Applied Surface Science 466 (2019) 425–432

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Competitive adsorption of arsenic and fluoride on {2 0 1} TiO_2

Zhen Zhou[a,b], Yaqin Yu[b,c], Zhaoxia Ding[a], Meimei Zuo[a], Chuanyong Jing[b,c,*]

[a] Department of Military Facilities, Army Logistics University, Chongqing 401311, China
[b] State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
[c] University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Keywords:
Arsenic
Fluoride
High-index TiO_2
Competitive adsorption
Molecular level mechanism

ABSTRACT

Elevated arsenic (As) and fluoride (F) in natural water present an urgent environmental concern. The demand for their effective removal underscores the fundamental understanding of their solid-liquid interface chemistry. Herein, the efficiency of {2 0 1} TiO_2 in As(III/V) and F was explored using macroscopic and molecular-level techniques. Their adsorption isotherms followed the Langmuir equation, and the maximum adsorption capacity was 50.5, 29.3, and 5.0 mg/g for As(III), As(V) and F, respectively. Their adsorption kinetics of As(III), As(V) and F conformed to the pseudo-second-order model. The XPS and *in situ* ATR-FTIR results identified that the active adsorption sites on {2 0 1} TiO_2 included surface hydroxyl groups, but not oxygen vacancies. As(III/V) and F form bidentate binuclear and monodentate mononuclear structures, respectively, regardless of exposed facets. Integrated with the molecular-level mechanism, the charge distribution multisite complexation model well predicted the pH edge behaviors in mono- and co-component systems. The shift of pH_{PZC} of {2 0 1} TiO_2 in competitive adsorption systems signified the formation of inner-sphere complexes. The results of this study shed new lights on the adsorption of coexisting ions using high-index faceted TiO_2.

1. Introduction

Elevated concentration of arsenic (As) and fluoride (F) in drinking water is an urgent environmental issue due to their health risks. Over 140 million people in at least 50 countries are affected by As contaminated water [1,2]. About 200 million people covering > 25 counties are at F risk via drinking water [3,4]. In fact, the coexistence of As and F has been reported (Table S1), further aggravating their toxicity and health hazard [5–7].

Adsorption is a suitable technique to remove As and F due to its cost-benefit balance [8,9], and anatase TiO_2 based adsorbent has exhibited its superior adsorption capability as well as chemical and mechanical stability [10,11]. Recent studies become aware of the dominant role of the exposed TiO_2 facets on As adsorption [12]. For example, As adsorption behavior on {1 0 1} TiO_2 has been investigated, illustrating that the maximum adsorption of As(V) and As(III) onto {1 0 1} TiO_2 surface occurred at pH 4 and 8, respectively [12]. Simultaneous As(III) and F removal were achieved by doping Lanthanum on {1 0 0} TiO_2 [9]. This {1 0 0} TiO_2-La adsorbent displayed a high F (78.4 mg/g) and As(III) (114.0 mg/g) adsorption density. Our previous research documented the antimony adsorption on different TiO_2 facets: {0 0 1}[13], {1 0 0}[14], and {1 0 1}[14], clarifying the relation between the exposed facets and antimony adsorption capacity. In contrast to the widespread interests on the low-index faceted TiO_2 adsorbents, few attention has been paid on the high-index facets. The active adsorption sites and adsorption modes of high-index faceted TiO_2 are even unclear. More recently, a dandelion-like hierarchical TiO_2 nanocrystals exposed {2 0 1} high-index facets has been documented [15]. Compared with low-index facets, {2 0 1} high-index faceted TiO_2 exhibited a unique atomic structure, abundant unsaturated coordination sites [16], and higher surface energy (1.72 J/m^2) [14]. It is speculated that {2 0 1} high-index faceted TiO_2 will possess high adsorption capacities and unique adsorption behavior.

Therefore, the purpose of this study was to explore the adsorption behavior and molecular level mechanisms of As and F using {2 0 1} TiO_2. Multiple techniques including macroscopic wet chemistry, X-ray photoelectron spectroscopy (XPS) analysis, *in situ* flow-cell attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy, and the charge distribution multisite complexation (CD-MUSIC) model were used to explore the interface reactions. Competitive adsorption of coexisting ions was also systematically studied. Our results further our understandings in the solid-liquid interfacial reactions for TiO_2 based adsorption.

---

[*] Corresponding author.
E-mail address: cyjing@rcees.ac.cn (C. Jing).

https://doi.org/10.1016/j.apsusc.2018.10.052
Received 1 September 2018; Received in revised form 2 October 2018; Accepted 5 October 2018
Available online 09 October 2018
0169-4332/

2. Experimental

2.1. Materials

$NaAsO_2$ and $Na_2HAsO_4{\cdot}7H_2O$ were purchased from Fisher Scientific (USA) and Sigma Chemical (USA), respectively. Other chemicals (e.g. NaOH, HCl, NaF, NaCl, $NaNO_3$, Na_2SO_4, $Na_2SiO_3{\cdot}9H_2O$, $Na_3PO_4{\cdot}12H_2O$, $CaCl_2$, $MgCl_2{\cdot}6H_2O$, and $FeCl_3{\cdot}6H_2O$) were obtained from Sinopharm Chemical Reagent (China). As(III/V) (500 mg/L) and F (1000 mg/L) stock solutions were adjusted via dissolving aforementioned reagents in deionized water (18.2 MΩ, Milli-Q, USA), individually, and refrigerated at 4 °C until needed. All reagents were analytical grade and utilized straight without other purification.

2.2. {2 0 1} TiO_2 fabrication

{2 0 1} TiO_2 was synthesized via a modified solvothermal approach based on [15]. The acetic acid (HAc) and 12 mL N, N-dimethylformamide (DFM) were served as capping agent, and titanium butoxide (TB) was act as Ti precursor. Detailed fabrication procedure was collected in Supplementary Material.

2.3. Adsorbent characterization

Exterior surface morphology of {2 0 1} TiO_2 was acquired by a field-emission scanning electron microscopy (FE-SEM, S-3000 N, Hitachi, Japan). The crystal morphology was further recorded using high resolution transmission electron microscopy (HRTEM, F20, FEI, USA). The crystalline fabric was obtained through the powder X-ray diffraction (XRD) using an X'Pert PRO diffractometer (PANalytical, Netherlands) with Cu Kα radiation at a scanning rate of 0.026°/s from 5° to 90°. Raman spectrometer (LabRAM HR Evolution, Horiba, Japan) with an excitation wavelength at 532 nm was adopted to reconfirm the crystal structure. The electron paramagnetic resonance (EPR) signal of oxygen vacancy was detected by a Bruker EMX plus spectrometer (LOT-Oriel Gmbh&Co. KG, Germany) at room temperature. To scan the chemical states of the materials' surface, XPS (Escalab 250Xi, Thermo Scientific, USA) was performed with monochromatized Al Kα radiation under vacuum. Methods of N_2 adsorption-desorption isotherms and the thermal curves of thermogravimetric analysis (TGA) were described in Supplementary Material.

2.4. Batch adsorption experiments

During all batch adsorption experiments, a 0.04 M NaCl was selected as the background electrolyte and the adsorbent-to-solution ratio was fixed at 0.5 g/L. The pH values were measured and modulated by an automatic potentiometric titrator (Mettler-Toledo T5, Switzerland) via NaOH and HCl. Before adding As(III/V) and F stock solution, the Milli-Q water was bubbled by N_2 for 60 min to eliminate dissolved O_2. The reaction containers including the As(III) were wrapped with aluminized paper to avoid light exposure and shaken at 200 rpm in room temperature (25 °C). After equilibrium, these samples were centrifuged and filtered via a 0.22 µm membrane. Meanwhile, the adsorbent-less blanks were also prepared to measure the initial amount of As(III, V) and F. The content of As was measured by inductively coupled plasma optical emission spectrometry (ICP-OES, PerkinElmer, USA) or furnace atomic absorption spectrometer (FAAS) (AAS-800, PerkinElmer, USA) according to their concentration level. The speciation of As was detected through high performance liquid chromatography atomic fluorescence spectrometry (HPLC-AFS, China). The amount of F was determined via F ion-selective electrode (Orion, Thermo Fisher Sci., USA).

2.4.1. Adsorption isotherms

In order to probe the adsorption behavior of {2 0 1} TiO_2 to As(III/V) and F, adsorption isotherms experiments were adopted at pH 5.0, 7.0, 9.0. The initial adsorbates were ranged from 0 to 400 mg/L (for As (III/V)) or 0–150 mg/L (for F). The acquired data were simulated using the Langmuir model:

$$Q_e = \frac{KC_eQ_m}{1 + KC_e} \tag{1}$$

here, Q_e (mg/g) is the equilibrium adsorption capacity on {2 0 1} TiO_2, Q_m (mg/g) is the maximum adsorption capacity, C_e (mg/L) is the equilibrium content of adsorbates, K (L/mg) is the Langmuir constant.

2.4.2. Adsorption kinetics

Adsorption kinetics experiments were conducted in 500 mL beakers with 5 mg/L As(III/V) and F as the adsorbate, respectively. During the entire test, the pH of the suspensions was kept in the value of 7.0 ± 0.2 via HCl or NaOH. Specifically, 1 mL sample was acquired with the following time intervals 5 min (during the first hour), 10 min (till the 2nd h), 15 min (till the 3rd h), 30 min (till the 6th h), 60 min (till the 12th h), and 120 min (till the 29th h). To simulate the experimental data, pseudo-second-order model was utilized:

$$q_t = \frac{q_e^2kt}{1 + q_ekt} \tag{2}$$

herein, qt (mg/g) represents the adsorption capacity as the function of time t, qe (mg/g) represents the equilibrium adsorption capacity, and k (mg/(mg·h)) represents the rate constant of the pseudo-second-order model.

2.4.3. Adsorption envelopes

Low (1 mg/L As(III/V) and 2 mg/L F) and high (5 mg/L As(III/V) and F) initial concentrations were chosen as the adsorbates in mono-adsorption pH edge experiments. The low concentration level is the average based on our previous groundwater survey at Shanxi, China [17,18]. Co-adsorption pH edge was carried out to evaluate the elimination efficacy of {2 0 1} TiO_2 towards F and As(III,V). The initial pH of As(III/V) and F solutions were modulated within the range of 2.0–12.0.

2.4.4. Competitive adsorption

A 1 mg/L As(III/V) or 2 mg/L F was chosen as the adsorbate. The competitors were employed at different ions-to-As molar rate (10 and 50 for SO_4^{2-}, NO_3^-, PO_4^{3-}, SiO_3^{2-}, Mg^{2+}, 50 and 100 for Ca^{2+}, 0.1 and 0.5 for Fe^{3+}) or ions-to-F molar rate(1 and 5 for SO_4^{2-}, NO_3^-, PO_4^{3-}, SiO_3^{2-}, Mg^{2+}, 5 and 10 for Ca^{2+}, 0.01 and 0.05 for Fe^{3+}), which occur in ground water ubiquitously. The influence of these competitive ions on adsorption was studied by comparing the adsorption percentile of the As or F at different ions-to- As or F molar rate covering the purview of pH 2.0–12.0. The Zetasizer Nano ZS (Malvern Instrument Ltd., UK) was utilized to measure the electrokinetic potential. The illustrated zeta potential value was the average of triple measurements.

2.5. In situ flow-cell ATR-FTIR

Similar to our previous works [19–21], 3.0 g/L {2 0 1} TiO_2 suspension was sonicated for 30 min in ultrasonic water bath. A preliminary equilibration step with 0.04 M NaCl solution at pH = 7.0 ± 0.2 was conducted under 0.5 mL/min flow rates. After stabilization (about 2 h), the spectra have no change and the background spectrum was recorded via a Thermo-Nicolet iS50R FTIR spectrometer (Thermo Nicolet, USA) coupling with a horizontal ATR cell (Pike Technologies, USA) and a mercury-cadmium-telluride (MCT) detector under liquid-nitrogen cooled circumstance. Adsorption spectra were monitored 256 scans every 10 min at 4 cm^{-1} resolution. Subsequently, the electrolyte solution containing 50 mg/L As(III/V) or 100 mg/L F was pumped into the ATR cell at the same pH to perform *in situ* adsorption tests.