were estimated and incorporated in the figures.

The equilibrium isotherms were determined by varying the initial uranium concentration in the range $30–5000\,\mu g\,L^{-1}$ and using a reaction time of 24 h, which was found sufficient to reach equilibrium (data not presented). The uranium uptake (q) was calculated by the following mass balance equation:

$$q = \frac{(C_0 - C_t)V}{w1000},\qquad(1)$$

where q is the metal uptake (mg metal/g of BIOS), C_0 (mg or $\mu g\,L^{-1}$) the initial metal concentration, C_t (mg or $\mu g\,L^{-1}$) the metal concentration at any time, V the volume of the solution and w is the mass of the adsorbent in grams.

2.4. Zeta potential measurements

Electrokinetic measurements were performed, using a zeta-potential analyzer (Rank Brothers Ltd., UK). All mobility measurements were carried out at ambient laboratory temperature ($20 \pm 1\,°C$). The solution pH was adjusted by adding various amounts of either 0.1 M NaOH or 0.1 M HCl. Twenty independent measurements were performed for each experimental condition and the zeta potential values were determined using the smoluchowski equation.

3. Results and discussion

3.1. Effect of adsorbent dosage

The sorption of U(VI) was initially examined onto BIOS at different adsorbent dosages ($0.1–5\,g\,L^{-1}$) for constant uranium concentration (2.1×10^{-7} M). It was found that the percentage uranium removal increased by increasing the BIOS concentration until the value of $0.5\,g\,L^{-1}$. After this concentration the removal remained constant (data not presented). This was attributed to the fact, that adsorption was optimum for the specific U(VI) initial concentration. Therefore, by increasing the adsorbent dosage, the effective surface area increased; up to the concentration of $0.5\,g\,L^{-1}$. Therefore, for the rest of the experiments an adsorbent dosage of $1\,g\,L^{-1}$ was used, to exclude entirely a possible effect caused from the adsorbent dosage.
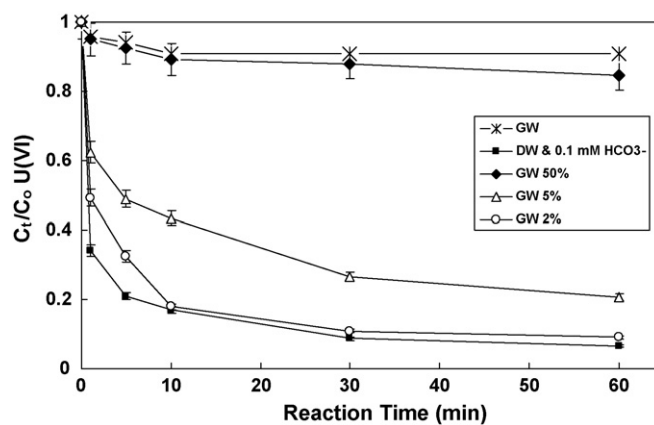

Fig. 1. Kinetics of U(VI) sorption onto BIOS at different ratios of groundwater in distilled water. Experimental conditions: initial U(VI) $= 2.1 \times 10^{-7}$ M; pH 7.0; adsorbent dosage $= 1\,g\,L^{-1}$.

3.2. Kinetics of U(VI) sorption onto BIOS in the real groundwater

The previous results indicated that the sorption of U(VI) onto BIOS was reasonably efficient, when the optimum adsorbent dosage was used, i.e., over $0.5\,g\,L^{-1}$. Nevertheless, these results were accomplished in distilled water with 0.1 M NaCl as the background electrolyte. To obtain a realistic view of the effectiveness of the BIOS in adsorbing U(VI), kinetic experiments have been performed by using the Marienfelde groundwater (Table 1) as water matrix for the experiments. The results of the kinetic experiments of various ratios of groundwater in distilled water are illustrated in Fig. 1.

Fig. 1 clearly shows that the sorption of U(VI) decreased, as the groundwater ratio increased. Particularly, when the groundwater was exclusively used as the water matrix (i.e., not mixed with distilled water), then the removal of U(VI) was very low. To explain these results, the composition of the groundwater was taken into consideration, since it contains relative high concentrations of carbonate, sulfate and chloride.

In the experiments carried out by distilled water, the major U(VI) species at neutral pH range are UO_2OH^+, $(UO2)_3(OH)_5^+$ in the absence of carbonate. Since the major aqueous species at pH > 5 in the absence of carbonate are uranyl-hydroxide complexes, it was assumed that these hydroxide complexes are adsorbed on the surface of iron oxides and cause the removal of U(VI) in the absence of carbonate at pH 7.0, as shown in Fig. 1.

However, when the real groundwater was used, in pH 7.0, the major U(VI) species change drastically, as shown in the speciation diagram of U(VI) in the groundwater (Fig. 2). At neutral pH, carbonate species of uranium such as $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ prevail. At lower pH values the complexes of sulfate of the type $UO_2(SO_4)$ appear. Consequently, in the pH range of most natural waters (i.e., 6.0–8.0) the uranyl-hydroxide complexes, are entirely missing and the predominant U(VI) carbonate complexes obviously cannot be efficiently adsorbed on the surface of BIOS. Therefore, the effect of carbonate concentration on the uranium sorption by BIOS was further examined.
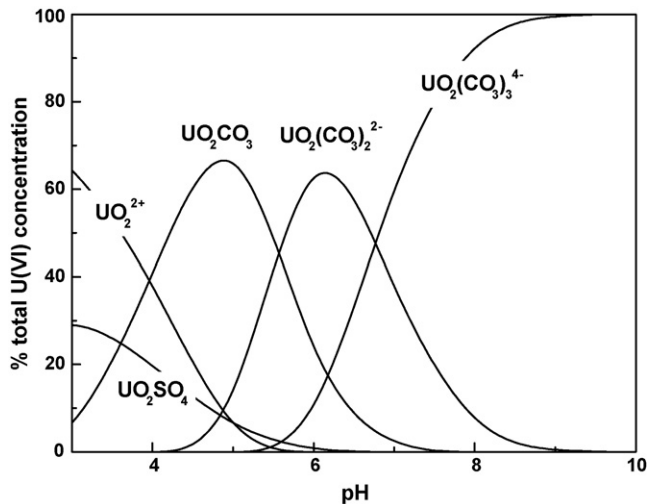
Fig. 2. Speciation of 2.1×10^{-7} M U(VI) in the groundwater of Marienfelde (Table 1). Ionic strength, 1.9×10^{-2} (calculated with PHREEQC applying the WATEQ4F database).
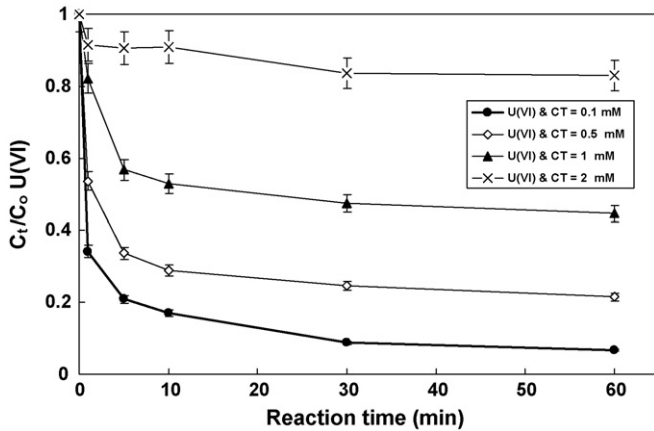

Fig. 3. Kinetics of U(VI) sorption onto BIOS at different carbonate concentrations in distilled water. Experimental conditions: initial U(VI) = 2.1×10^{-7} M; pH 7.0; adsorbent dosage = $1 \, \text{g} \, \text{L}^{-1}$.

3.3. Effect of carbonate concentration

To assess the effect of carbonate concentration, experiments were carried out with distilled water spiked with carbonate (NaHCO$_3$) at pH 7.0 and the results are illustrated in Fig. 3. The adverse effect of carbonate on U(VI) sorption onto BIOS was apparent. At lower carbonate concentrations, U(VI) was efficiently sorbed onto BIOS and around 90% uranium removal was accomplished. By increasing the carbonate concentration to val-

ues higher than 1 mM, the removal of uranium was considerably decreased and at carbonate concentration of 2 mM practically no removal occurred.

The effect of carbonate on U(VI) sorption onto iron oxides can be attributed to several factors. The solution speciation of U in the presence of carbonate largely determines how it partitions with the solid phase of bacteriogenic iron oxides, as already was shown in Fig. 2. Under acidic conditions, uranium is present in the uranyl form (UO$_2{}^{2+}$). However, at pH > 5 uranyl carbonate complexes are formed, which become anionic at higher pH values and therefore cannot be efficiently adsorbed onto iron hydroxides.

Nevertheless, the surface charge of the bacteriogenic iron oxides is likely to play the most important role, according to zeta potential measurements, which were carried out for the case of BIOS (data not presented) and compared with the values reported in the literature for the amorphous iron oxides [7]. The zeta potential values of BIOS are negative in the examined pH range (3.0–9.0) with no clear trend. On the other hand, the surface charge of amorphous iron oxides changes from positive at pH values below 7.6 to negative at higher pH values, because the point of zero charge is 7.6. Therefore, it was suggested that the use of BIOS caused electrostatic repulsion between the surface of iron oxides and the anionic U(VI)-carbonate species.

3.4. Equilibrium modeling of U(VI) sorption onto bacteriogenic iron at different carbonate concentrations

The commonly used Langmuir and Freundlich models have been applied to describe the feasibility of U(VI) sorption onto BIOS at different carbonate concentrations. The empirical Freundlich equation based on sorption on a heterogeneous surface is as follows [15]:

$$q_e = K_f(C_e)^{1/n}, \tag{2}$$

where q_e is the amount adsorbed at equilibrium (mg g^{-1}), C_e the equilibrium concentration (mg L^{-1}). K_f and n are constants indicative of sorption capacity and sorption intensity, respectively. Eq. (2) can be linearized and obtain the following logarithmic equation:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e. \tag{3}$$

The Langmuir equation is based also on several assumptions and has the following form:

$$q_e = \frac{K_L b C_e}{1 + b C_e}, \tag{4}$$

Table 2
Freundlich and Langmuir constants associated to adsorption isotherms of U(VI) onto BIOS at different carbonate concentrations

Carbonate concentration (CT, mM)	Freundlich constants			Langmuir constants		
	K_f	n	R^2	K_L (mg g^{-1})	b (L mg^{-1})	R^2
0.1	14.8	1.14	0.99	9.25	3.01	0.99
0.25	11.4	1.15	0.99	8.54	2.56	0.99
0.5	6.4	1.2	0.99	6.93	1.98	0.98

where q_e is the amount adsorbed at equilibrium (mg g^{-1}), C_e the equilibrium concentration (mg L^{-1}), b a constant related to the energy or net enthalpy of adsorption (L mg^{-1}) and K_L is the mass of adsorbed solute required to saturate a unit mass of adsorbent (mg g^{-1}). The Langmuir equation can be also linearized and obtain the following form:

$$\frac{C_e}{q_e} = \frac{1}{K_L b} + \frac{C_e}{K_L}. \qquad (5)$$

The adsorption constants derived from the elaboration of the isotherms (not shown) are given in Table 2. In both cases (Langmuir or Freundlich) the pronounced effect of the inhibition of U(VI) sorption by increasing the carbonate concentration is depicted. The K_L and the K_f values decreased by increasing the carbonate concentration. However, the values of the Freundlich constant n, pointed out that the sorption of U(VI) onto BIOS was favorable, as it lies between 1 and 10 and the relatively large value of b implied strong bonding with the BIOS [15]. Nonetheless, the obtained values are lower than the values reported in literature for the sorption of U(VI) onto synthetic ferrihydrite or goethite. For example Giammar and Hering [6] have reported a sorption capacity of 27.3 mg g^{-1} of goethite in open air system adsorption and Wazne et al. [7] have reported 0.125 mol U(VI)/mol Fe, for closed system adsorption, which was reduced to 0.034 mol U(VI)/mol Fe in the presence of 1.68 mM carbonate concentration.

3.5. Effect of pH on the sorption of U(VI) onto BIOS in the presence and absence of carbonate

The effect of pH on the U(VI) sorption onto BIOS was additionally examined. Fig. 4 shows that in the absence of carbonate, the variation of pH in the range 4.0–7.8 did not have any significant impact on the U(VI) removal. A slight decrease has been observed as the pH was increased and this can be attributed to the fact that the presence of hydroxyl complexes of uranyl increased and therefore, they caused a shift of the surface charge to more negative values. The results, regarding the removal of U(VI) in the absence of carbonate, are consistent with literature findings,
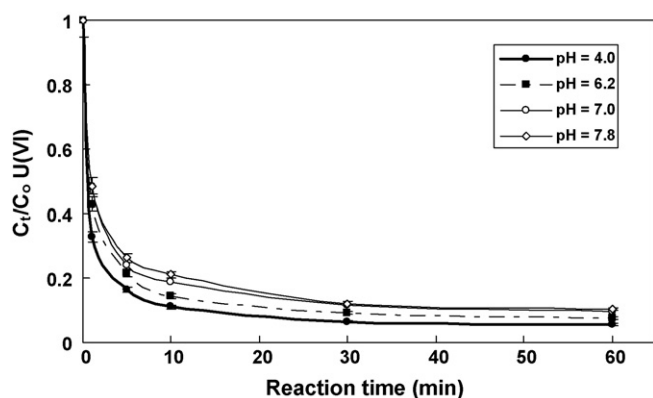

Fig. 4. Kinetics of U(VI) sorption onto BIOS at different pH values from distilled water with 0.1 M NaCl. Experimental conditions: initial U(VI) = 2.1 × 10^{-7} M; adsorbent dosage = 1 g L^{-1}.
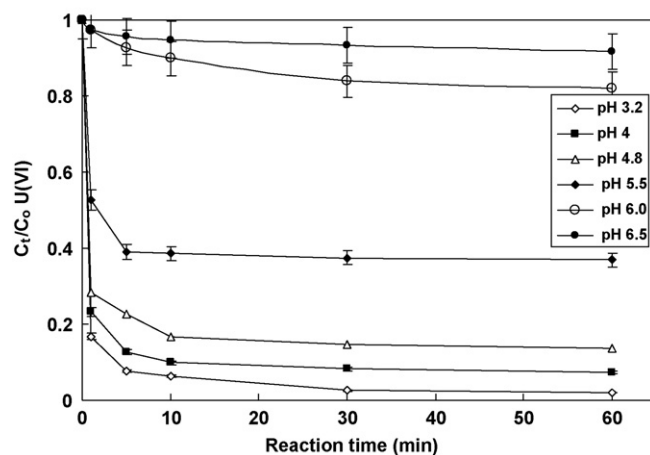

Fig. 5. Kinetics of U(VI) sorption onto BIOS at different pH values from the Marienfelde groundwater. Experimental conditions: initial U(VI) = 2.1 × 10^{-7} M; adsorbent dosage = 1 g L^{-1}.

applying several iron oxides [16]. Nevertheless, the results were entirely reverse, when the effect of pH was examined using the real groundwater. The results are illustrated in Fig. 5. It can be noticed that the removal of U(VI) was very efficient at lower pH values, i.e., in the range of 3.2–4.8. As the pH increased, then the U(VI) sorption decreased and at pH values over 6.0, U(VI) sorption onto BIOS was inhibited. It can be also noticed that the reaction after 30 min is almost completed, while most of the removal takes place in the first minute of reaction.

Previous studies of U(VI) sorption onto iron oxides [4,7] and onto other materials [17] depicted that, in the presence of carbonate, the removal of U(VI) was adversely affected. Using iron oxides as adsorbents, uranium removal is in almost all cases optimum in the pH range 5.0–6.0. In the case of BIOS, the optimum pH range was found to be 3.2–4.0. At pH 5.5, the removal decreased to 50%, after 60 min reaction time, which was practically considered as the end point of adsorption.

In this case also, the negative zeta potential values of BIOS in the pH range 3.0–9.0 can give explanation to the fact that, the removal of U(VI) was very efficient at lower pH values, while at these pH values, common iron oxides show lowest U(VI) removal [6].

At lower pH values (i.e., 3.0–4.0), the carbonate complexes of uranyl were absent (as shown in Fig. 2) and therefore the predominant uranium species was the uranyl-cation (UO$_2$$^{2+}$), which most likely can be adsorbed onto BIOS. On the contrary, common amorphous iron oxides present a positive surface charge and therefore at lower pH values, uranyl-cation adsorption was not favored.

3.6. Adsorption kinetic modeling

Mathematical models, which are frequently used to describe the kinetics of sorption, are the pseudo-first and the pseudo-second order equations, after the assumption that measured metal concentrations are equal to cell surface concentrations. The pseudo first order Lagergen kinetic model and the 1st order reversible reaction model [18] were initially applied in this

Table 3
The second order reaction rate constants for the sorption of U(VI) onto BIOS from different ratios of groundwater with distilled water at pH 7.0

% of GW in DW	q_e (mg g^{-1})	K_{ads} (g mg^{-1} min^{-1})	h (mg g^{-1} min^{-1})	R^2
2	0.025	37.11	0.023	0.99
5	0.023	20.33	0.01	0.99
50	0.0038	75.4	0.001	0.98

study but did not correlate well to the obtained results (data not presented). Therefore, the experimental data were described with the second order equation, for which much higher regression coefficient was obtained. Briefly, the pseudo second-order kinetic model is expressed as:

$$\frac{dq}{dt} = k_{ads}(q_e - q)^2, \tag{6}$$

where k_{ads} (g mg^{-1} min^{-1}) is the rate constant of second order adsorption. The integration of Eq. (6) is:

$$\frac{1}{q_e - q} = \frac{1}{q_e} + k_{ads}t, \tag{7}$$

which can be rearranged and linearized to obtain:

$$\frac{t}{q} = \frac{1}{k_{ads}q_e^2} + \frac{1}{q_e}t. \tag{8}$$

The plot t/q versus t should give a straight line if second order kinetics are applicable and q_e and k_{ads} can be determined from the slope and intercept of the plot, respectively. Additionally the initial sorption rate h (mg g^{-1} min^{-1}) can be determined based on the following equation:

$$h = k_{ads}q_e^2. \tag{9}$$

The kinetic constants are presented in Tables 3–6. It can be noticed that in all cases the initial sorption rate decreases by increasing the carbonate concentration. In comparison, it can be

Table 4
The second order reaction rate constants for the sorption of U(VI) onto BIOS from distilled water spiked with different concentrations of carbonate at pH 7.0

Carbonate (mM)	q_e (mg g^{-1})	K_{ads} (g mg^{-1} min^{-1})	h (mg g^{-1} min^{-1})	R^2
0.1	0.029	37.16	0.031	0.99
0.5	0.021	45.62	0.02	0.99
1	0.012	40.05	0.006	0.99
2	0.006	24.16	0.0008	0.96

Table 5
The second order reaction rate constants for the sorption of U(VI) onto BIOS from distilled water with 0.1 M NaCl at different pH values

pH	q_e (mg g^{-1})	K_{ads} (g mg^{-1} min^{-1})	h (mg g^{-1} min^{-1})	R^2
4.0	0.030	77.82	0.07	0.99
6.2	0.030	54.16	0.048	0.99
7.0	0.031	44.4	0.042	0.99
7.8	0.032	38.1	0.039	0.99

Table 6
The second order reaction rate constants for the sorption of U(VI) onto BIOS from groundwater at different pH values

pH	q_e (mg g^{-1})	K_{ads} (g mg^{-1} min^{-1})	h (mg g^{-1} min^{-1})	R^2
3.2	0.027	178.6	0.131	0.99
4.0	0.027	171.8	0.125	0.99
4.8	0.019	168.1	0.061	0.99
5.5	0.012	388.7	0.056	0.99
6.0	0.0044	39.83	0.00077	0.98
6.5	0.002	143.1	0.00057	0.98

observed that when the effect of pH was examined in the absence of carbonate, then the initial sorption rate remained almost constant, demonstrating the significant role of pH on the sorption efficiency of U(VI) onto BIOS and consequently the effect of carbonate.

4. Conclusions

Given the results of this study, certain conclusions can be drawn. The potential of bacteriogenic iron oxides in adsorbing U(VI) clearly depends on the carbonate concentration and the pH value of the water. U(VI) adsorption was enhanced by decreasing the concentration of carbonate in water. The variation of pH played an important role only when the experiments have been accomplished in the real groundwater, consequently in water containing carbonate. Under these conditions, highest U(VI) adsorption was achieved in the pH range 3.2–4.0 and at higher pH values the sorption was decreased. On the contrary, the pH variation did not have a significant impact when the experiments were carried out in distilled water, i.e., in the absence of carbonate. The absence of carbonate resulted in the dominance of uranyl-hydroxo complexes, which in general were effectively adsorbed on the bacteriogenic iron oxide surfaces. Zeta potential measurements have been performed and the results have showed that BIOS surface was negatively charged in the pH range 3.0–9.0. This explain the obtained results on the basis of electrostatic repulsion of the negative surface of BIOS and anionic uranyl-carbonate species in carbonate medium at pH values higher than 4.0 and the attraction of the positive hydrolyzed uranium species by the negative surface of BIOS in the lower pH values. The results have been further elaborated with the Freundlich and Langmuir models and the pronounced effect of carbonate was depicted. The maximum adsorption capacity with the Langmuir model was determined 9.25 mg g^{-1} in 0.1 mM carbonate medium and was decreased to 6.93 mg g^{-1} when the carbonate concentration was set to 0.5 mM. Similar decrease by increasing carbonate concentration was observed with the Freundlich constants. These results are related to the other examined parameters, since it was shown that the variation in carbonate concentration as well as in the pH value did affect the sorption capacity of the bacteriogenic iron oxides. However, the higher performance of BIOS in the low pH area (i.e., below 4) was different from the respective performance of other iron oxides such as synthetic ferrihydrite or goethite reported in the literature.

The experimental data were analyzed by the pseudo-second order model to determine the kinetic constants. In all cases, it was noticed that the initial adsorption rate as well as the adsorption capacity increased by decreasing the concentration of carbonate or the pH value of the water.

Acknowledgements

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