Mechanism and kinetics of Pb(II) adsorption on ultrathin nanocrystalline titania coatings

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ABSTRACT

Pb(II) is a highly toxic substance, exposure to which can cause various diseases. To better understand the application of titania as an adsorbent for removing Pb(II) from wastewater, quartz crystal microbalance (QCM) technique was employed to investigate the adsorption behavior of Pb(II) on ultrathin nanocrystalline titania coatings. The present study focused on the mechanism and kinetics of Pb(II) adsorption. The obtained results show that the driving force of Pb(II) adsorption on titania coatings is electrostatic interaction, and that Pb(II) is adsorbed onto titania coatings by Pb(II) ions coordinating with hydroxyl groups of titania surface. In terms of the in situ frequency measurements of QCM, the adsorption kinetic parameter is estimated to be 4.12×10^5 L/mol. QCM measurement provides a useful method for monitoring the adsorption process of Pb(II) on titania coatings.

1. Introduction

In recent years, the removal of heavy metal ions from aqueous solution has been taking on great importance. Pb(II), a typical heavy metal ion, is frequently found in wastewater coming from lead smelter, municipal sewages, mining, battery manufacturer, paper industry, alloy manufacturing and pigments [1,2]. Pb(II) is a highly toxic substance, exposure to which can produce severe damage to human health, causing the onset of various diseases such as mental retard, nerve disorders, joint pain, learning disabilities, stunted growth, impaired hearing, kidney damage, memory and behavioral problems [3–5]. To prevent this from happening, many techniques have been developed for the removal of Pb(II) from wastewater, such as ion exchange, flocculation, membrane filtration, solvent extraction, biosorption, chemical precipitation, reverse osmosis, adsorption [6,7]. Among them, adsorption is considered as the simplest and most economical technique at present [8]. Numerous adsorbents such as carbon nanotubes [9], activated carbon [10], fiber [11], starch [12], clay minerals [13], aquatic plants [14], plant wastes [15], industrial and agriculture by-products [16] have been tested for their potential application to remove heavy metal ions from wastewater. Generally, adsorbents used to remove metal ions require to possess high adsorption capacity, adequate mechanical and physical properties. It has been demonstrated that the large surface area (often 1000 times higher than its geometric area) of the mesoporous anatase titania coatings, produced by depositing the oxide in colloidal form onto a solid substrate, allows high levels adsorption of metal ions [17,18]. Recently, titania has been used to remove Pb(II) by means of adsorption and photocatalysis [19,20]. To the best of our knowledge, previous investigation mainly focused on the removal of Pb(II), the mechanism and kinetics of Pb(II) adsorption on titania coatings have not been explored in detail, so far.

A piezoelectric quartz crystal microbalance is an effective tool due to its extreme sensitivity to the nanogram level of mass change loaded onto its surface. As a mass sensor, QCM has been widely used in biochemistry, environment, food, and clinical analysis because the technology provides a label-less method for the direct study of biospecific interaction process [21,22]. With immobilized antibodies on the surface of crystal, some QCM immunosensors have been used for the detection of viruses [23], proteins [24], bacteria [25]. In addition, it has also been demonstrated that it is useful for the study of adsorption/desorption process at solid/solution interface [26,27].

In the present work, to obtain a comprehensive understanding of the mechanism and kinetics of Pb(II) adsorption on ultrathin nanocrystalline titania coatings, a QCM device was employed to investigate the mechanism of Pb(II) adsorption on titania coatings, and the kinetics of Pb(II) adsorption was also investigated in detail.

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2. Experimental

2.1. Materials

Anatase titania sol (particle size 5 nm) was purchased from Guangzhou Mende Co. (Guangzhou, China). All other chemicals were of analytical reagent grade obtained from Shanghai Chemical Reagent Co. (Shanghai, China). Deionized (DI) water (resistivity of 18 MΩ cm) was obtained from a Milli-Q system (Millipore Inc.), and was used for rinsing and for makeup of all aqueous solutions.

2.2. Apparatus

QCM measurements were performed using a Q-sense instrument (Gothenburg, Sweden). Mechanically polished AT-cut 9-MHz quartz crystals (diameter of 12 mm, Beijing Chenjing Co., Beijing, China) were vacuum deposited with gold electrodes (6-mm diameter) on both sides of the surface. To reduce background frequency drift, one electrode was completely insulated from the test liquid. This was accomplished by mounting a glass cover slip over one side of the quartz crystal, which was held in place by two silicon o-rings. The o-rings were so large (10 mm) that they could make contact only with the exposed quartz peripheral to the centrally located electrode and not with the electrode itself. Thus, the covered electrode was in contact only with air. This covering assembly was held in place using silicone glue. The electrical contacts were insulated from the test solution using silicon tubing and silicon glue, and only one electrode was exposed to the test solution. The working crystal was connected to an IC-TTL oscillator. Both the detector cell and the oscillator were put in a copper Faradaic cabin to remove the surrounding electromagnetic noise. The frequency was monitored by a frequency counter (Iwatsu, Model SC-7201), and the recorded data were stored in a computer.

The infrared spectrum was recorded using Fourier transformed infrared spectroscopy (FTIR: Model 883, Perkin-Elmer Optoelectronics Inc., USA).

2.3. Preparation of nanocrystalline titania coatings at the surface of quartz crystal

After the gold-plated quartz crystals were treated with 3 M NaOH solution for 20 min and washed with water, the titania ultrathin coatings at the surface of quartz crystal were prepared using the original titania sol by spin coating at 3500 rpm for 3 min. Thicker coatings were achieved by repeating the coating process. A narrow strip of the titania coatings at the edge of the quartz crystal were removed using a methanol-soaked tissue. Before and after the titania coating modification, the frequency of the quartz crystal was measured, and the thickness of titania coatings was estimated from the amount of deposited titania particles. The titania coatings with 0.6 μm thickness were employed in our study, unless otherwise stated. The coatings were finally heat-treated at 300 °C for 1.5 h, and after its cooling to room temperature, all titania coatings were stored in water.

2.4. QCM monitoring of Pb(II) adsorption at the surface of titania coatings

To monitor the in situ adsorption process of Pb(II) ions at the surface of titania coatings, the following procedure was adopted. After mounting the crystal in the cell, a small amount of aqueous solution was introduced into the cell. When the frequency became stable, the Pb(II) solution was introduced into the cell within 5 s. Time-dependent change in the frequency was recorded continu-
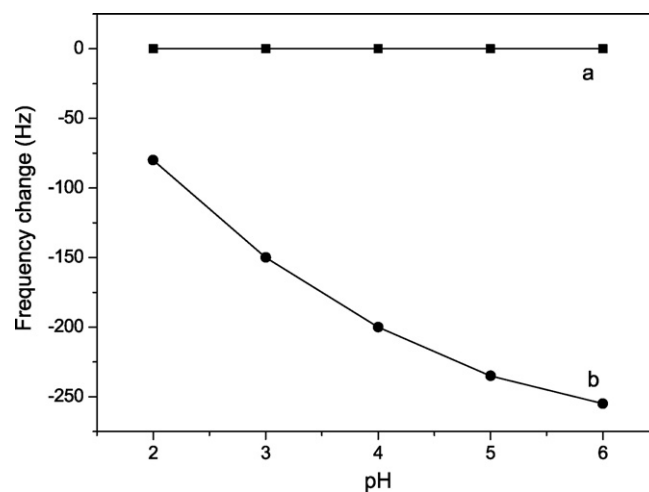

Fig. 1. Effect of pH on frequency response of QCM with titania coatings in different solutions: (a) water and (b) 0.1 mM Pb(NO$_3$)$_2$ solution.

ously by a frequency counter and stored in a microcomputer during the adsorption process of Pb(II).

3. Results and discussion

3.1. Mechanism of Pb(II) adsorption on titania coatings

Usually, the interaction on the solid interface is closely related to the characteristics of the solid interface. The surface of nanocrystalline titania coatings exhibits high hydrophilicity (the site density of >TiOH groups on colloidal titania is about 5 sites per nm^2 [28]). Therefore, the adsorption of Pb(II) onto titania coatings is expected to depend primarily on ions coordinating and electrostatic interaction. Our investigation indicated that pH significantly affected the adsorption of Pb(II) on titania coatings. Considering that titania coatings were unstable in acidic solution and precipitation occurred in Pb(II) solution at higher pH, the adsorption of Pb(II) in solutions of pH ranging from 2 to 6 was determined by QCM. As seen in Fig. 1, the titania coatings were stable in aqueous solution when the pH was varied from 2 to 6. QCM study showed that the value in frequency change increased with the increasing pH, suggesting that alkaline solution was favorable for Pb(II) adsorption. This can be attributed to the fact that the surface charge of titania coatings varies with solution pH, namely the decrease of pH initially decreasing negative and subsequently increasing positive surface charge. As for anatase titania, the isoelectric point is approximately 5, when the solution pH is below 5, hydroxyl groups of titania surface will react with protons [29]:

$$> Ti{-}OH + H^+ \rightarrow\ > Ti{-}OH_2^+ \tag{1}$$

Therefore, the surface protonation/deprotonation equilibria strongly affect the adsorption behavior of Pb(II) ions on the titania surface. At lower pH solution, titania surface possesses mainly positive charge, which makes Pb(II) ions in solution hardy interact with titania due to the electrostatic repulsion. With the increase of pH, the negative charge of titania surface increases, and more Pb(II) ions will be adsorbed onto titania surface by electrostatic attraction.

To further understand the adsorption behavior of Pb(II) on titania coatings, the adsorption/desorption process of Pb(II) ions on titania coatings was monitored by QCM (Fig. 2). Pb(NO$_3$)$_2$ solution (0.1 mM, pH 4) was firstly introduced into the cell and left to adsorb until reaching adsorption equilibrium (stage I), then a small
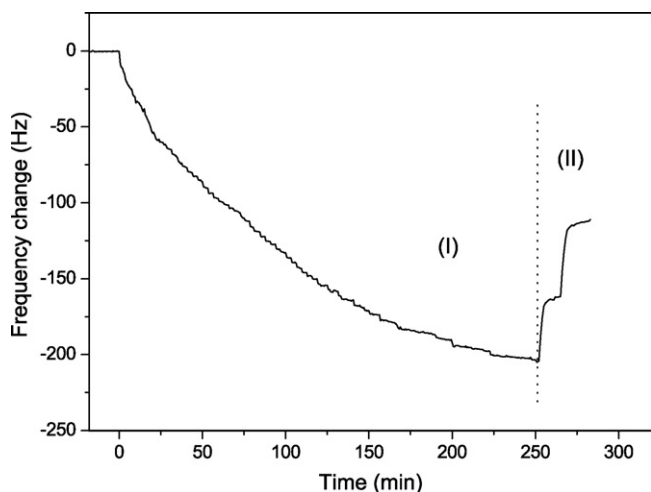
Fig. 2. Plot of frequency change against time. (I) Adsorption of Pb(II) ions (0.1 mM, pH 4) and (II) desorption of Pb(II) caused by introduction of H$^+$ ions.
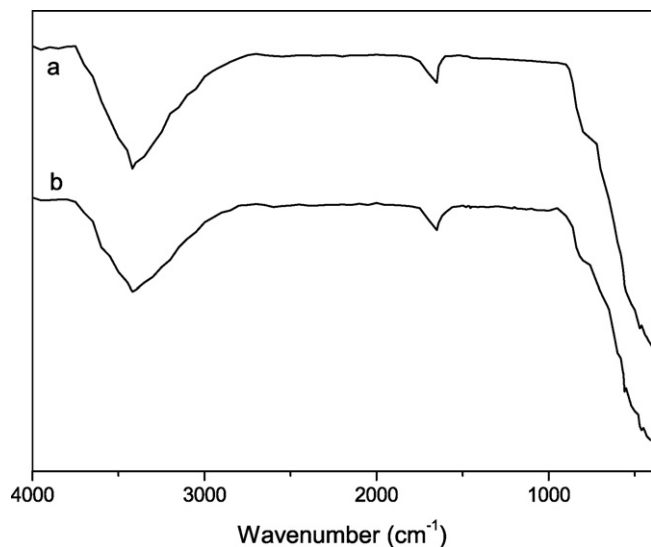

Fig. 5. Frequency change of QCM after the addition of Pb(NO$_3$)$_2$ solution (pH 4) to the detector cell. Quartz crystal (a) with Au electrode, (b) with titania coatings/Au and (c) with titania coatings/Au.

the driving force of Pb(II) adsorption, the essential of adsorption process is Pb(II) ions coordinating with hydroxyl groups of titania surface:

$$> Ti-OH + Pb(II) \rightarrow > Ti-OH\cdots Pb(II) \qquad (2)$$
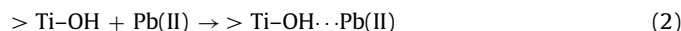
In order to validate the above equation, the infrared spectra of titania before and after Pb(II) adsorption were preformed (Fig. 3). The infrared spectra of titania showed no obvious change after the adsorption of Pb(II) ions. The phenomena further confirm the binding between Pb(II) and titania is ions coordinating. Thus, the mechanism of Pb(II) adsorption on titania coatings can be illustrated in Fig. 4. The Pb(II) ions in solution are initially attracted to the negatively charged sites on titania coatings by electrostatic interaction, and then Pb(II) ions coordinating with hydroxyl groups of titania surface.

3.2. Kinetics of Pb(II) adsorption on titania coatings

Fig. 5 shows the frequency change of QCM with time at various concentrations of Pb(NO$_3$)$_2$ at pH 4. In comparison with the response to the bare gold electrode, a larger frequency response to the adsorption of Pb(II) was observed on titania coatings and a longer time was required for the crystal to attain a frequency plateau. In addition, the change in frequency was found to increase with the increasing Pb(NO$_3$)$_2$ concentration at a given time. Herein, the adsorption rate constant rather than the total frequency change was used to characterize the adsorption behavior of Pb(II) on titania coatings, as the in situ frequency measurement includes additional frequency changes caused by over-adsorption and the change in the property of titania coatings. The results exhibited in Fig. 5 indi-

Fig. 3. Infrared spectra of (a) titania and (b) titania/Pb(II).

quantity of protons were introduced into the cell two times (stage II). Addition of Pb(II) ions caused a decrease in frequency due to the adsorption of Pb(II) on titania coatings. Introduction of protons resulted in an immediate increase in frequency, indicating a rapid desorption of Pb(II) adsorbed from titania coatings. Such results not only indicate that the Pb(II) adsorbed on titania can be displaced by the introduction of protons, but also further confirm that the electrostatic interaction plays an important role in the process of Pb(II) adsorption. Actually, the electrostatic interaction is only
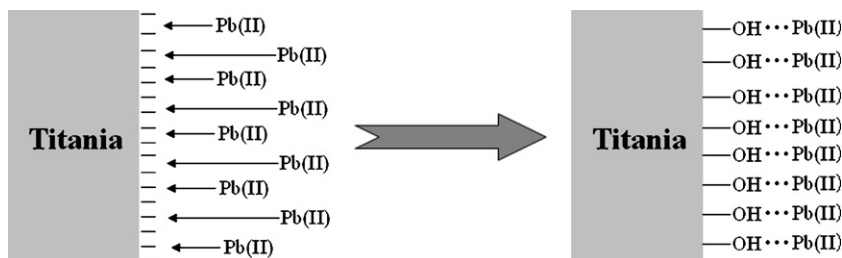

Fig. 4. Scheme of the adsorption process of Pb(II) on ultrathin nanocrystalline titania coatings.
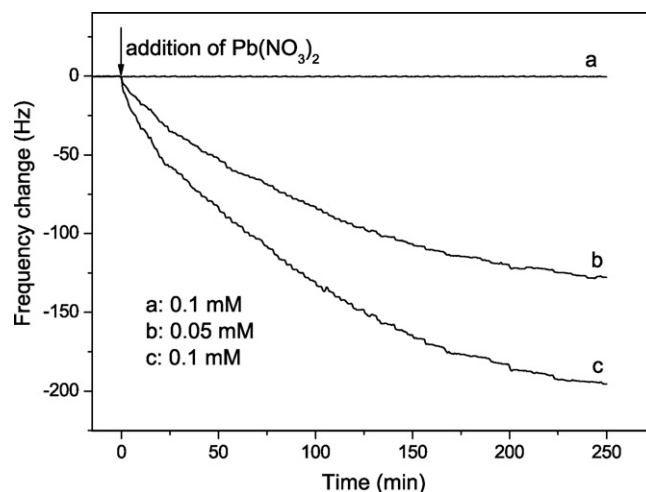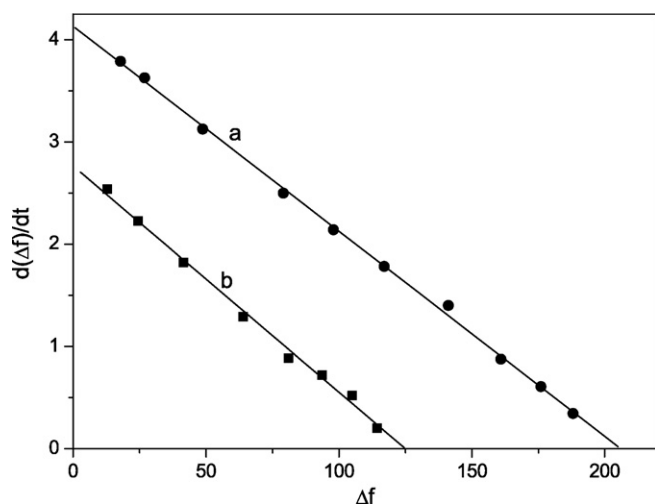
Fig. 6. Plot of $d(\Delta f)/dt$ vs. Δf. (a) Corresponding to curve (c) of Fig. 5 and (b) corresponding to curve (b) of Fig. 5.

cate that the interaction between the remaining unbound sites on titania (T) coatings and Pb(II) (P) in solution can be described as a pseudo-first-order reaction as shown below:

$$T + P \rightleftharpoons TP \qquad (3)$$

The reaction rate can be described as follows:

$$\frac{d[TP]}{dt} = k_a[T][P] - k_d[TP] \qquad (4)$$

where k_a and k_d are the association constant and the dissociation constant respectively. $\Delta f(\Delta f = f_0 - f)$ is proportional to [TP], and $\Delta f_m - \Delta f$ to [T] (Δf_m = the maximum value of frequency change). Thus, Eq. (4) can be expressed as follows:

$$\frac{d(\Delta f)}{dt} = k_a C(\Delta f_m - \Delta f) - k_d(\Delta f) \qquad (5)$$

where C is the concentration of Pb(II) assumed to be a constant in the test solution. For the estimation of k_a and k_d, the values of $d(\Delta f)/dt$ were plotted against the corresponding Δf (see Fig. 6, corresponding to curves of Fig. 5). The slope (SL) and intercept (INT) of the line are related to the kinetic constants, i.e., SL $= -(k_a C + k_d)$ and INT $= k_a \Delta f_m C$.

The equilibrium constant K for the formation of the titania/Pb(II) complex could be estimated as follows:

$$K = \frac{k_a}{k_d} \qquad (6)$$

The value of K obtained from Fig. 6 is 4.11×10^5 L/mol in 0.05 mM Pb(II) solution and the value of K is 4.12×10^5 L/mol in 0.1 mM Pb(II) solution. The two values are approximately equal, indicating that the interaction between titania and Pb(II) is not independent on the Pb(II) concentration.

4. Conclusions

The study demonstrates that QCM is a useful technique for studying the mechanism and kinetics of Pb(II) adsorption on ultrathin nanocrystalline titania coatings. The results of QCM measurements reveal that the adsorption process of Pb(II) is composed of two different processes. The Pb(II) ions in solution are initially attracted to the negatively charged sites on titania coatings by electrostatic interaction, and then Pb(II) ions coordinating with hydroxyl groups of titania surface. The adsorption kinetic parame-

ter estimated from the frequency measurements is 4.12×10^5 L/mol based on the pseudo-first-kinetic model.

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