



## Polymerization of silicate on TiO<sub>2</sub> and its influence on arsenate adsorption: An ATR-FTIR study



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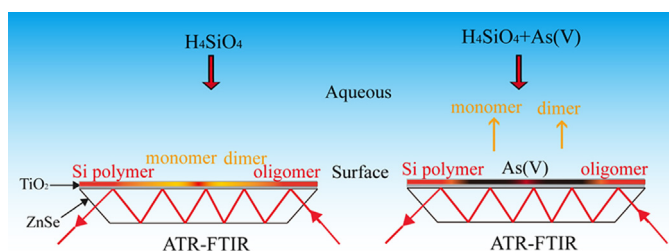
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### HIGHLIGHTS

- Molecular-level interaction of Si and As(V) on TiO<sub>2</sub> 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 TiO<sub>2</sub> 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 TiO<sub>2</sub>, 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 TiO<sub>2</sub>, but the silicate oligomer and polymer were not influenced by As(V) adsorption. The silicate oligomeric and polymeric surface species will gradually occupy the TiO<sub>2</sub> surface sites to inhibit As adsorption and TiO<sub>2</sub> regeneration. Our findings provide spectroscopic evidence and clearly elucidate the molecular-level interactions of silicate and As(V) on TiO<sub>2</sub>, 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 (TiO<sub>2</sub>) 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  $\text{H}_4\text{SiO}_4$  due to its  $\text{p}K_1$  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  $\text{p}K_1$  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,  $\text{TiO}_2$  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  $\text{TiO}_2$  in a geogenic groundwater pH environment and (ii) the molecular-level interactions and adsorption kinetics of silicate and As(V) on  $\text{TiO}_2$ . 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  $\text{CO}_2$  contamination, DI water used in the present experiments was purged with nitrogen for at least an hour. The  $\text{TiO}_2$  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 $\text{TiO}_2$ 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  $45^\circ$  beveled faces (infrared angle of incidence,  $\theta$ ) was used and the infrared spectra were collected using 256 scans per spectrum at a resolution of  $4\text{ cm}^{-1}$ .

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  $\text{TiO}_2$  were similar to our previous reports with minor modifications [30,31]. Briefly, a 300  $\mu\text{L}$  suspension containing 3.5 g/L of  $\text{TiO}_2$  was evenly spread on the ZnSe crystal and air-dried overnight to form a uniform  $\text{TiO}_2$  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  $\text{TiO}_2$  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  $\text{N}_2$  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 $\text{TiO}_2$

The 0.013 mM As(V) adsorption on  $\text{TiO}_2$  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  $785\text{ cm}^{-1}$ ,

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