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Sorption of uranyl and arsenate on SiO_2 , Al_2O_3 , TiO_2 and FeOOH

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Abstract Migration of uranium and arsenic in aquatic environments is often controlled by sorption on minerals present along the water flow path. To investigate the sorption behaviour, batch experiments were conducted for uranium and arsenic as single components and also solutions containing both uranium and arsenic in the presence of SiO_2 , Al_2O_3 , TiO_2 and FeOOH at a pH ranging from 3 to 9. In solutions containing only U(VI) or As(V) with the minerals, the sorption of U(VI) was low at acidic pH range and increases with increasing pH, whereas As(V) showed opposite sorption behaviour to Al_2O_3 , TiO_2 and FeOOH from acidic pH range to alkaline condition. For the As(V)– SiO_2 system, the sorption was low for almost all pH. Sorption of U(VI) and As(V) on SiO_2 and FeOOH is almost similar in solutions containing either U(VI) or As(V) separately, or both together. In the U(VI)–As(V)– Al_2O_3 system, a significant retardation in uranyl sorption and an enhancement in arsenate sorption on Al_2O_3 were observed for a wide range of pH. The sorption behaviour of U(VI) and As(V) was changed when Al_2O_3 was replaced by TiO_2 , where an increase in sorption was observed for both elements. The sorption behaviour of uranyl and arsenate in the U(VI)–As(V)– TiO_2 system gives evidence for the formation of uranyl–arsenate complexes. The change in sorption retardation/enhancement of U(VI) and

As(V) could be explained by the formation of uranyl–arsenate complexes or due to the competitive sorption between uranyl and arsenate species.

Keywords Uranium · Arsenic · Sorption · Uranyl–arsenate

Introduction

Natural uranium is a mixture of 99.27 % ^{238}U and 0.72 % ^{235}U . According to the high half life of ^{238}U , radiotoxicity of natural uranium is rather low in comparison to the chemical toxicity (ATSDR 2013). Understanding the fate and the transport of uranium at surface as well as subsurface conditions is important to evaluate the long-term effects of these radionuclides in the environment. U(VI) is the most stable and mobile oxidation state of uranium under oxidising conditions. One of the important factors which affects the migration of U(VI) in subsurface is sorption at the solid/solution interface. Many factors control the sorption of radionuclides on mineral surfaces and the important candidate amongst them is the aqueous speciation of elements. Hence, it is important to know the major species to predict the sorption behaviour of U(VI) in the environment. The importance of U(VI) speciation with respect to different ligands has been previously studied (Bernhard 2005; Dong and Brooks 2006; Nair and Merkel 2011). The interaction of U(VI) with phosphate has been investigated extensively (e.g. Cheng et al. 2004; Guo et al. 2009; Sandino and Bruno 1992; Jerden et al. 2003). Arsenic is analogous to phosphate and also a potential candidate for environmental pollution in many countries including Bangladesh, India, Thailand and the United States. Prolonged exposure of arsenic through drinking water can cause human cancer (Chen et al.

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2003; Smith et al. 1992). The formation of uranium–phosphate complexes was investigated rather well (Bachmaf et al. 2008; Brendler et al. 1996; Cheng et al. 2004; Payne et al. 1996; Sandino and Bruno 1992), but on the contrary, less information is available about the formation of uranium–arsenate complexes despite its adverse effect as mentioned above. pKa for arsenate, uranyl and many other U-complexes is available. However, the formation of aqueous uranyl–arsenate species is sparsely investigated. Rutsch et al. (1999) reported the formation of three uranium–arsenate species [UO_2HAsO_4 , $\text{UO}_2\text{H}_2\text{AsO}_4^+$, $\text{UO}_2(-\text{H}_2\text{AsO}_4)_2$] which were identified using time-resolved laser-induced fluorescence spectroscopy (TRLFS) within acidic pH conditions ranging from 1.5 to 3. The formation of uranyl–arsenate complex under alkaline pH conditions was studied by Gezahegne et al. (2009) and reported the formation of $\text{UO}_2\text{AsO}_4^-$, as similar to the formation of uranyl–phosphate complex (UO_2PO_4^-). However, this study has not proposed a formation constant ($\log K$) value for the $\text{UO}_2\text{AsO}_4^-$ complex. The challenges involved to identify the uranyl–arsenate species in aquatic environment and to estimate $\log K$ values were discussed in (Gezahegne et al. 2011, 2012). Existence of natural minerals such as Trögerite, $\text{H}_2(\text{UO}_2\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ and $\text{UO}_2(\text{HAsO}_4) \cdot 4\text{H}_2\text{O}$ is a good evidence for the affinity between uranium and arsenic to form aquatic species as well. Hence, the knowledge of uranyl–arsenate species is important especially for the proper remediation strategies for uranium mine water which often contains arsenic. One of the two main objectives of this study is to further investigate the formation of uranyl–arsenate complexes and its influence on the sorption behaviour of uranium and arsenic in the presence of environmentally relevant minerals such as SiO_2 , Al_2O_3 , TiO_2 and FeOOH . These minerals are wide spread in nature and also present as major or minor components in other mineral groups (e.g.: clay minerals).

Transport process of toxic inorganic contaminants such as uranium and arsenic is retarded by means of sorption on metal oxides presented on sediments. One of the commonly found metal oxides on natural sediments is goethite (Wang et al. 1993), which is also thermodynamically stable. However, there is no sufficient information available on the sorption of U(VI) and As(V) onto goethite and SiO_2 in a system containing both elements. When considering U(VI)– SiO_2 and As(V)– SiO_2 systems, U(VI) has rather strong affinity to SiO_2 especially from near neutral to alkaline pH conditions (Stamberg et al. 2003; Nair and Merkel 2011). However, SiO_2 is not a good sorbent of As(V) over a wide pH range and geochemical conditions (Xu et al. 1988). A recent study by (Tang and Reeder 2009) showed an enhancement in U(VI) sorption on Al_2O_3 in the presence of As(V). The study reported precipitation of uranyl–arsenate complexes at a system containing U(VI)–

As(V)– Al_2O_3 , which causes a major reduction of U(VI) concentration in the system. The mineral titanium oxide (TiO_2) is also extensively used for sorption experiments due to its well-known structure, surface characteristics, chemical stability, less solubility and near neutral point of zero charge. Sorption of various actinides on TiO_2 has been previously reported (Comarmond et al. 2011; Jakobsson 1999; Olsson et al. 2003). Removal of arsenic from drinking water by TiO_2 has been proposed as a novel method (Dutta et al. 2005, 2004). To our knowledge, sorption experiments on the system U(VI)–As(V)– TiO_2 are not reported elsewhere so far. To get more insights into the sorption behaviour of U(VI) and As(V) (as single element system and combined system), present study was conducted only with uranium (0.5×10^{-6} mol/L), arsenic (0.5×10^{-6} mol/L) and uranium–arsenic together ($0.5:0.5 \times 10^{-6}$ mol/L) with the aforementioned minerals at a pH ranging from 3 to 9.

Materials and methods

Solid and solution preparation

The silica sand used for the experiment is known as F32 and was obtained from Quarzwerke Frechen, Germany. The average grain size and the surface area were 0.24 mm and $0.1 \text{ m}^2/\text{g}$, respectively. The X-ray diffraction characterisation shows that F32 contains $98.6 \pm 0.26 \%$ quartz and $1.4 \pm 0.26 \%$ calcite. Chemical analysis of the silica sand shows that it has 99.7 % SiO_2 , 0.2 % Al_2O_3 and 0.03 % Fe_2O_3 . Process of removing calcite and iron oxides as well as the purification of F32 was explained in Nair and Merkel (2011). For this experiment, goethite was prepared as described by Schwertmann and Cornell (2000). The surface area of goethite was measured using BET method and was found to be $44.77 \text{ m}^2/\text{g}$. Al_2O_3 and TiO_2 were obtained from Sigma-Aldrich (Germany). The assay, specific surface area and particle size of Al_2O_3 were 99.7 %, $0.6 \text{ m}^2/\text{g}$ and $10 \mu\text{m}$, respectively. In case of TiO_2 , the aforementioned properties were $\geq 99.9 \%$, $2.5 \text{ m}^2/\text{g}$ and $<5 \mu\text{m}$, respectively. U(VI) and As(V) stock solutions ($0.5 \mu\text{M}/\text{L}$) were prepared from $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Chemapol, Czech Republic) and As_2O_5 (Alfa Aesar, Karlsruhe Germany), respectively, by dissolving in deionised and purified water (TKA, Germany). To avoid precipitation or sorption of U(VI), the water was pre-acidified with HNO_3 to pH 2.5. All chemicals used were of ACS grade reagent or better.

Batch experiments

All experiments were conducted with uniform concentration of uranium ($0.5 \mu\text{M}/\text{L}$), arsenic (0.5×10^{-6} mol/L)

and uranium–arsenic together ($0.5:0.5 \times 10^{-6}$ mol/L) under normal laboratory conditions (temp. 23 ± 1 °C) in 500 mL Teflon (PTFE) beakers. We noticed a considerable U(VI) sorption on glass wares during preliminary experiments with low U(VI) concentration at neutral to alkaline pH conditions. Therefore, every tool used for this experiment was made of Teflon. Twelve sets of experiments were carried out with different sorbing materials such as SiO₂ (100 g/L), Al₂O₃ (10 g/L), TiO₂ (2 g/L) and FeOOH (0.04 g/L) as follows;

(1) U(VI)–SiO₂, (2) As(V)–SiO₂, (3) U(VI)–As(V)–SiO₂, (4) U(VI)–Al₂O₃, (5) As(V)–Al₂O₃, (6) U(VI)–As(V)–Al₂O₃, (7) U(VI)–TiO₂, (8) As(V)–TiO₂, (9) U(VI)–As(V)–TiO₂, (10) U(VI)–FeOOH, (11) As(V)–FeOOH and (12) U(VI)–As(V)–FeOOH

These experiments were conducted for a pH ranging from 3 to 9. The pH of the solution (500 mL) was initially adjusted to 9 using NaOH and then decreased to a pH of 3 by HNO₃ at an interval of 0.5. A period of 20-min equilibrium time was kept between each pH level, and the samples (5 mL) were collected at each pH interval for further analysis. A magnetic stirrer (IAK, Germany) was used to obtain steady contact of the solution with the solid material throughout the experiments. The collected samples were filtered using cellulose acetate filters (0.2 µm) and analysed for uranium as well as arsenic using ICP-MS (XSeries 2, Thermo Fisher Scientific). The sorption percentage of U(VI) and As(V) on the sorbents was calculated using the Eq. 1;

$$\text{Sorption (\%)} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where C_i and C_f were the initial and the final concentration of U(VI) and As(V) in the solution. Background electrolytes were avoided from the current investigation to prevent the alteration of the composition of uranyl–arsenate aqueous species. Alkali and alkaline earth metals are known for forming complexes with uranyl–arsenates (e.g. sodium uranyl arsenate). All the experiments were carried out in duplicates and the percentage of error was $< \pm 5$.

Results and discussion

U(VI)/As(V)/U(VI)–As(V)–SiO₂ system

Sorption of U(VI) and As(V) on SiO₂ was almost similar in solutions containing either U(VI) or As(V) separately, or both together (Fig. 1). At pH 3, the sorption of uranium was low and sharply increased in the pH range ~ 4 –5.5 (from 30–40 % to < 80 %) and becomes constant afterwards in the pH range 5.5–9 (80–90 %). This sorption behaviour at different pH range can be explained as

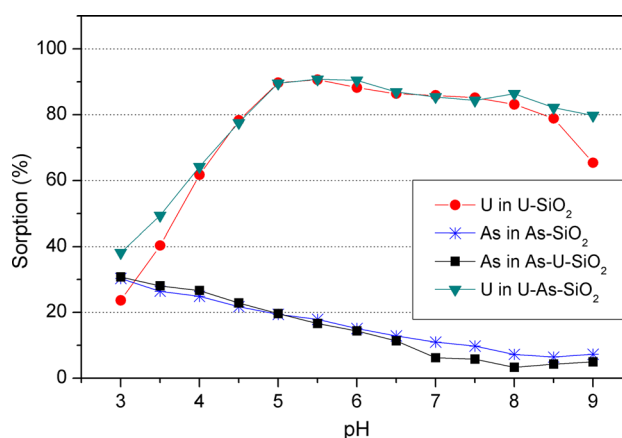


Fig. 1 U(VI), As(V) and U(VI)–As(V) sorption on SiO₂ as a function of pH. (0.5×10^{-6} mol/L U, 0.5×10^{-6} mol/L As, $0.5:0.5 \times 10^{-6}$ mol/L U:As, 100 g/L SiO₂, temp.: 23 °C, $p\text{CO}_2$: $10^{-3.5}$ bar)

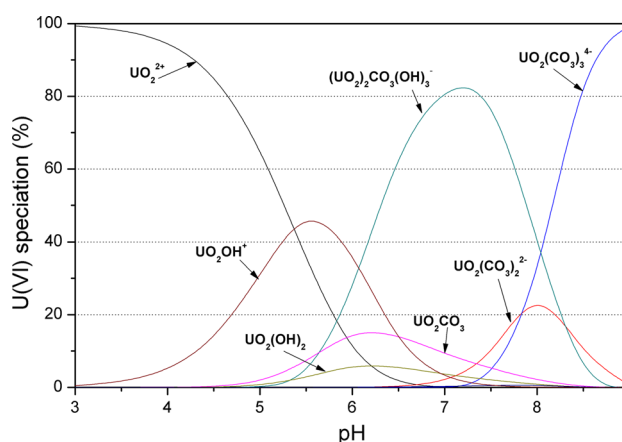


Fig. 2 Aqueous speciation calculation of U(VI) in relation to pH using PHREEQC with NEA_2007 database. ($\Sigma\text{U} = 0.5 \times 10^{-6}$ mol/L, temperature = 23 °C, $p\text{CO}_2 = 10^{-3.5}$ bar)

follows. At low pH, uranium mainly occurs as UO_2^{2+} which shows less affinity to silica surface. The increase in U(VI) sorption on quartz with respect to the pH was due to the changes in uranium speciation. The most dominant species at near neutral to alkaline conditions were UO_2OH^+ , $\text{UO}_2(\text{OH})_2$, UO_2CO_3 ($(\text{UO}_2)_2\text{CO}_3(\text{OH})^{3-}$, $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$, respectively, under our experimental conditions (Fig. 2). A previous study also showed and discussed similar sorption behaviour for U(VI) on quartz (> 90 %) (Nair and Merkel 2011). Moreover, (Stamberg et al. 2003) observed similar sorption behaviour for uranium–silica system under alkaline pH conditions. Silica is not a good sorbent of As(V) for a wide range of pH. As(V) sorption on quartz was considerably low for a wide range of pH (Fig. 1). Less affinity of As(V) to silica is well known and reported elsewhere (Darland and Inskeep 1997; Xu et al. 1988). The formation or impact of uranyl–

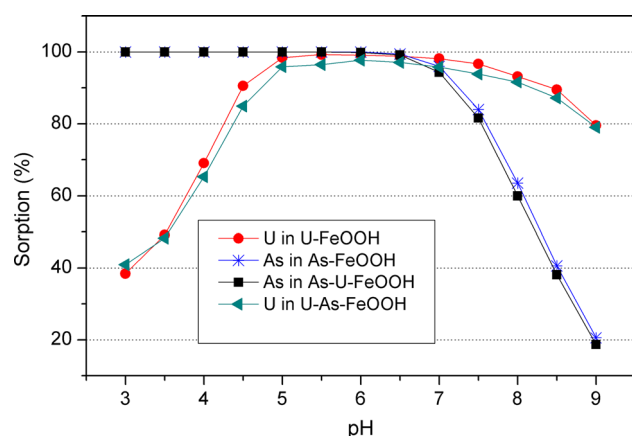


Fig. 3 U(VI), As(V) and U(VI)–As(V) sorption on FeOOH as a function of pH. (0.5×10^{-6} mol/L U, 0.5×10^{-6} mol/L As, $0.5:0.5 \times 10^{-6}$ mol/L U:As, 0.04 g/L FeOOH temp.: 23 °C, $p\text{CO}_2$: $10^{-3.5}$ bar)

arsenate complex was not visible in the sorption behaviour of U(VI)/As(V) on silica in U(VI)–As(V)– SiO_2 system.

U(VI)/As(V)/U(VI)–As(V)–FeOOH system

As(V) sorption on goethite was similar in both systems containing either As(V) alone or As(V) and U(VI) together (Fig. 3). For a pH ranging from 3 to 6.5, As(V) was sorbed completely (100 %) on goethite and the sorption decreased to 20 % at pH 9. The high sorption behaviour was attributed to the presence of major As(V) species (H_2AsO_4^-) in this pH range (Fig. 4) and the positively charged surface of goethite (Stollenwerk 2003). Elevated pH causes changes in As(V) speciation (HAsO_4^{2-}) and also makes the goethite surface to become less positive which consequently reduces the sorption (Stollenwerk 2003). U(VI) sorption on goethite was similar in U(VI)–FeOOH and/or U(VI)–As(V)–FeOOH system (Fig. 3). 40 % of U(VI) was sorbed at pH 3 and the sorption was complete (100 %) at a pH from 5 to 7. A gradual decrease in sorption can be observed from pH 7.5 to 9 (from 98 to 80 %). As mentioned above, the U(VI) sorption on minerals depends on the aqueous speciation of uranium. Identical sorption behaviour of U(VI) on goethite was also observed in Sherman et al. (2008) and Guo et al. (2009). Moreover, goethite is a good sorbent for U(VI) for a wide range of pH. The impact of As(V) on U(VI) sorption or vice versa was not noticeable in the U(VI)–As(V)–FeOOH system.

U(VI)/As(V)/U(VI)–As(V)– Al_2O_3 System

In the As(V)– Al_2O_3 system, significant amount (50 %) of arsenate was sorbed on Al_2O_3 at pH 3 and the sorption decreases with increase in pH level (Fig. 5). Under neutral to alkaline conditions, the sorption was very low and

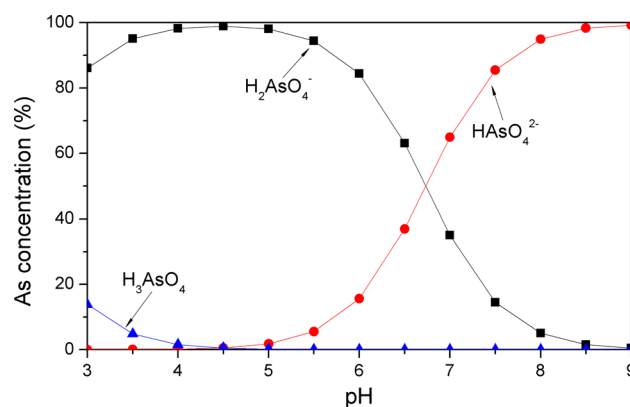


Fig. 4 Aqueous speciation calculation of As(V) in relation to pH using PHREEQC with Ilnl database. ($\Sigma\text{As} = 0.5 \times 10^{-6}$ mol/L, temperature = 23 °C, $p\text{CO}_2 = 10^{-3.5}$ bar)

declined to <5 % at a pH ranging 8–9. When compared with the As(V)– TiO_2 system, the sorption of arsenate on Al_2O_3 was less than that of TiO_2 (Fig. 6) at acidic pH range. Minor sorption of arsenate onto Al_2O_3 can be explained by the dissolution of Al_2O_3 and the liberation of Al^{3+} ions at acidic pH (~ 4.5 –5) which may lead to the formation of $\text{AlH}_2\text{AsO}_4^{2+}$ or AlHAsO_4^+ ions. Wieland and Stumm (1992) observed the dissolution of kaolinite at acidic pH range and the liberation of Al^{3+} . These aqueous complexes show little affinity to Al_2O_3 or their possible competitive sorption with H^+ ions. Another plausible reason is that 20-min equilibration time might not be enough for As(V) to reach the sorption equilibrium with the Al_2O_3 surface. There was a little increase in sorption behaviour for arsenate on Al_2O_3 from pH 4 to 5 and is not significant with respect to aqueous speciation. This could be due to possible experiment error (~ 5 %). In the U(VI)–As(V)– Al_2O_3 system, an enhanced As(V) sorption on Al_2O_3 was observed for a wide range of pH. The increase in sorption was predominant at the pH range 4.5–7 and can be attributed to the formation of uranyl–arsenate complex ($\text{UO}_2\text{AsO}_4^-$), which dominates at this pH range. Sorption of U(VI) on Al_2O_3 shows a similar trend as obtained for U(VI)– SiO_2 or U(VI)–FeOOH system (Fig. 5). At pH 3, the sorption was ~ 30 %, increased gradually to ~ 76 % at pH 5.5–7 and then decreased to ~ 50 % at pH 9. But a reduction in U(VI) sorption on Al_2O_3 was observed for the system U(VI)–As(V)– Al_2O_3 , especially from near neutral to alkaline range. Conversely, Tang and Reeder (2009) found an enhanced uranium sorption on Al_2O_3 in the presence of arsenate. In their study, the reduction in uranium concentration was not only by the sorption but also due to the precipitation of uranyl–arsenate complexes. Competitive sorption between uranyl and arsenate species could be another reason for the reduction of U(VI) sorption in our studies. Further investigations are required to provide a

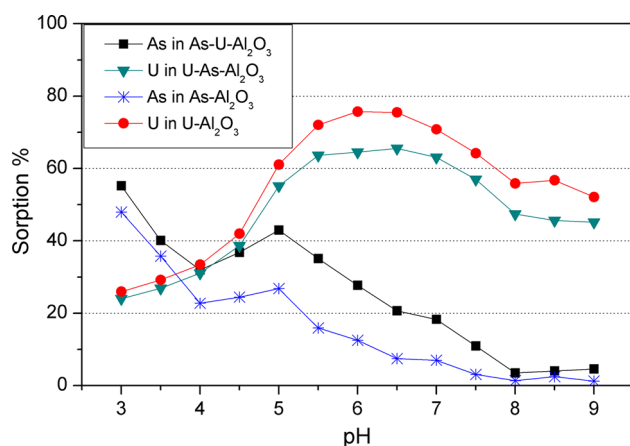


Fig. 5 U(VI), As(V) and U(VI)–As(V) sorption on Al₂O₃ as a function of pH. (0.5×10^{-6} mol/L U, 0.5×10^{-6} mol/L As, $0.5:0.5 \times 10^{-6}$ mol/L U:As, 10 g/L Al₂O₃, temp.: 23 °C, $p\text{CO}_2$: $10^{-3.5}$ bar)

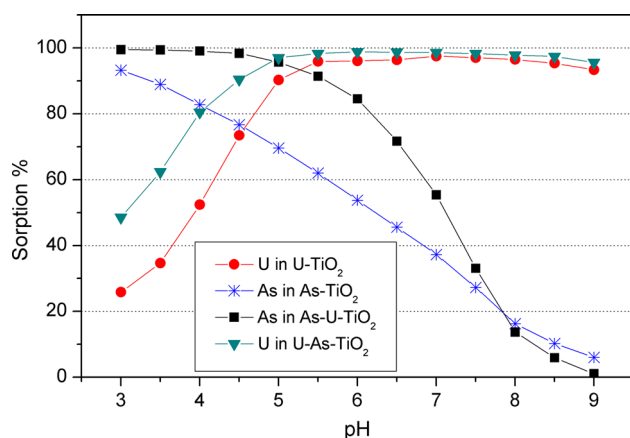


Fig. 6 U(VI), As(V) and U(VI)–As(V) sorption on TiO₂ as a function of pH. (0.5×10^{-6} mol/L U, 0.5×10^{-6} mol/L As, $0.5:0.5 \times 10^{-6}$ mol/L U:As, 2 g/L TiO₂, temp.: 23 °C, $p\text{CO}_2$: $10^{-3.5}$ bar)

valid explanation for the increase in sorption of As(V) and the decrease in U(VI) sorption on Al₂O₃ in the system U(VI)–As(V)–Al₂O₃.

U(VI)/As(V)/U(VI)–As(V)–TiO₂ System

TiO₂ has a high affinity to U(VI) for a broad pH range. At low pH, the sorption was ~30 % and reached to ~100 % at pH 5.5 (Fig. 6). From pH 5.5–9, the sorption behaviour was constant irrespective of pH. The result is consistent with other studies of U(VI) sorption onto TiO₂ (Comarmond et al. 2011; Zhijun et al. 2004). Bachmaf and Merkel (2011) and Payne et al. (2004) noticed high affinity of uranyl carbonate species towards anatase present as impurity phase in kaolinite. The high sorption of U(VI) on

TiO₂ at near neutral to alkaline condition was due to the affinity of uranyl hydroxides as well as the uranyl carbonate species to the mineral surface. The sorption of As(V) on TiO₂ was higher at acidic pH and decreased with increasing pH (Fig. 6). At pH 3, ~95 % of As(V) was sorbed on TiO₂ and the sorption decreased to ~60 % at pH 6 and finally to ~10 % at pH 9. The pH_{pzc} of TiO₂ is ~5.6 (Kosmulski 2009) and at $pH < pH_{pzc}$, the surface of TiO₂ has positive charge and As(V) anions sorbs better at acidic pH conditions. The surface charge is related to the release of either H⁺ or OH[−] ions during the sorption process (Dutta et al. 2004). Hence, the surface charge as well as the aqueous species plays a major role in the sorption of As(V). Further, it has been well investigated that the sorption of As(V) onto TiO₂ is higher at low pH and lower at high pH values (Dutta et al. 2004; Pena et al. 2005). The greater affinity of TiO₂ towards arsenate has been already mentioned in “Introduction”. In the presence of equimolar U(VI) and As(V) together, an enhancement of U(VI) as well as As(V) sorption on TiO₂ was observed (Fig. 6). The sorption of As(V) to TiO₂ was high for a wide pH range and was more prominent than sorption of U(VI). At certain pH range (e.g. pH 4–7), the As(V) sorption was increased to nearly 20 %, whereas the sorption of U(VI) increased only at acidic pH (from 3 to 5) and showed similar sorption as in U(VI)–TiO₂ for higher pH values. The elevated sorption behaviour of both elements is a good indication of the formation of uranyl–arsenate complex ($\text{UO}_2\text{AsO}_4^-$), particularly in the pH range 4.5–7. $\text{UO}_2\text{AsO}_4^-$ has more affinity to TiO₂ surface than other U(VI) or As(V) aqueous species.

Conclusions

The batch experiments conducted to investigate the sorption behaviour of U(VI) and As(V) revealed that the uranyl and arsenate sorption on minerals highly depend on the pH conditions. The aqueous speciation of both elements changes with pH and supports the fact that the sorption changes with respect to the speciation. The general sorption capacities of the above-said minerals towards U(VI) and As(V) are in the following order of $\text{FeOOH} > \text{TiO}_2 > \text{Al}_2\text{O}_3 > \text{SiO}_2$ under the aforementioned experimental conditions. Sorption behaviour of U(VI) and As(V) on SiO₂ as well as FeOOH was similar in solutions containing either both elements together or separately. On contrary, a considerable retardation of U(VI) sorption and an increase in As(V) sorption on Al₂O₃ were observed in the U(VI)–As(V)–Al₂O₃ system. This change in sorption retardation or enhancement can be explained by the formation of uranyl–arsenate complexes or competitive sorption between uranyl and arsenate species. In the U(VI)–As(V)–

TiO₂ system, both elements showed an enhancement in sorption behaviour, which is an evidence for the formation of uranyl–arsenate complexes. Further investigations are necessary to make firm conclusions about the uranyl–arsenate complexes, which facilitates the implementation of proper remediation strategies for uranium mine waters that often contain arsenic.

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