

Adsorption of Ag(I) on H₂TiO₃ from aqueous solutions

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Received 23 June 2006; accepted 17 May 2007

Abstract: Adsorption of silver ions from aqueous solution onto H₂TiO₃ was studied. Equilibrium experimental studies were performed to determine the adsorption capacity of H₂TiO₃ for silver ion at various pH values. Batch experiments were conducted in the range of pH value 3–7 and silver ions concentration 10–200 mg/L. The results show that the adsorption is strongly dependent on pH value. The equilibrium absorption capacity of H₂TiO₃ increases significantly with the increase of pH value from 3 to 7. The adsorption of silver ion obeys the Langmuir isothermal equation well in the concentration range studied, the adsorption constant is 0.054 7, 0.052 4, 0.088 1 at pH 5, 6 and 7, respectively, and the maximum adsorption capacities are 23.64, 29.76 and 40.82 mg/g.

Key words: silver ions; adsorption; hydrous titania

1 Introduction

Titania is well known as an attractive photocatalyst. However, the photocatalytic activity of titania is not strong enough in practical application so that the modification of titania with metal ions[1–4] such as Fe, Au, Ag and Sn to improve its photocatalytic efficiency has been investigated by many researchers. It is widely known that titania containing various inorganic substances such as silver, copper and zinc, shows antibacterial property[5–7]. Ionic silver has the highest antibacterial activity among metal ions[8–10]. Recently, silver-doped titania antibacterial materials have been developed and some of them are in commercial use.

There are several techniques to make silver-doped materials (e.g. sol-gel method, high-temperature glass fusion, ion implantation, ion exchange, sputtering, etc.). Especially, the ion exchange method has several advantages such as uniform distribution, low processing temperatures, perfect antibacterial activity, and it is possible to get rid of reduction of silver ions with a high mass fraction. Therefore, many efforts have been paid for the preparation of silver-containing materials by the ion exchange method. FENG et al[11] prepared Ag/HAp by the ion exchange between Ag⁺ and Ca²⁺ in Hap and studied the morphology and structure of Ag/HAp by

SEM and XRD. AYBEN and ULKU[12] studied the ions exchanges activity of Ag⁺, Zn²⁺, and Cu²⁺ in a Na-clinoptilolite and the effect of preparing parameters on antibacterial properties. PARK and JANG[13] prepared Ag/ACF and investigated the adsorption behavior and antibacterial activity of ACF supported with silver (Ag/ACF). But for the preparation of silver-doped titania antibacterial materials, there were very few reports in the survey of the adsorption behavior on H₂TiO₃. In this paper, we investigated the adsorption behavior of silver ions on H₂TiO₃.

2 Experimental

2.1 Materials

The H₂TiO₃ was prepared by forced-hydrolysis of titanium sulfate (Ti⁴⁺: 0.375 mol/L, H⁺: 3 mol/L) in autoclave at 125 °C for 2 h. The H₂TiO₃ was used without any heat or chemical treatment for adsorption studies. The size of H₂TiO₃ was measured by particle size analyzer (MS-2000). The average size of the particles is 0.2 μm, and its specific surface is 13.8 m²/g. The stock solution of Ag⁺ (1 g/L) was prepared by dissolving 0.157 4 g of AgNO₃ into 10 mL HNO₃ (0.01 mol/L) and making the volume to 1 L with distilled water. All working solutions were prepared by diluting the stock solution with distilled water.

2.2 Methods

2.2.1 Dynamic adsorption

Before conducting the equilibrium adsorption experiments, the dynamic adsorption experiments were conducted to determine the time required to reach equilibrium. The dynamic adsorption measurements were carried out at room temperature ($(25 \pm 1)^\circ\text{C}$) on a rotary shaker using 500 mL capped conical flask. 0.2 g of H_2TiO_3 was mixed into 200 mL of silver containing solution of known concentration. Solution was taken at various periods of time and analyzed for silver ions concentration (c_t). The adsorption density q (mg/g) at different time was calculated by the equation:

$$q = (c_s - c_t)V/M \quad (1)$$

where c_s is the initial concentrations of silver ions in the solution (mg/L), V is the volume of the solution (L), M is the amount of the H_2TiO_3 used (g).

2.2.2 Equilibrium adsorption

Five solutions of pH (3, 4, 5, 6 and 7) were prepared by adding appropriate volumes of 0.1 mol/L HNO_3 or 0.1 mol/L NaOH solution of distilled water. The pH of solution was measured using microprocessor pH meter model H18417 by Hunan instruments. The shaking experiment was carried out in a thermostat shaker bath. Adsorption measurements were carried out in a batch technique at room temperature (25 ± 1) $^\circ\text{C}$, 200 mL of silver containing solution of known concentration were shaken with H_2TiO_3 (0.2–1.0 g) in 500 mL reagent glass bottle for 2h. The solution was filtered through filter paper and analyzed for silver ions concentration.

The equilibrium adsorption density q_e (mg/g) was computed using the following equation:

$$q_e = (c_s - c_e)V/m \quad (2)$$

where c_s and c_e stand for the initial and final concentrations of silver ions in the solution (mg/L), respectively, V stands for the volume of the solution (L), m stands for the amount of the H_2TiO_3 used (g).

2.2.3 Analysis method

The solution was filtered through filter paper; the first 5 mL portion of the filtrate was rejected because of the adsorption of silver ions on filter paper. The concentration of silver ions in measuring filtrate was determined with Atomic Absorption Spectrophotometer (AAS 200A Buck Scientific Model) and corrected for losses due to adsorption on the walls of the glass bottles by running blank experiments (without H_2TiO_3 added).

3 Results and discussion

3.1 Dynamics of Ag^+ absorbed

The results (Fig.1) showed that the absorption equilibrium was quickly reached with an initial concentration c_s of silver ion 50 mg/L in 5 min. For

higher values of c_s reached, the equilibrium took about 10 min. After 10 min of the suspension skating, more than 20% of Ag^+ ($c_s=200$ mg/L) was already adsorbed from the aqueous solution, about 50% of Ag^+ was adsorbed from the aqueous solution with the smaller value of c_s (50 mg/L). To ensure equilibrium was attained, we choose contact time equal to 2 h to undertake the following experiments.

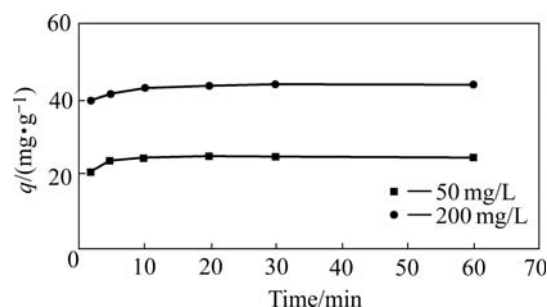
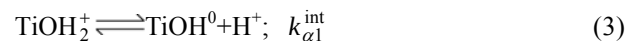


Fig.1 Dynamics of Ag^+ absorbed by H_2TiO_3 (pH=7, $t=25^\circ\text{C}$)

3.2 Effect of pH

According to surface complexation theory, the reactive surface sites of hydrated metal oxides are comprised of metal-hydroxyl sites that can react with ions in solution. The surface acidity of these sites on H_2TiO_3 surface can be described as[14]



where TiOH_2^+ , TiOH^0 and TiO^- represent the protonated, neutral and ionized surface hydroxyl groups, respectively, $k_{\alpha 1}^{\text{int}}$ and $k_{\alpha 2}^{\text{int}}$ the respective acidity constants.

Surface acidity is an important property of hydrous titania (H_2TiO_3) which relates to the extent of interfacial reactions including adsorption of metal ions. Since the surface charge of an adsorbent can be modified by changing pH of the solution, pH is one of the most important parameters affecting the adsorption process of silver ions. Therefore, the effect of pH on the silver ions adsorption was investigated in the pH range of 3–7 using 0.2 g of H_2TiO_3 at the concentration of silver ions as 20, 30 and 40 mg/L, respectively. The variation of equilibrium adsorption density (q_e) with rise in pH of the solution is shown in Fig.2. It is obvious from this figure that the q_e value for silver ions adsorption on H_2TiO_3 increases with increasing pH from 3 to 7, and it increases very sharply at pH above 5. With an initial concentration (c_s) 20 mg/L of silver ion, the q_e value increases from 8.2 mg/g to 9.4 mg/g as pH increases from 3 to 5. While the pH value increases up to 7, the q_e value attains 15.3 mg/g. The q_e value also increases with increasing silver ions concentration at the same pH value, but the extent of q_e

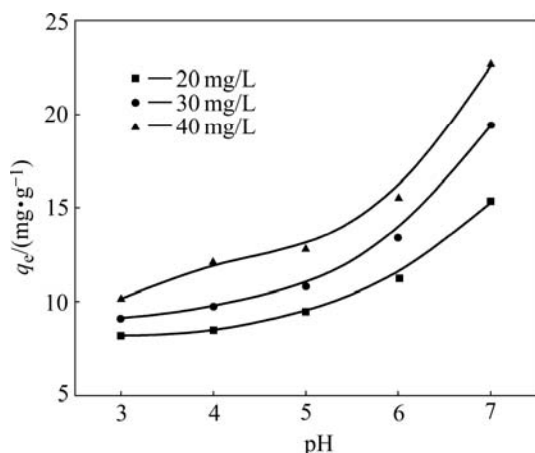


Fig.2 Effect of pH on adsorption

increase is different at the various pH values.

The influence of pH on silver ions adsorption can be explained as follows: low adsorption of silver ions on H_2TiO_3 at low pH is due to strong H^+ ion competition for the available exchange sites or a surface adsorption phenomenon in which the adsorbent surface does not favor the adsorption of positively charged ions at low pH.

3.3 Effect of silver ions concentration

The adsorption of silver ions on the H_2TiO_3 was studied as a function of initial concentration of silver ions in the range of 10–150 mg/L while keeping all other parameters constant, and the results are shown in Fig.3 and Fig.4. The equilibrium concentration of silver ions (c_e) obtained was plotted against initial concentration of silver ions (c_s) at various pH values in Fig.3. The adsorption density values obtained were plotted versus equilibrium concentration of silver ions in Fig.4.

It is obvious that the increase of the initial concentration in silver ion gives a substantial increase in the quantity of retained silver ion in bulk solution for the same quantity of H_2TiO_3 (Fig.3). The increase in initial

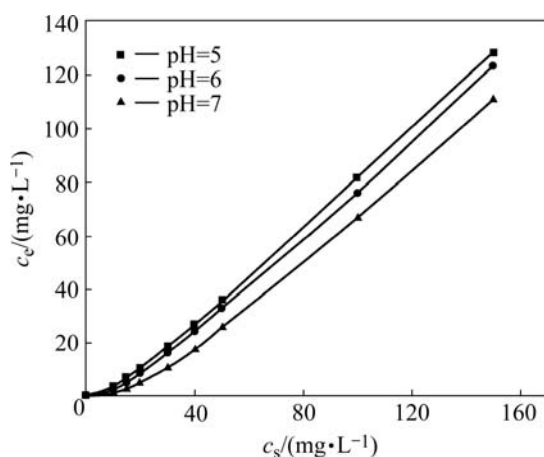


Fig.3 Curves of equilibrium concentration of silver ions (c_e) vs initial concentration of silver ions (c_s) at various pH values

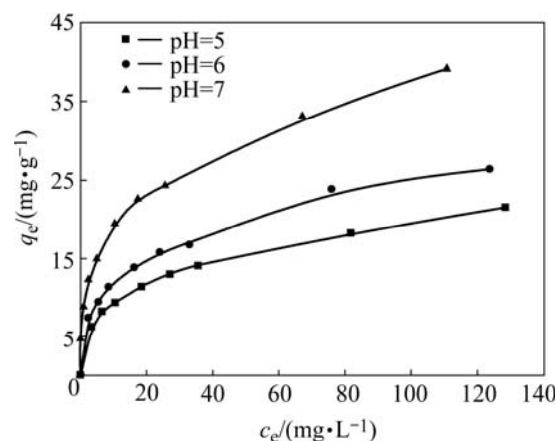


Fig.4 Curves of equilibrium concentration of silver ions (c_e) in bulk solution vs its adsorption density (q_e) at various pH values

concentration of silver ion for the same mass of H_2TiO_3 creates a great increase of molecules of silver ion adsorbed on the free sites of the surfaces of particles H_2TiO_3 , the equilibrium adsorption density (q_e) increases quickly with increasing equilibrium concentration of silver ions between 0.05 and 20 mg/L, especially at pH=7 (Fig.4). When the equilibrium concentration of silver ions is higher than 20 mg/L, most of sites are occupied, more and more silver ion remain in the liquid phase and equilibrium adsorption density (q_e) approaches to its maximum limit q_m .

3.4 Effect of adsorbent dosage

The effect of adsorbent dosage on the adsorption of silver ions was studied by varying the amount of H_2TiO_3 from 0.2 to 1.0 g in 200 mL solutions ($c_s=50$ mg/L) at pH=7 and 2h of contact time. The adsorption percent values $((c_s - c_e)/c_s) \times 100\%$ obtained are plotted versus adsorbent dosage in Fig.5.

It can be seen from Fig.5 that the amount of silver ions adsorption increases quickly with increasing adsorbent dosage. This is an expected result that as the amount of the adsorbent increases, the number of adsorbent particles surrounded by silver ions or the ratio of the number of adsorbent particles to that of silver ions increases in the solutions, resulting in thus more ions adsorbed onto the adsorbent surfaces.

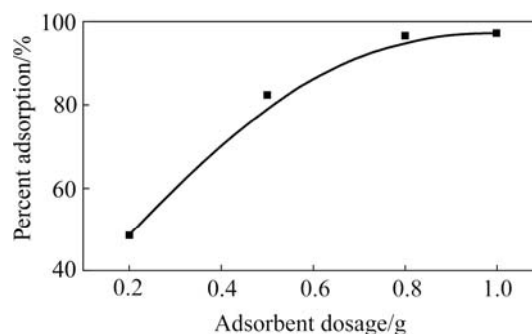


Fig.5 Effect of adsorbent dosage on adsorption of silver ions

3.5 Adsorption models

The Langmuir adsorption isotherm[15] is one of the most widely used models for describing of the adsorption of a solute from a liquid solution and it has been successfully applied in many studies on adsorption of various metal ions. A basic assumption of the Langmuir law is that the adsorption takes place on specific homogeneous sites of the adsorbent surface. It is then assumed that once a metal ion occupies a site, no further adsorption can take place at that site. The rate of adsorption to the surface should be proportional to a driving force per unit area. The driving force is the concentration in the solution, and the area is the amount of bare surface. The saturated monolayer isotherm can be represented as

$$q_e = \frac{q_m k c_e}{1 + k c_e} \quad (5)$$

The above equation can be rearranged to the following linear form:

$$\frac{c_e}{q_e} = \frac{1}{k q_m} + \frac{1}{q_m} c_e \quad (6)$$

where c_e is the equilibrium concentration in bulk solution (mg/L); q_e is the amount of metal ion absorbed (mg/g); q_m is the maximum adsorption capacity (mg/g); k is the adsorption equilibrium constant (L/mg). A plot of c_e/q_e versus c_e should indicate a straight line of slope $1/q_m$ and an intercept of $1/(k q_m)$. The straight line was obtained by plotting c_e/q_e against c_e . Fig.6 indicates the conformity of the data to the Langmuir equation as well. Values of constants q_m and k were calculated from the slope and intercept. The calculated results of the adsorption constant k and the specific maximal quantity q_m are shown in Table 1.

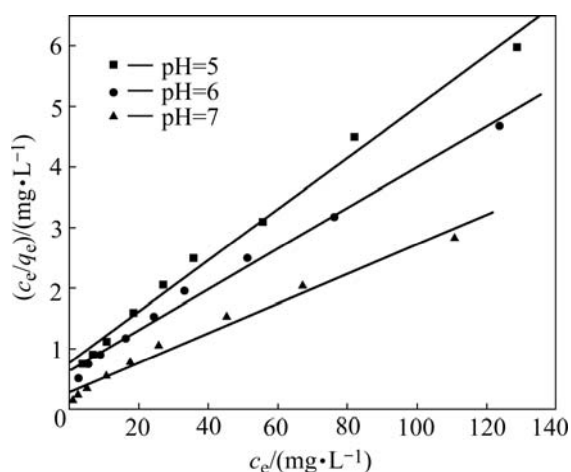


Fig.6 Langmuir isotherm plots for adsorption of silver ions on H_2TiO_3 at various pH values

Table 1 Constants of Langmuir isotherm at various pH values

pH	$k/(L \cdot mg^{-1})$	$q_m/(mg \cdot g^{-1})$
5	0.054 7	23.64
6	0.052 4	29.76
7	0.088 1	40.82

It can be seen from Table 1 that the specific maximal quantity q_m increases with increasing pH, the adsorption constant k is almost the same at pH=5 and pH=6, but it has a high value at pH 7.

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(Edited by HE Xue-feng)