



Article Adsorption Mechanism of Pb²⁺ Activator for the Flotation of Rutile

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Received: 23 May 2018; Accepted: 22 June 2018; Published: 25 June 2018



Abstract: In general, the flotation of minerals containing titanium needs to be activated by metal ions due to a lack of activating sites on their surface. However, the activating process is indirectly inferred due to the lack of direct experimental observation. In this study, atomic force microscopy (AFM) was used to observe the activation process. The results revealed that the hydroxyl compounds of Pb²⁺ ions were adsorbed on the rutile surface in the form of multiple molecular associates, rather than through single molecule adsorption. Styryl phosphoric acid (SPA) could largely be adsorbed on the activated rutile surface. The results of contact angle measurements also revealed that the hydrophobicity of the activated rutile surface was significantly greater than that of the un-activated rutile surface after SPA was adsorbed. This study will be helpful to understanding the activating process from the microscale.

Keywords: rutile activation flotation; atomic force microscope (AFM); activation sites

1. Introduction

In recent years, titanium and its alloys have been extensively used in the aviation, aerospace, marine, chemical, pharmaceutical industries and other fields due to characteristics including its light weight, high strength, corrosion resistance, magnetic resistance, etc., [1-4]. Due to the high consumption of titanium materials, the demand for the extraction and purification of raw materials is increasing. The raw materials currently used in the industrial extraction of titanium and its oxides are mainly rutile (TiO₂) and ilmenite (FeTiO₃). These materials reportedly have poor hydrophobicity and the highly selective chelating collector molecules are difficult to adsorb on their surfaces due to the lack of activating sites. In general, their flotation separation necessitates the addition of metal ions as activators. Pb^{2+} , Cu^{2+} , Fe^{3+} and Bi^{3+} ions were reported to be relevant metal ions. Pb^{2+} ions have been widely used as the activator for ilmenite flotation, and the activating mechanism was studied by XPS (X-ray photoelectron spectroscopy), zeta potential, FTIR (Fourier transform infrared spectroscopy) and solution chemical composition calculation [5-7]. In previous studies, it was found that Pb²⁺ ions were physically adsorbed in the form of hydroxide $([Pb(OH)_n]^{(2-n)})$ on the ilmenite surface, which was the main adsorbate form. A few Pb²⁺ ions could also react with Fe elements on the ilmenite surface to form -Fe-O-Pb- compounds. Li et al. [8] also found that Pb^{2+} ions had a strong activating ability for rutile flotation, and the activating mechanism was explained by XPS and zeta potential measurements. Xiao et al. [9] used Bi^{3+} ions to activate the rutile flotation, and found that Bi^{3+} ions adsorbed on the rutile surface in the form of the hydroxyl species of Bi^{3+} ions $(Bi(OH)_n^{+(3-n)})$ and the hydroxylated rutile surface, producing the compounds of -Ti-O-Bi²⁺. After metal ion activation, chelators that bind to these metal ions were often used as collectors to improve the hydrophobicity of the rutile surface, such as styryl phosphoric acid (SPA) [9–11].

On the basis of these previous studies, we found that the activation mechanisms of metal ions for mineral flotation were indirectly deduced by some measures, such as XPS, zeta potential, FTIR and simulation calculation [5,6,8–13]. However, at the micro level, there was no intuitive evidence for the explanation of the activation mechanisms of Pb^{2+} ions for rutile flotation. In order to further understand the mechanism of how metal ions activate mineral flotation, it was necessary to observe the activation process of metal ions from the microscopic scale. In this study, contact angle measurements were used to investigate the effect of Pb^{2+} ions on the rutile flotation from the macro scale, and atomic force microscopy (AFM) was used to observe the Pb^{2+} ions and provided some information on the adsorption of SPA on the rutile surface from the microscopic scale due to its high spatial resolution. We found that the hydroxyl compounds of the Pb^{2+} ion were adsorbed on the rutile surface in the form of multiple molecular associates rather than through single-molecule adsorption.

2. Materials and Methods

2.1. Materials and Reagents

A block of rutile sample from Zaoyang, Hubei, was selected as the substrate for AFM and contact angle measurements. Firstly, the sample was cut into a cuboid shape with dimensions $12 \text{ mm} \times 12 \text{ mm} \times 2 \text{ mm}$. The sample was then sequentially ground by diamond grinding wheels of 100, 40 and 9 µm roughness to obtain a flat surface. The sample was successively polished by a microcloth using 1.0, 0.3 and 0.05 µm alumina powder solution. After being polished, the sample was washed with Milli-Q water and cleaned in a microwave bath to remove any adhering alumina. Lastly, the polished sample was washed by alcohol, and treated with a plasma cleaner (Harrick Plasma, Plasma Cleaner PDC-32G from Harrick Plasma Co., Ltd., New York, NY, USA) for 2 min to remove any adhering organic matter. Styryl phosphoric acid (SPA) with 68% purity was obtained from Zhuzhou Flotation Reagents, and then purified by recrystallization in methanol–water solvent in the lab. Its recrystallization product (95% purity) was used in all experiments. Lead nitrate (Pb(NO₃)₂) (99.8%) was purchased from Sinopharm Chemical Reagent Co., Ltd. All aqueous solutions were prepared using Milli-Q water (Millipore deionized, 18.2 M Ω resistivity).

2.2. Methods

2.2.1. Contact Angle Measurements

A contact angle measuring device (JC2000C, Shanghai Zhongchen Digital Technology Company, Shanghai, China) was used determine the wettability of the rutile surface before and after 10^{-5} mol/L SPA adsorption on the un-activated/activated rutile surface. The polished rutile sample was immersed in the solution containing Pb²⁺ ions (10^{-5} mol/L) or SPA (10^{-5} mol/L) for 10 min, respectively, and then taken out and blow dried with N₂ as the control groups. The sample preparation procedure was that the polished rutile sample was first immersed in the solution with Pb²⁺ ions (10^{-5} mol/L) for 10 min, and then taken out to be immersed in the solution with SPA (10^{-5} mol/L) for 10 min, and lastly taken out and blown dried with N₂. The contact angles of samples were measured with Milli-Q water, which were placed using a calibrated syringe. Fifty microliters (50μ L) of Milli-Q water was used for each measurement. The equilibrium contact angle of the water droplet was measured in four different positions with $\pm 2^{\circ}$ of error, and the mean value was reported as the result. All measurements were conducted at 25 °C.

2.2.2. PF-QNM Imaging

AFM measurements were performed by a Bruker Multimode 8 SPM with NanoScope 8 software installed and a NanoScope V controller. Silicon nitride cantilevers with a nominal spring constant of 0.35 N/m (NDP-10, Bruker, Billerica, MA, USA) were used, and the probes were treated using a Plasma Cleaner for 2 min beforehand. Samples were treated in the same way as the contact angle measurements.

All AFM experiments were performed in a liquid cell at room temperature. Fifty microliters (50 μ L) of Milli-Q water was injected into the liquid cell. The deflection sensitivity and spring constant for each cantilever were measured using the built-in cantilever calibration, ramp and thermal noise method, respectively. The peakforce amplitude was set at 100 nm, the peakforce frequency was set to 2 kHz and the scan rate was set to 0.977 Hz. The peakforce setpoint was carefully set at a small loading force ranging from 200 to 600 pN.

3. Results and Discussions

3.1. Contact Angle Measurements

In order to characterize the effect of Pb²⁺ ions, the hydrophobicity of the rutile surface was investigated under different conditions by performing measurement of the contact angles and the results are shown in Figure 1. In Figure 1, it can be found that the contact angle of the rutile surface was $37.6^{\circ} \pm 1.5^{\circ}$ in the natural condition, suggesting that the natural hydrophobicity of rutile surface was very poor. This is in agreement with the results reported in previous studies [9,12]. After SPA adsorption on the un-activated rutile surface, the contact angle of the rutile surface only increased from 37.6° to $48.7^{\circ} \pm 2.0^{\circ}$, which indicated that it was very difficult for SPA to be adsorbed on the un-activated rutile surface. Many reports suggested that minerals containing titanium, such as rutile and ilmenite, lacked the activating sites on their surfaces for surfactant adsorption [5,6,11]. However, after SPA adsorption on the activated rutile surface, the contact angle of the rutile surface sharply increased from 37.6° to 86.1°, which revealed that SPA could significantly improve the hydrophobicity of the rutile surface after Pb²⁺ ion activation. Again, this finding was in accordance with the earlier observation of Li et al. [8]. In earlier studies, the activation mechanisms of metal ions to mineral flotation were indirectly deduced by some measures, such as XPS, zeta potential and simulation calculation [2,3,5,6,9,12–15]. To investigate the activation mechanism at the microscale, AFM was used to observe the morphology of the rutile surface before and after Pb²⁺ ions treatment, due to its high spatial resolution.



Figure 1. The contact angles of water on the rutile surface. (**A**) Rutile surface without any treatment; (**B**) rutile surface after styryle phosphoric acid (SPA) adsorption; (**C**) rutile surface first adsorbed with Pb²⁺ ions, and then with adsorbed SPA.

3.2. AFM Imaging

In order to observe the activating process of Pb^{2+} ions on the rutile surface, we designed the AFM experiments to investigate the adsorption morphology of SPA on the rutile surface in the absence and presence of Pb^{2+} ions. Figure 2a shows the morphology of the rutile surface in water without any treatment. It can be seen that the rutile surface is very smooth, and the Rq was only 0.890 nm, which suggested that the polished rutile surface met the requirement of AFM measurements at a nanoscale resolution.

The appearance of the rutile surface treated with SPA is shown in Figure 2b. It can be seen that there is no obvious change on the rutile surface after SPA adsorption. The Rq (0.985 nm) is slightly higher than that in Figure 2a, which indicates that only a small amount of SPA was adsorbed on the rutile surface.

The result of Pb²⁺ ion adsorption on the rutile surface is shown in Figure 2c. According to Figure 2c, we found that many round matters appeared on the rutile surface, and they covered the whole rutile surface. Their diameters were very uniform, and they were distributed around 40 nm. Even if the tip effect was considered, such a large radius could not be made up of a single molecule; therefore, it must be composed of molecular associations. However, the difference in height was very large—from 0.5 nm to 3.0 nm—due to the existence of multilayer adsorption. Referring to previous results, the round materials may be composed of lead hydroxide and hydrate, which was adsorbed on the rutile surface due to the electrostatic attraction force [5–8,15].

The appearance of the activated rutile surface after SPA adsorption is shown in Figure 2d,f. In order to observe the overall adsorption morphology, we conducted a scan of a large area—20 μ m \times 20 μ m. In Figure 2f, it is shown that SPA is adsorbed on the rutile surface in the form of aggregation, and it can be clearly seen that the more intensive SPA gathered onto the film. There was also some SPA aggregation on the surface of the formed SPA film. The adsorption of SPA on the activated rutile surface was not uniform, while the height of the adsorption film (including the height of lead hydroxide and hydrate, and water layer) was mainly between 5.2 nm and 10.3 nm. This phenomenon was very similar to that reported in the literature on the adsorption of surfactants on the mineral surface [16,17]. In order to further explore the activating effect of Pb²⁺ ions on the rutile surface, we selected an ordinary area (the area of the blue line in Figure 2f) for magnification scan. The scan range (5 μ m \times 5 μ m) and height bar value (-10 to 10 nm) were the same as Figure 2a–c, and the results are shown in Figure 2d. It can be clearly seen that there are also many round matters which appear on the activated rutile surface, t as in Figure 2c, but there are significant differences compared with Figure 2c. The adsorption matters in Figure 2d are much higher and their diameters are much larger than those in Figure 2c. Those characteristics are obviously caused by the SPA adsorption on the activated rutile surface. On the other hand, the obvious agglomeration phenomenon is found in Figure 2d, which is difficult to observe in Figure 2c. In hydrophobic induction, hydrophobic collectors in aqueous solution were more likely to produce association [14,18].

Figure 3 shows the analyses of AFM section lines listed in Figure 2a–d, respectively. In Figure 3, the vertical distance slightly increases after SPA adsorption on the un-activated rutile surface. This complies with the contact angle measurements, suggesting that it is very different for SPA adsorption on the natural rutile surface. After Pb²⁺ ion treatment, it was evident from the distinct vertical peaks that Pb²⁺ ions had been successfully deposited on the rutile surface. It was further found from Figure 3 that Pb²⁺ ions showed single-layer and double-layer adsorption on the rutile surface. After SPA was adsorbed on the activated rutile surface, the vertical distance dramatically increased, suggesting that SPA could be adsorbed on the activated rutile surface with Pb²⁺ ion hydroxide as the activating site.



Figure 2. Atomic force microscope (AFM) topographic images of rutile surface. (**a**) Rutile surface without treatment; (**b**) rutile surface after adsorbing SPA; (**c**) rutile surface after adsorbing Pb²⁺ ions; (**d**,**f**) rutile surface first adsorbed with Pb²⁺ ions, and then adsorbed with SPA; and (**e**) an optical image of the rutile surface and scanning probe. Scan size: (**a**–**d**) 5 μ m × 5 μ m, (**f**) 20 μ m × 20 μ m.



Figure 3. AFM height profile of rutile surface: (A) no treatment; (B) SPA adsorption on the un-activated rutile surface; (C) Pb²⁺ ions adsorption; and (D) SPA adsorption on the activated rutile surface.

4. Conclusions

In summary, AFM was first used to observe the activating process of Pb^{2+} ions on the rutile surface. The results indicated that the hydroxyl compounds of Pb^{2+} ion was adsorbed on the rutile

surface in the form of multiple molecular associations, rather than as a single molecule. SPA could largely be adsorbed on the activated rutile surface with single and double layers, rather than on the un-activated rutile surface. This finding will be very helpful to understanding the activating process of metal ions on mineral surfaces and will promote the activating effect in flotation.

Author Contributions: H.Z. and J.W. conceived of and designed the experiments; W.X. prepared the samples and performed the experiments; W.X. and H.Z. analyzed the data; and W.X., H.Z., W.Q. and G.Q. contributed to the writing and revising of the paper.

Funding: This research was jointly funded by the National Natural Science Foundation of China (No. 51474254), Young Elite Scientists Sponsorship Program by CAST (2017QNRC001), Innovation-Driven Project of Central South University (2018CX019).

Acknowledgments: We sincerely appreciate the detailed and constructive reviews and suggestions from three anonymous reviewers, which greatly improved this paper. We especially thank Weiguang Zhou for help with the English modification.

Conflicts of Interest: The authors declare no conflict of interest.

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