Polymerization of silicate on TiO₂ and its influence on arsenate adsorption: An ATR-FTIR study

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HIGHLIGHTS

- Molecular-level interaction of Si and As(V) on TiO₂ was studied with *in situ* ATR-FTIR.
- The As(V) surface structure remained unchanged in the presence of Si.
- The As(V) adsorption released the adsorbed Si monomers and dimers.
- Si oligomers and polymers greatly inhibited As(V) adsorption.

GRAPHICAL ABSTRACT

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ABSTRACT

The exposure risks of toxic arsenic in the environment are dependent on the adsorption and desorption processes at solid/aqueous interfaces, which could be greatly influenced by co-existing oxyanions such as silicate. In the present work, the adsorption of arsenate [As(V)], silicate (Si), and the influence of silicate on As(V) adsorption are investigated at the molecular level by *in situ* attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. Silicate monomer, dimer, oligomer, and polymer were detected on the TiO₂ surface after 3 h, and silicate oligomer was the predominant surface species under the experimental conditions. The presence of silicate with different silicate and As(V) adsorption sequences did not interfere with As(V) surface species on TiO₂, but only affected the As(V) adsorption capacity. For silicate, the adsorption of As(V) could greatly inhibit the formation of Si monomer and dimer on TiO₂, but the silicate oligomer and polymer were not influenced by As(V) adsorption. The silicate oligomeric and polymeric surface species will gradually occupy the TiO₂ surface sites to inhibit As adsorption and TiO₂ regeneration. Our findings provide spectroscopic evidence and clearly elucidate the molecular-level interactions of silicate and As(V) on TiO₂, which will further our understanding of the removal of As in groundwater.

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1. Introduction

Groundwater arsenic contamination and its adverse effects have been reported all over the world [1,2]. Arsenate [As(V)], the dominating As species in oxic environments, is present as an oxyanion in natural environments ($pK_1 = 2.8$, $pK_2 = 6.7$, $pK_3 = 11.8$). As(V) can be strongly adsorbed on metal oxides such as goethite, ferrihydrite, and nano-crystallized titanium dioxide (TiO₂) with inner-sphere

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surface complexes [3,4]. Therefore, adsorption is considered to be one of the most effective methods for the removal of As in groundwater. However, the groundwater As adsorbents were commonly exhausted after two or three times of adsorption, even though the As regeneration rates (80–90%) were extremely high [5–7]. The exhaustion of As adsorbents can be attributed to the adsorption of co-existing ions in groundwater.

Groundwater As(V) adsorption can be influenced by natural competing oxyanions such as silicate, phosphate, and bicarbonate [8–10]. Silicate (Si) is present as H_4SiO_4 due to its pK_1 at 9.8, and is widely distributed with high concentrations ranging from 5 to 35 mg/L in groundwater [11]. Similar to As(V), silicate has a high affinity for metal oxides, and can compete with As(V) for the adsorption sites to form inner-sphere surface complexes through a ligand exchange mechanism [12]. The interferences of silicate to arsenate adsorption capacities have been comprehensively studied, and results showed the arsenate adsorption capacities decreased with the increasing of silicate concentrations [13–15]. Furthermore, depending on pH, concentration, and other factors, silicate can be combined as silicate polymers both in the aqueous phase and on metal oxide surfaces [11,16,17]. These silicate polymers on metal oxides could greatly increase silicate adsorption capacities and affect the adsorption/desorption behavior of As(V) in groundwater [11,18,19].

The competitive effects of silicate with As(V) are greatly dependent on the silicate concentrations and pH values. For example, at a total silicate concentration of 0.1 mM, the adsorption of As(V) was decreased only at pH above 8, but when silicate concentrations were increased to 1.8 mM, As(V) adsorption was already decreased at pH 6 due to the polymerization of silicate [20]. Only under strongly acidic conditions ($\text{pH} < 3$), could As(V) adsorption not be interfered with by silicate [18]. Due to their different dissociation properties, adsorption of As(V) is strong under acidic conditions and gradually decreases with increasing pH, while silicate has the opposite adsorption behavior owing to its pK_1 at 9.8. Thus, at the pH of the majority of As contaminated groundwater ($\text{pH} = 7.5\text{--}8.5$) [21], As(V) has low affinity for metal oxides while the adsorption of Si is relatively high [18]. Therefore, the influence of silicate on As(V) adsorption in groundwater should be seriously considered.

Moreover, the adsorption competition could be strongly influenced by the adsorption kinetics. Silicate adsorption is slower than that of As(V) because of its polymerization on surfaces [22,23]. In the presence of silicate, the kinetics and total quantity of arsenic adsorption are found to be reduced [22]. Although the competitive interactions between silicate and As(V) adsorption on metal oxides have been previously investigated, the molecular-level mechanisms and kinetic effects of silicate on As(V) adsorption are still not fully understood.

The spectroscopic technique of attenuated reflectance-Fourier transform infrared (ATR-FTIR) is useful for the *in situ* study of the molecular-level interactions of silicate and As(V) on surfaces. With this technique, the monomeric, oligomeric, and polymeric silicate surface species can be distinguished based on the position of the Si–O stretching bands [16,24,25]. Moreover, the molecular As(V) adsorption structures on metal oxides were also extensively studied with ATR-FTIR spectroscopy [26,27]. Therefore, the competitive effects of monomeric and polymeric silicate on As(V) adsorption can be investigated.

In this study, TiO_2 was selected as an adsorbent due to its large surface area, chemical stability, and potential in groundwater As treatment [4,28]. ATR-FTIR spectroscopy was employed to study (i) the adsorption and polymerization of silicate on the surface of TiO_2 in a geogenic groundwater pH environment and (ii) the molecular-level interactions and adsorption kinetics of silicate and As(V) on TiO_2 . The insights gained from this study should improve

our knowledge in groundwater As removal and the regeneration of As adsorbents.

2. Materials and methods

2.1. Materials

The stock solutions of 13.35 mM (1000 mg/L) As(V) and 35.71 mM (1000 mg/L) silicate were prepared by dissolving $\text{Na}_2\text{AsO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Na}_4\text{SiO}_4 \cdot 9\text{H}_2\text{O}$ in deionized (DI) water, respectively. In order to prevent CO_2 contamination, DI water used in the present experiments was purged with nitrogen for at least an hour. The TiO_2 was prepared by hydrolysis of titanyl sulfate, as described in our previous report [29].

2.2. FTIR spectra of As(V) and Si adsorption on TiO_2 film

The ATR-FTIR measurements were performed using a Thermo-Nicolet Nexus 6700 FTIR spectrometer equipped with a horizontal attenuated total reflectance (HATR) cell (PIKE Tech) and a liquid-nitrogen-cooled mercury–cadmium–telluride (MCT) detector. A multibounce ZnSe ATR crystal with 45° beveled faces (infrared angle of incidence, θ) was used and the infrared spectra were collected using 256 scans per spectrum at a resolution of 4 cm^{-1} .

To simulate a geogenic As-contaminated groundwater in Shanxi, China [21], all ATR-FTIR experiments were carried out at pH 8, and the silicate and As(V) concentrations were set to 0.36 mM (10 mg/L) and 0.013 mM (1 mg/L), respectively. Solutions of As(V), silicate, and As(V) in the presence of silicate were prepared in 0.01 M NaCl background electrolyte at pH 8. The FTIR measurements of As(V) and silicate adsorption on TiO_2 were similar to our previous reports with minor modifications [30,31]. Briefly, a 300 μL suspension containing 3.5 g/L of TiO_2 was evenly spread on the ZnSe crystal and air-dried overnight to form a uniform TiO_2 film. The flow cell with the coated film was washed with 0.01 M NaCl solution using a LC pump (LC 10A, Shimadzu Corp.) at a flow rate of 0.3 mL/min for 3 h to flush out the loose particles and equilibrate the TiO_2 film at the experimental pH values. The background IR spectrum was collected and saved. The electrolyte solution was then changed to the As(V), silicate or As(V) plus silicate solution at the same pH as that of the electrolyte solution. Spectra were recorded as a function of time until the sorption reached equilibrium (at least 3 h). All samples were purged with N_2 in the dark during the spectra collection.

The spectra were baseline corrected using the Omnic baseline correction algorithm. Because the second derivative crosses the x-axis at the point of maximum slope of the underlying (first derivative) curve, and presents a much sharper band than the underlying absorbance band does. The second derivative IR spectra were employed in the IR spectra analysis and bands fitting. The Savitsky–Golay second derivatives were calculated to assist band identification using an order of 3 and with the number of points depending on the signal-to-noise ratio in the original spectra [25], and negative second derivative spectra were presented corresponding to the initial spectra. The peak fitting of all IR spectra was carried out with Peakfit v.4.12 software using the second derivative fitting algorithm, and *R* factors in all of the fitted spectra were more than 0.999.

3. Results and discussion

3.1. As(V) adsorption on TiO_2

The 0.013 mM As(V) adsorption on TiO_2 at pH 8 was monitored over time by ATR-FTIR spectroscopy (Fig. 1). The adsorbed As(V) spectra exhibited three bands at 875, 830, and 785 cm^{-1} ,

Fig. 1. ATR-FTIR spectra of 0.013 mM As(V) adsorbed on TiO₂ over time at pH 8 in 0.01 M NaCl.

corresponding to vibrations of As–O, As–OTi, and As–OH, respectively (Fig. 1). The IR band at 875 cm^{−1} corresponded to the uncomplexed As–O vibrations in aqueous H₂AsO₄[−] species. Because metal ions are not as strongly coordinated to oxygen ions as protons, the As–OTi bond should be stronger than As–OH. Therefore, the IR band at 830 cm^{−1} was due to the vibrations of the As–OTi bond, and the band at 785 cm^{−1} corresponded to the As–OH vibrations. The results are in agreement with previous studies of As(V) adsorption on iron oxides [26,28,32], and the peak assignments are shown in Table 1.

3.2. Polymerization of silicate on TiO₂

To investigate the adsorption and polymerization of silicate on TiO₂, the IR spectra of 0.36 mM silicate adsorption at pH 8 were monitored over time (Fig. 2A). Increasing IR bands in the range between 800 and 1200 cm^{−1} were characteristic of the adsorbed silicate. The negative second derivative spectra were employed to distinguish peaks between 800 and 1200 cm^{−1}, and IR bands at 1120, 1020, 952, 902/922, and 830 cm^{−1} were detected (Fig. 2B).

According to the previous studies, the IR band at 830 cm^{−1} (Fig. 2B) could be attributed to the mixed monomeric and oligomeric Si–OH stretching vibrations [16]. The bands at 902 and 952 cm^{−1} were attributed to monomeric silicate surface complexes [16,25,33]. IR bands at 922 and 1020 cm^{−1} were due to oligomeric silicate surface complexes [16,18,25,33]. The main oligomeric silicate anions found in minerals are the dimer (Si₂O₇^{6−}) and cyclic

Table 1
FTIR peak positions and assignments for adsorbed As(V) and silicate on TiO₂.

Frequency (cm ^{−1})	Description	Reference
785	As–OH vibration	[26–28,32]
830	Complexed As–O–Ti vibration, Si–OH vibrations of Si monomers and oligomers	[11,16,19,25,28,33]
875	Uncomplexed As–O vibrations	[26–28,32]
902	Monomeric Si–O vibrations	[11,16,19,25,33,35]
922	Dimeric Si–O vibrations	[11,16,19,25,33,35]
952	Monomeric Si–O vibrations	[11,16,19,25,33,35]
1020	Oligomeric Si–O vibrations	[11,16,19,25,33,35]
1110–1140	Polymeric Si–O vibrations	[11,16,19,25,33,35]

anions such as (SiO₃^{2−})_n with *n* = 3, 4 or 6. The maximum IR absorption band for the silicate dimer occurs in the range of 900–950 cm^{−1}, while the cyclic anions often show IR bands above 1000 cm^{−1} [16]. Therefore, the bands at 922 and 1020 cm^{−1} corresponded to vibrations of the silicate dimer and cyclic oligomer, respectively. The broad peak at 1120 cm^{−1} was attributed to the silicate polymer on the TiO₂ surface [18,34,35]. The peak assignments are shown in Table 1.

During the first 20 min of silicate adsorption, silicate monomer with IR bands at 902 and 952 cm^{−1}, and silicate oligomer with a peak at 1020 cm^{−1} (Fig. 2A), were the predominant surface species on TiO₂. With reaction time increasing, the peak at 902 cm^{−1} shifted to higher wavenumber at 922 cm^{−1}. The IR band 922 cm^{−1} corresponded to the vibrations of the silicate dimer (Si₂O₇^{6−}) [16,33]. The shifting of the peak suggested that the silicate monomer was disposed toward forming the linear dimer by condensation reactions [25]. After the first 20 min, IR bands at 922 and 1020 cm^{−1} increased rapidly and became the dominant IR bands, indicating the growth of the silicate linear dimer and cyclic oligomer on TiO₂. Moreover, an increasing broad shoulder at 1110–1150 cm^{−1} due to the vibrations of polymeric silicate surface species was also detected.

The IR results suggested the silicate oligomer and polymer could be easily formed in a relatively short period of reaction time (0.2 h) under a groundwater silicate concentration, and Si oligomer was the dominant Si surface species on TiO₂ at 0.5–7 h. In line with our present results, oligomeric and polymeric Si species were also detected when silicate adsorption on TiO₂, ferrihydrite, and hematite in both short-term (0.1–35 h) and long-term (210 days) experiments [11,18,33]. The adsorption and polymerization of silicate would occupy most of the surface sites and inhibit the adsorption of other oxyanions.

3.3. Interference of Si on As(V) adsorption

Due to the different affinities of silicate and As(V) for the TiO₂ surface, the surface species of As(V) and silicate formed on TiO₂ can be influenced by different adsorption sequences. To study the molecular-level interactions of silicate and As(V) on TiO₂, ATR-FTIR spectra of silicate pre-adsorption, As(V) pre-adsorption and silicate and As(V) simultaneous adsorption were monitored over time.

3.3.1. Interference of silicate pre-loading on As(V) adsorption

The ATR-FTIR spectra of 0.36 mM silicate pre-loading on TiO₂ for 3 h, followed with silicate adsorption in the presence of 0.013 mM As(V) at pH 8, are shown in Fig. 3A. The negative second derivative spectra and peak fitting results are shown in Fig. 3B and C, respectively. For silicate adsorption without As, the IR bands of the silicate monomer at 952 cm^{−1}, silicate dimer at 922 cm^{−1}, cyclic silicate oligomer at 1020 cm^{−1}, and silicate polymer at 1120 cm^{−1} were detected on TiO₂ surfaces. After adsorption for 3 h, the silicate oligomer was the dominant surface species, and the silicate surface species gradually reached equilibrium at the end of 3 h.

After silicate preloading for 3 h, As(V) was added to the silicate adsorption system. As a result of As(V) adsorption, IR bands at 830, 922, and 952 cm^{−1} corresponding to silicate adsorption decreased with increasing time (Fig. 3B). The rapid decreasing of the main monomeric Si–O band at 952 cm^{−1} and the Si–O–Si stretching vibrations at 922 cm^{−1} suggested the desorption of the silicate monomeric and dimeric surface species (Fig. 3B). However, there was no obvious decrease of the cyclic silicate oligomer at 1020 cm^{−1} and polymeric silicate vibrations at 1120 cm^{−1} with the addition of As(V), indicating that the silicate oligomer and polymer on TiO₂ were not influenced by As(V) adsorption. The two possible reasons are (i) the surface silicate oligomer and polymer always

Fig. 2. ATR-FTIR spectra of 0.36 mM silicate adsorbed on TiO_2 over time at pH 8 in 0.01 M NaCl (A) and their negative second derivative IR spectra (B).

grow with increasing time, while the monomeric and dimeric silicate surface species would not increase once the surface sites were completely occupied (ii) the adsorption of As(V) partially desorbed the silicate monomer and dimer, which are not strongly bound with TiO_2 , then the TiO_2 surface sites were captured by As(V), resulting in the diminution of surface silicate monomer and dimer.

With the addition of As(V), the uncomplexed As–O stretching vibrations at 875 cm^{-1} corresponding to adsorbed As(V) gradually increased (Fig. 3B). The As–OTi band at 830 cm^{-1} was overlapped with the mixed monomeric and oligomeric Si–OH vibrations at 830 cm^{-1} , and the bands could not be distinguished with the second derivative spectra (Fig. 3B). Thus, the peak at 830 cm^{-1} is not discussed in the present study. The As(V) adsorption bands were the same as the As(V)-only adsorption system, indicating the As(V) adsorption structures on TiO_2 were not influenced by silicate pre-loading. Because there was no static IR band in the single and binary adsorbate system, the IR spectra could not be normalized to compare the As(V) and silicate adsorption quantitatively. However, peak fitting results clearly showed that the peak area of the uncomplexed As–O vibration at 875 cm^{-1} was much lower than that of in the As(V)-only adsorption system (Fig. 6A and B), and the qualitative analysis suggested silicate pre-loading definitely

decreased As(V) adsorption, which is in line with the previous macroscopic experimental results.

A previous study showed that the competitive effect of silicate with As(V) would increase with increasing silicate pre-loading time [18]. This can be explained with our IR results showing that silicate oligomer and polymer could not be desorbed by As(V) adsorption, and the oligomer and polymer would grow with increasing time, so that as a result, the oligomer and polymer would take over TiO_2 surface sites and the competitive effects of silicate with As(V) would increase with increasing silicate pre-loading time.

3.3.2. As(V) pre-adsorption system

For the As(V) pre-adsorption system, the IR spectra were collected for 0.013 mM As(V) pre-loading on TiO_2 for 3 h followed by 0.013 mM As(V) and 0.36 mM silicate competitive adsorption (Fig. 4A). The negative second derivative spectra and peak fitting results are shown in Fig. 4B and C, respectively. After As(V) pre-loading for 3 h, there were three bands at 875 , 830 , and 785 cm^{-1} corresponding to vibrations of As–O, As–OTi, and As–OH, respectively.

With the addition of silicate, the peak at 875 cm^{-1} corresponding to uncomplexed As–O stretching decreased slightly (Fig. 6B),

Fig. 3. ATR-FTIR spectra over time of 0.013 mM As(V) adsorbed on TiO_2 pre-treated with 0.36 mM Si for 3 h at pH 8 in 0.01 M NaCl (A) and their negative second derivative IR spectra (B) and peak fitting results (C).

Fig. 4. ATR-FTIR spectra of 0.013 mM As(V) adsorbed on TiO₂ pre-treated with 0.36 mM silicate for 3 h over time at pH 8 in 0.01 M NaCl (A) and their negative second derivative IR spectra (B) and peak fitting results (C).

indicating the addition of silicate partially desorbed the adsorbed As(V). For silicate adsorption, a small band at 922 cm⁻¹ corresponding to the silicate dimer was detected (Fig. 4B). However, the peak area of the silicate dimer was much smaller than for the silicate-only adsorption system (Fig. 6A and B). The IR band at 952 cm⁻¹ corresponding to monomeric silicate surface species in the silicate-only adsorption system was not detected in the As(V) pre-loading system, suggesting As(V) pre-loading greatly inhibited monomeric and dimeric silicate adsorption. However, the strong peak and the shoulder at 1020 and 1120 cm⁻¹ corresponding to the surface silicate oligomer and polymer were not influenced by As(V) pre-loading. The phenomena can be explained by the As(V) pre-loading occupying most of the TiO₂ surface sites, so that there were not enough surface sites for silicate adsorption. Once the monomeric silicate surface species were formed, extra silicate in solution would complex with the monomeric silicate to form silicate dimer, oligomer, and polymer. Therefore, there was no monomeric silicate surface species formed in the As(V) pre-loading system.

Our different adsorption sequence results suggested that only the silicate monomer and dimer can be influenced by As(V) in both

the Si and As(V) pre-loading system, while the formation of silicate oligomer and polymer was not influenced. The results suggested that once the stable oligomeric and polymeric silicate surface complexes were formed, they could not easily be desorbed by other oxyanions such as As(V) in groundwater. Even during the adsorbent regeneration process, the polymeric silicate surface species could not be completely eluted with NaOH or HCl solutions [36]. Due to the large adsorption capacity and polymerization of silicate on surfaces, we deduce the formation of silicate oligomer and polymer could be one of the most important reasons why most of the groundwater As adsorbents were exhausted after two or three times of regeneration [5–7]. Effective silicate desorption methods should be explored to achieve the As adsorbents' regeneration in groundwater treatment.

3.3.3. As(V) and silicate simultaneous adsorption

The IR spectra of 0.013 mM As(V) and 0.36 mM silicate simultaneous adsorption on TiO₂ were collected over time (Fig. 5A), the negative second derivative spectra and peak fitting results are shown in Fig. 5B and C, respectively.

Fig. 5. ATR-FTIR spectra of 0.013 mM As(V) and 0.36 mM silicate simultaneous adsorption over time at pH 8 in 0.01 M NaCl (A) and their negative second derivative IR spectra (B) and peak fitting results (C).

Fig. 6. Peak fitting results of the IR spectra of silicate pre-loading (A), As(V) pre-loading (B), and silicate and As(V) simultaneous adsorption (C) over time.

As with the As(V)-only adsorption system, the increase of the uncomplexed As–O band at 875 cm^{-1} and As–OH stretching vibration at 785 cm^{-1} were detected (Fig. 5B), suggesting the increased adsorption of As(V) on TiO_2 surfaces. For silicate adsorption, similar to the silicate-only adsorption and Si preloading systems, the monomeric band at 952 cm^{-1} , dimeric band at 922 cm^{-1} , oligomeric band at 1020 cm^{-1} , and polymeric silicate band at 1120 cm^{-1} were detected (Fig. 5B). Moreover, the peak areas of surface silicate monomer and dimer were much lower than for the silicate-only adsorption system, while the silicate oligomer and polymer were not influenced by As(V) adsorption. The results are in line with the silicate or As(V) pre-loading systems, indicating that the adsorption affinities of As(V) and silicate monomers/dimers on TiO_2 are similar, while the silicate oligomer and polymer have stronger adsorption affinity than As(V).

In all adsorption sequences, the As(V) adsorption structures on TiO_2 were not influenced by silicate; only the As(V) adsorption quantities were decreased by silicate adsorption. Regarding silicate adsorption, the silicate monomer and dimer could be partially desorbed with As(V) adsorption, while the formation of silicate oligomer and polymer was not influenced. Because the surface silicate oligomer and polymer would increase with increasing time, and could not be easily desorbed, the formation of silicate surface polymers would greatly inhibit As adsorption in long time adsorption processes, especially in field groundwater As filtration treatment. Moreover, the polymeric silicate surface species could not be completely eluted with NaOH or HCl solutions in the regeneration process of the groundwater As adsorbent. Therefore, the surface sites would be gradually occupied by silicate polymers, after which the adsorbents were exhausted.

3.4. Adsorption kinetics

To study the As(V) and silicate adsorption kinetics in the different adsorption sequences, the IR spectra were fitted with the second derivative algorithm. Fitting results of silicate pre-loading (Fig. 6A), As(V) pre-loading (Fig. 6B), and silicate and As(V) simultaneous adsorption (Fig. 6C) over time are shown with increasing time. In accordance with previous studies, the peaks at 875 , 1120 , 1020 , 922 , and 952 cm^{-1} were chosen to represent As(V), silicate polymer, silicate oligomer, silicate dimer, and silicate monomer, respectively.

The IR spectra of different adsorption sequences indicate that adsorption sequence would not influence As(V) surface species on TiO_2 , but only influence the As(V) adsorption amount. The peak area of the As–O band at 875 cm^{-1} was As(V) pre-adsorption > simultaneous adsorption > Si pre-adsorption (Fig. 6), which suggested the As(V) adsorption capacities of the three sequences, and our observations are in line with the previous water chemistry study results [18].

For silicate adsorption, the formation of silicate monomer and dimer were greatly inhibited in all three adsorption sequences, but formation of silicate oligomer and polymer were not influenced by As(V) adsorption. Silicate monomer was not detected in the As(V) pre-loading system, which was because As(V) preloading had occupied most of the surface sites on TiO_2 ; as a result, silicate condensation rapidly took place on the basis of adsorbed silicate. However, in the silicate pre-loading and simultaneous adsorption system, a small amount of monomeric silicate was detected because there were more surface sites for Si adsorption; once the monomeric silicate was formed, it could not be completely desorbed by As(V) or completely condensed to form silicate dimer and oligomer. From the peak fitting results (Fig. 6), the adsorption capacities of the silicate monomer and dimer were silicate pre-adsorption > simultaneous adsorption > As(V) pre-adsorption. The results were in agreement with the previous water chemistry experiments at pH 3–9 [18].

Previous studies showed that the adsorption kinetics of silicate were much slower than As(V) [22,23]. Our IR results indicated that the adsorption kinetics of silicate monomer and dimer were similar to that of As(V), and the adsorption of silicate monomer, dimer, and As(V) were equilibrated within 90 min (Fig. 6). However, the formation of oligomeric and polymeric silicate surface species (equilibrated at about 200 min) was much slower than adsorption (Fig. 6). Silicate polymerization is a long-term process on metal oxides, and the silicate oligomer and polymer would increase with increasing time. To prevent the greatly inhibiting effect of silicate on As(V), the As(V) removal in groundwater should be completed in a relatively short time.

4. Conclusions

ATR-FTIR was employed to study the polymerization of silicate and the molecular-level interactions of silicate and As(V) on the TiO_2 surface. Silicate monomer, dimer, oligomer, and polymer were detected on the TiO_2 surface in 0.5–3 h, and the silicate oligomer was the predominant surface species under the experimental conditions. Different silicate and As(V) adsorption sequences would not interfere with As(V) surface species on TiO_2 , but only interfere with the As(V) adsorption capacity. In contrast, the adsorption of As(V) could desorb the Si monomer and dimer surface species on TiO_2 , while silicate oligomer and polymer were not influenced by As(V) adsorption. The surface silicate oligomer and polymer increased with increasing time, and could not be easily desorbed by other oxyanions. Therefore, the presence of silicate in groundwater is one of the most important reasons for the exhaustion of As adsorbents in groundwater treatment processes. The interference of silicate on As adsorption in groundwater should be seriously considered, the As(V) removal in groundwater should be completed in a short time before silicate oligomer and polymer colonize TiO_2 surface sites, and approaches should be developed to remove the surface silicate oligomers and polymers during the adsorbents' regeneration process.

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