

Article

Activation Mechanism of Lead(II) to Ilmenite Flotation Using Salicylhydroxamic Acid as Collector

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Received: 20 May 2020; Accepted: 17 June 2020; Published: 24 June 2020



Abstract: In this study, salicylhydroxamic acid (SHA), which exhibits superior flotation performance to conventional collector benzohydroxamic acid (BHA), was first introduced in ilmenite flotation. The addition of lead(II) can significantly increase the recovery of ilmenite using SHA as collector. Thus, the adsorption mechanism of SHA on lead(II)-activated ilmenite surface was systematically studied using micro-flotation tests, adsorption analysis, zeta potential measurements, Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS). Micro-flotation results revealed that SHA had stronger collecting ability than BHA, and ilmenite floatability could be activated by lead ions with either SHA or BHA as collector. Ilmenite showed good floatability at pH 6–8 (over 90% recovery) in the presence of Pb^{2+} and SHA. In such conditions, the main lead species of $Pb(OH)^+$ and Pb^{2+} acted as active sites and caused positive surface potential shifts, thereby increasing the adsorbed amounts of negatively charged SHA on the surface of the mineral. FTIR and XPS analyses suggested that the lead species was chemically adsorbed on the surface of ilmenite to form active sites chelated by SHA. Moreover, the free lead ions in solution might form the Pb–SHA complexes to adsorb on the mineral surface, thereby increasing the floatability of ilmenite.

Keywords: ilmenite; lead ion; flotation; salicylhydroxamic acid; adsorption mechanism

1. Introduction

Titanium, which is a rare metal, has been widely applied in the aerospace sector, in the military industry, for medical devices, and for environmental protection, due to its high strength-to-weight ratio and inertness to many corrosive conditions [1,2]. Titanium ores, which are the important cornerstone of the titanium industry, comprise ilmenite ($FeTiO_3$) and rutile (TiO_2). In China, ilmenite ore has ranked first for the production of Ti metal, primarily due to the excessive exploitation and progressive exhaustion of rutile ore in the past [3,4]. Gravity, magnetic, and electrostatic separations, which have been traditionally used to obtain ilmenite concentrate, are increasingly becoming unsuitable for the finely disseminated ilmenite ore [5]. Meanwhile, froth flotation with surface modification has become a rapidly developing method for the beneficiation of ilmenite from raw ore in recent years, and has been receiving increasing attention from researchers [6–8].

To date, anionic surfactants (such as sodium oleate, naphthenic soap, oxidized paraffin soap, and hydroxamate) and cationic reagents (including undecyl propyl ether amine and dodecylamine acetate) are commonly used as collectors for the beneficiation of ilmenite ores [4,7,9,10]. Among these collectors, benzohydroxamic acid (BHA) was considered as an effective collector for the flotation of ilmenite, and the flotation mechanism was systematically studied [11]. However, the individual usage of hydroxamate has failed to attain the desired floatability, even in the presence of the large dosage of collector. The potential reason may be the small active sites of ilmenite, which is similar to the cases of wolframite, scheelite, and cassiterite [12]. A common practice to increase surface sites of mineral is surface modification, including microwave irradiation, surface oxidation, and introducing metal ions on its surface [12–15]. Lead(II) is widely used because it can enhance the floatability of oxide minerals with low cost [16,17], and BHA has been used for the flotation of ilmenite with the activation of lead ions [18]. Nevertheless, previous flotation results showed that BHA does not work as efficiently as expected, because of the poor hydrophobicity and floatability of ilmenite [11]. Thus, a hydroxamate collector with a strong adsorbability on the ilmenite surface should be developed.

Among hydroxamate collectors, salicylhydroxamic acid (SHA) is a promising chelator, due to its one more phenolic group than BHA and has been utilized in cassiterite, malachite, and rutile flotation [19–21]. In this work, SHA and BHA as ilmenite collector in the absence and presence of lead(II) were compared using single mineral flotation tests. Moreover, the activation mechanism of lead(II) to ilmenite flotation using SHA as collector was systematically studied by zeta potential measurements, adsorption analysis, Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS).

2. Materials and Methods

2.1. Materials

Ilmenite samples were sourced from Panzhihua (Sichuan Province, China). X-ray powder diffraction data (Figure 1) and chemical composition (Table 1) confirmed that the ilmenite samples were of over 90% purity. After the samples were crushed and screened, the 38–75 μm fractions were used in the flotation tests and $-2 \mu\text{m}$ fractions were utilized for the zeta potential measurements. SHA, BHA, and lead nitrate ($\text{Pb}(\text{NO}_3)_2$) of analytical reagent grade were purchased from Hengxing Co., Ltd., Tianjin, China. H_2SO_4 and NaOH solutions were adopted to adjust the pH of the system, and demineralized water was used throughout the experiments.

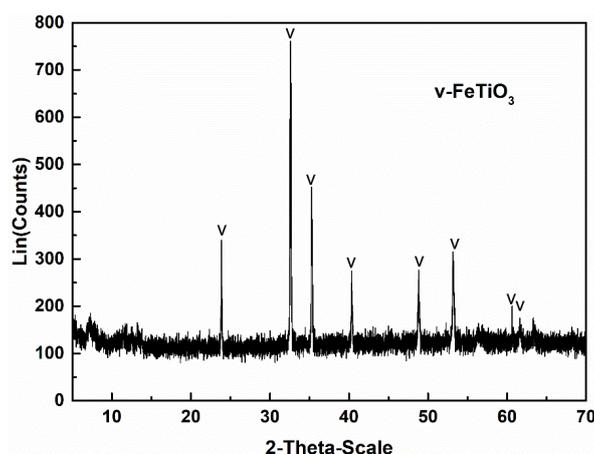


Figure 1. XRD pattern of the ilmenite.

Table 1. Chemical composition of the ilmenite samples.

Component	TiO ₂	Fe ₂ O ₃	SiO ₂	CaO	MgO	Al ₂ O ₃	MnO
Content (%)	50.97	41.79	1.96	1.48	2.17	0.89	0.74

2.2. Flotation Test

Single mineral flotation tests were carried out in an XFG flotation machine with a 40 mL plexiglass cell and at an impeller speed of 1650 rpm. A total of 2.0 g of ilmenite samples was added to 40 mL of distilled water, and the mineral suspension was placed into the flotation cell. After suitable quantities of flotation reagents and pH regulators were added, the pulp was stirred for 3 min and then floated for 4 min. The concentrate and tailing samples were filtered, dried, and weighed, to calculate the flotation recovery under various flotation conditions on the basis of the dry mass of the products. The results calculated in the form of mean value \pm standard deviation were plotted and reported using Origin 2015 software.

2.3. Adsorption Measurements

The adsorption measurements of SHA on the ilmenite surfaces treated and not treated with lead(II) were carried out using a TU-1810 UV–visible spectrophotometer (Purkinje General, Beijing, China). For this experiment, 2.0 g of ilmenite sample was introduced to a beaker with 40 mL of distilled water. The suspension was stirred for 1 h after the desired reagent was added to the solution. Then, the solution was centrifuged for solid–liquid separation to obtain the supernatant, which was subsequently used for concentration measurements of the residual reagents. Each experimental sample was tested 3 times to obtain the mean and variance. The adsorption of SHA on the ilmenite surface can be calculated as follows:

$$\Gamma = (C_0 - C \times V)/m, \quad (1)$$

where Γ is the amount of SHA adsorbed on the ilmenite surface (mol/g), C_0 is the initial quantity of SHA in the solution (mol), C is the residual concentration of the reagent in the supernatant (mol/L), V is the volume of the solution (L), and m is the weight of the mineral (g).

2.4. Zeta Potential Measurements

Zeta potentials were measured using a Delsa-440sx Zeta meter (Malvern Instruments, UK). The suspension was prepared by adding 16 mg of the ilmenite powder (particle diameter: $-2 \mu\text{m}$) in the beaker with 80 mL of electrolyte solution ($\text{KNO}_3 = 0.01 \text{ mol/L}$). The pH of the suspension was regulated to a required value by the addition of NaOH or H_2SO_4 solution. The desired amount of reagents was added in the order of lead(II) (when activation occurred) and SHA. The solution was stirred for 15 min by a magnetic stirrer and then allowed to settle for 10 min. The supernatant was filtered and kept for zeta potential measurements. The results presented in this study were averaged from over three independent measurements.

2.5. FTIR Measurements

The ilmenite samples were crushed to less than $3 \mu\text{m}$ with an agate mortar. A total of 1.0 g of pure minerals and the desired amounts of reagents were placed in a 100 mL beaker of 40 mL distilled water with 30 min of conditioning time. Then, the filtered and dried samples were recorded in the FTIR spectrometer (type NEXUS-470, Nicolet instrument company, Madison, WI, USA).

2.6. XPS Measurements

The Thermo Scientific ESCALAB 250Xi spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) was used to determine the XPS spectra of ilmenite powders with and without lead(II), at the desired

pH and dosage of SHA. The Al K α X-rays meter with an energy of 12 kV and 6 mA was operated for observations.

3. Results

3.1. Effect of Lead Ions on the Flotation Behavior of Ilmenite

Figure 2 shows the effects of pH value on the flotation results of ilmenite ores. As shown in Figure 2 (a₁), ilmenite displayed a relatively poor floatability with the treatment of BHA alone as collector, and the maximum flotation recovery was only 57.81% at pH 6.0. Figure 2 (a₂) follows the same trend as Figure 2 (a₁), but the maximum recovery reached 80.54%. This result indicated the activation effect of lead ions on the flotation of ilmenite using BHA, which was considerable in accordance with the results of Xu et al. [11] Figure 2 (b₁) shows that, without the addition of lead ions, the recovery of ilmenite increased from 54% to a maximum of 78.54%, with the increase in pH from 4 to 6, remained constant in the pH range of 6.0–8.0, and decreased slowly with the increase in pH from 8 to 11. As shown in Figure 2 (b₂), the floatability of ilmenite under the action of SHA was enhanced significantly from pH 4–11 after treatment with Pb²⁺. The maximum recovery value reached 92% over the optimum pH range from 6.0 to 8.0, and the recovery increases reached approximately 13.7% and 11.7% compared with those treated with SHA alone and BHA–Pb²⁺, respectively. This finding showed that SHA had better collection ability than BHA, and the flotation recovery of ilmenite could be enhanced greatly with the addition of lead ions.

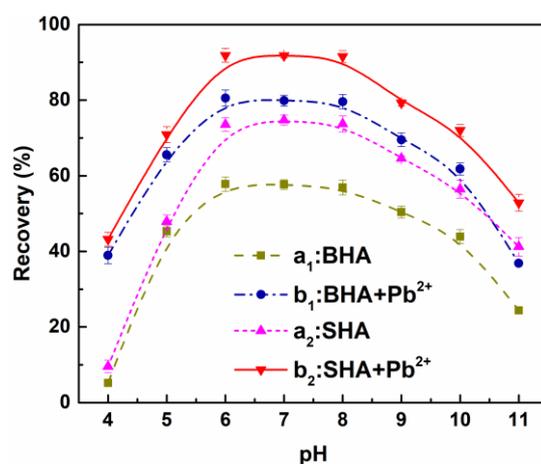


Figure 2. Effects of pH on ilmenite flotation recovery in the absence and presence of Pb²⁺ ions, using salicylhydroxamic acid (SHA) and benzohydroxamic acid (BHA) as collectors ($C(\text{BHA}) = 2 \times 10^{-4} \text{ M}$, $C(\text{SHA}) = 2 \times 10^{-4} \text{ M}$, $C(\text{Pb}^{2+}) = 1 \times 10^{-4} \text{ M}$).

Figure 3 shows a monotonic increase in the recovery of ilmenite with the increase in lead nitrate concentration. Over 80% and 92% of ilmenite particles were floated out when Pb²⁺ concentration reached approximately $1 \times 10^{-4} \text{ M}$, using SHA and BHA as collectors, respectively. The addition of Pb²⁺ significantly improved the recovery of ilmenite using SHA or BHA as collectors. The activation mechanism of lead ions in the flotation of ilmenite using SHA as collector was regarded as the key research object in the subsequent analysis, in view of the fact that the adsorption mechanism of BHA on ilmenite in the presence of lead species has been investigated by [11,22].

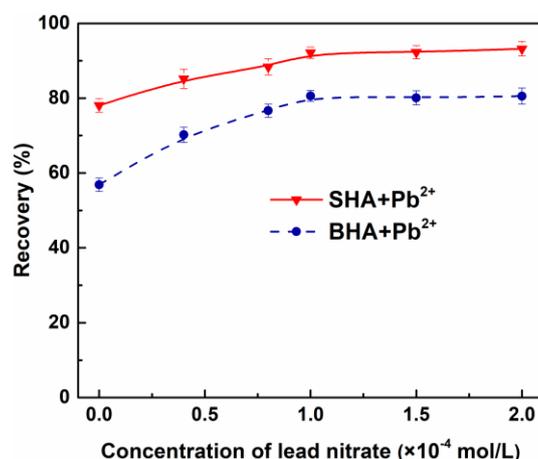


Figure 3. Effect of Pb^{2+} concentration on ilmenite flotation recovery using SHA and BHA (C (BHA) = 2×10^{-4} M, C (SHA) = 2×10^{-4} M, pH = 6.0).

3.2. Effect of Lead Ions on the Adsorbed Amounts of SHA on the Surface of Ilmenite

To characterize the effects of Pb ions on the adsorbed amount of SHA on the surface of ilmenite, the adsorption amounts of SHA on the surface of ilmenite in the absence and presence of Pb^{2+} ions as a function of pH were investigated. The results are shown in Figure 4. In the presence of 1×10^{-4} M of lead nitrate and SHA concentration of 2×10^{-4} M, the adsorbed amount of SHA on the surface of ilmenite with and without lead nitrate addition increased from pH 4 to 6, remained constant from pH 6–8, and fell gradually in the end. These findings were in accordance with the flotation results in Figure 2. The maximum adsorption amount of SHA reached 2.12×10^{-6} mol/g using SHA alone and 3.78×10^{-6} mol/g using Pb^{2+} ions. The adsorption amount of SHA on the surface of ilmenite in the presence of Pb^{2+} ions reached nearly 2 times that in the absence of Pb^{2+} ions within the investigated pH range. The adsorption results generally indicated that lead ions significantly increased the adsorption of SHA on the surface of ilmenite, thereby increasing the recovery of the mineral. To further verify the effect of lead ions on the adsorbed amount of SHA, zeta potential measurements were performed. The following section describes these measurements.

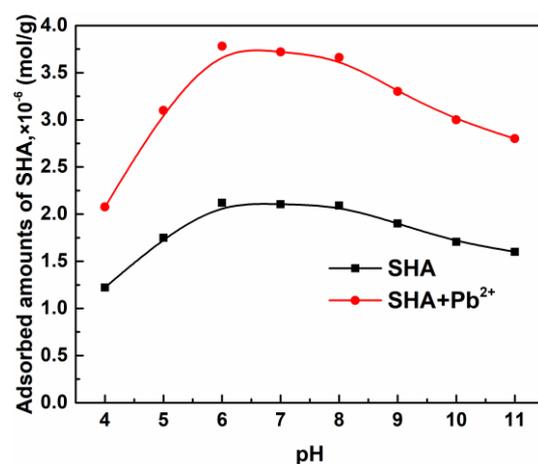


Figure 4. Effect of pH on the SHA adsorption in the absence and presence of Pb^{2+} ions (C (SHA) = 2×10^{-4} M, C (Pb^{2+}) = 1×10^{-4} M).

3.3. Effect of Pb^{2+} and SHA on the Zeta Potential of Ilmenite

The zeta potential of minerals is extremely sensitive to the flotation reagents added in the pulp. Thus, the zeta potentials of ilmenite particles in the absence and presence of Pb^{2+} ions and using SHA as the collector as a function of pH was measured, to investigate the interaction between

ilmenite and reagents. The results are presented in Figure 5. The figure shows that the isoelectric point (IEP) of ilmenite was approximately pH 5.40, which was between the previous reports [6,14]. Therefore, the surface of ilmenite was positively charged at a pH less than 5.40 and negatively charged at a pH greater than 5.40. When SHA was added to the pulp suspension, the zeta potential of ilmenite was decreased throughout the entire pH range, and the IEP negatively shifted to the pH 5.05. This result was due to the interaction between the SHA and the ilmenite surface. SHA mainly exists in its molecular form in acid solution and ionizes increasingly to produce additional negatively charged SHA ions with the increase in pH value, due to the dissociation of the hydroxyl group from hydroxamic and phenolic acids [19]. The low magnitude of SHA ions is generated in acidic solutions to interact with the surface of ilmenite. As a result, the negative shift of the zeta potential of ilmenite upon the addition of SHA under acidic conditions was smaller than that under alkaline conditions (Figure 5).

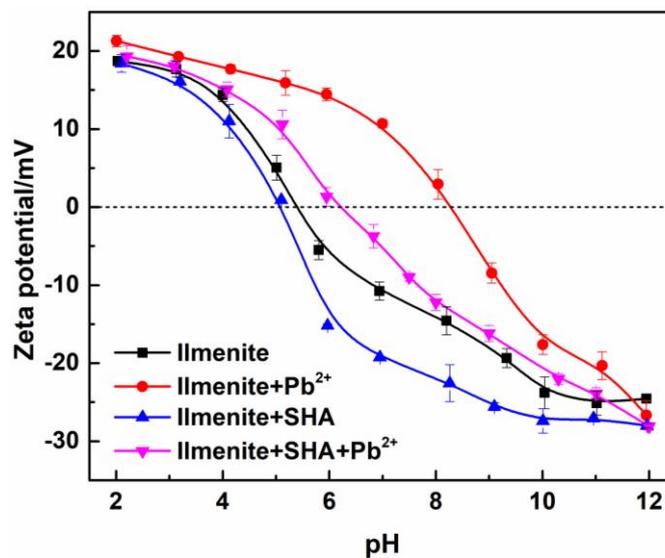


Figure 5. Zeta potentials of ilmenite as a function of pH ($C(\text{Pb}^{2+}) = 1 \times 10^{-4}$ mol/L. $C(\text{SHA}) = 2 \times 10^{-4}$ mol/L).

Figure 6 shows the distribution coefficients of various lead hydroxyl complexes in aqueous solutions as a function of pH [23]. The predominant lead species varied with the pH as follows: the dissociated Pb^{2+} and $\text{Pb}(\text{OH})^+$ dominated in the aqueous solution, with pH less than 7 and pH between 7 and 10, respectively. Therefore, in the optimum pH range for ilmenite flotation (pH = 6–8), the main species were $\text{Pb}(\text{OH})^+$ and Pb^{2+} . At pH > 8, the amounts of $\text{Pb}(\text{OH})_2$, $\text{Pb}(\text{OH})_3^-$, and $\text{Pb}(\text{OH})_4^{2-}$ gradually increased. These species became the major lead ingredients in the solutions at pH > 10. As shown in Figure 5, the addition of lead ions greatly enhanced the zeta potential of ilmenite, especially within the pH range between 6 and 8, due to the adsorption of $\text{Pb}(\text{OH})^+$ and Pb^{2+} . Furthermore, the IEP appeared at approximately 8.4. The maximum positive shift of the zeta potentials of ilmenite was observed at pH 6.0–8.0, and the zeta potential shift gradually decreased above pH 8. A negative shift occurred in the zeta potential of the mineral near pH 12 because of the adsorption of $\text{Pb}(\text{OH})_3^-$, $\text{Pb}(\text{OH})_4^{2-}$, and OH^- .

When Pb^{2+} and SHA were present, the zeta potential of activated ilmenite had a larger negative shift (decreased by approximately 16 mV in the pH region from 6.0 to 8.0) than that with SHA addition alone. This result was consistent with the those of previous flotation and adsorption experiments. Owing to lead species that adsorbed on the ilmenite surface and acted as active sites, SHA could be firmly chelated on the mineral surface. Compared with the direct ilmenite flotation without lead ions, the anion SHA collector did not have to overcome electrostatic repulsion and was therefore more easily adsorbed on the positively charged ilmenite surface.

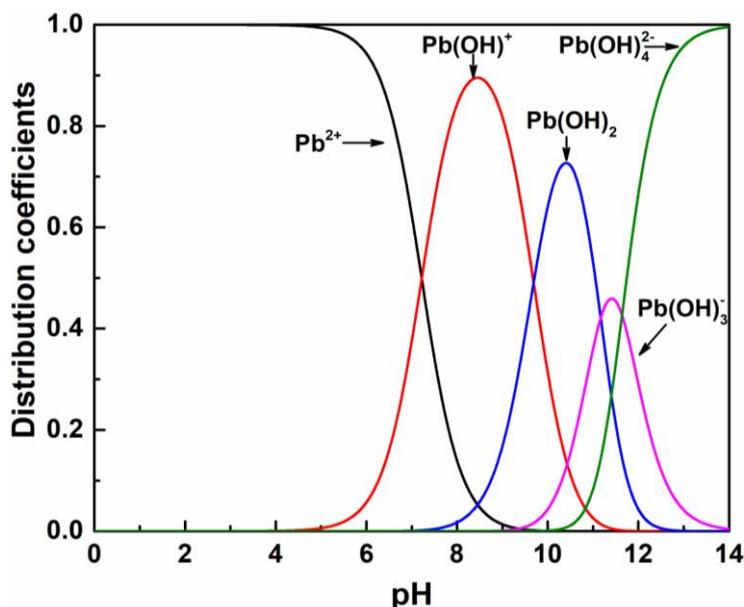


Figure 6. Distribution coefficients of various lead hydroxyl complexes in aqueous solutions as a function of pH [23].

3.4. FTIR Analysis

The experiments of the adsorption measurements and zeta potential proved that lead ions played a positive role in the adsorption of SHA on the surface of ilmenite. To further clarify the reaction mechanism between reagents and minerals, the FTIR analyses of SHA, ilmenite without any disposal, ilmenite treated with SHA alone, and ilmenite treated with lead ions and SHA at pH 6.0 were conducted. The results are shown in Figure 7.

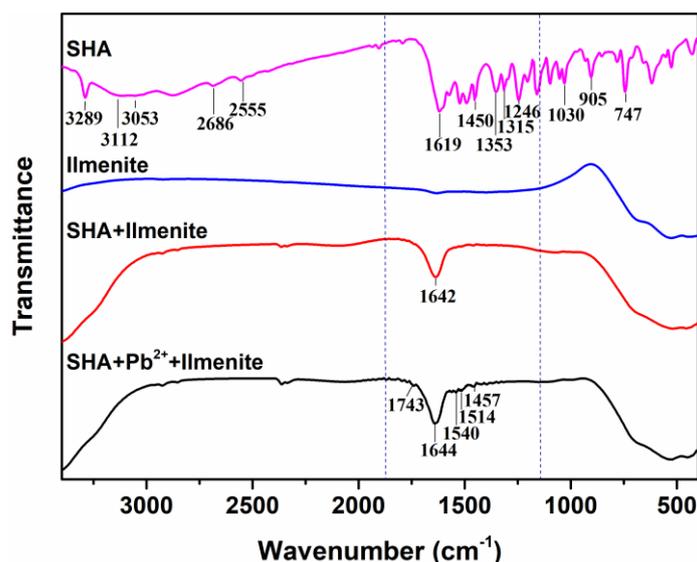


Figure 7. FTIR spectra of ilmenite before and after conditioning with Pb^{2+} and SHA.

In the infrared (IR) spectrum of SHA, the band at 3289 cm^{-1} was attributed to the stretching vibration absorption of the phenolic hydroxyl group [24]. The peaks developed at 3112 and 3053 cm^{-1} were due to the N–H stretching vibration [25]. The peak appearing at 1619 cm^{-1} was the C=O stretching vibration peak, and the broad bands at 2686 and 2555 cm^{-1} were attributed to the O–H group that formed intermolecular hydrogen bonds with C=O. The absorption peak at 1353 and 1315 cm^{-1} was ascribed to the N–O stretching vibrations [26], and the peak at 1246 and 1030 cm^{-1} was attributed

to the aromatic C–H in-plane deformation of the aromatic ring [27]. The bands at 905 and 747 cm^{-1} were due to the C–H out-of-plane bending vibrations of benzene rings [22]. After treatment with SHA alone at pH 6, a new IR absorption peak at 1642 cm^{-1} appeared on the IR spectrum of ilmenite. A shift of 23 cm^{-1} occurred relative to the peak at 1619 cm^{-1} , that belonged to the C=O stretching vibration peak in the SHA spectrum, thereby suggesting that SHA was chemically adsorbed on the ilmenite surface. After treatment with Pb^{2+} and SHA, the absorption intensity at 1644 cm^{-1} increased (shifted by 25 cm^{-1}). This phenomenon revealed that the content of SHA adsorbed on the surface of the ilmenite significantly increased with the activation of lead ions. A strong chemisorption occurred for SHA species on the lead(II)-activated ilmenite surface. The disappearance of the O–H stretching peak might be attributed to the formation of O-metal bonds [28], which indicated chelation from the C=O and O–H groups. In addition, several new peaks from 1300 cm^{-1} to 1900 cm^{-1} appeared, due to the changes in the benzene ring structure caused by the chelating group of Pb–SHA [11]. The FTIR spectra of ilmenite before and after conditioning revealed that SHA not only adsorbed on the surface of ilmenite by chemical adsorption, but also chelated with lead species that adsorbed on the ilmenite surface. This phenomenon increased the collector adsorption.

3.5. XPS Analysis

XPS analysis is widely used for the investigation of the atomic composition and chemical state of the matter surface. An XPS analysis of ilmenite before and after Pb^{2+} and SHA treatment at pH 6.0 was conducted to further study the adsorption mechanism between SHA and ilmenite activated with lead ions, and the results were shown in Figure 8.

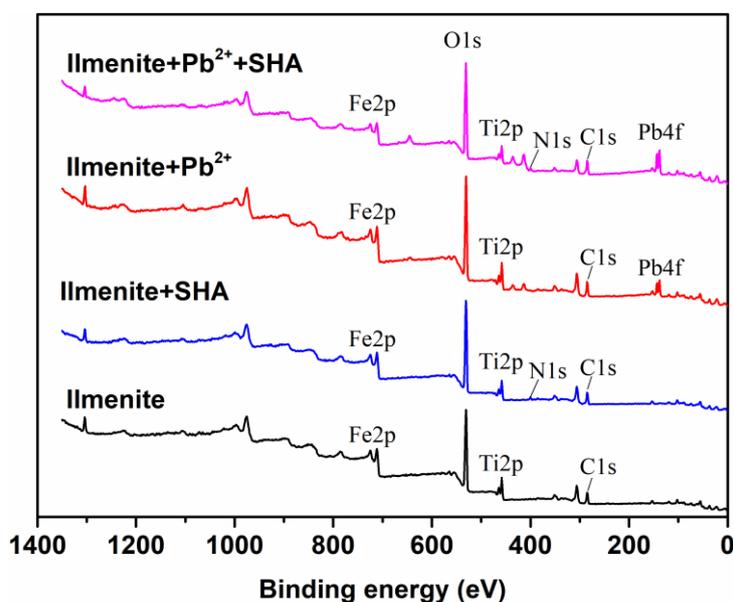


Figure 8. XPS survey spectra of ilmenite, before and after Pb^{2+} and SHA treatment.

The XPS spectra in Figure 8 and the relative amounts of elements in Table 2 showed that the Fe(2p), O(1s), Ti(2p), and C(1s) peaks were observed at the XPS spectra of pure ilmenite [29], and the C(1s) peak ascribed mainly to the carbon background peak introduced during XPS measurement and partially to the contamination of CO_2 and hydrocarbons on the process of sample preparation. After SHA treatment, a new weak peak for N(1s) was detected on the ilmenite surface. Moreover, the relative amount of N(1s) on the surface of the ilmenite was 0.62%, which was attributed to the chelation of SHA to the surface of ilmenite. When ilmenite was only treated with lead ions, an evident Pb(4f) peak appeared at around 138.5 eV. The relative content of Pb(4f) on the ilmenite surface was 1.43%, which suggested that lead species largely adsorbed on the surface of ilmenite. Compared with SHA or lead ion treatment alone, the presence of lead ions and SHA generated more evident peaks

at Pb(4f) and N(1s). The relative amounts of Pb(4f) and N(1s) doubled to 2.4 and 1.21%, respectively. The mutual promotion of the adsorption of lead ions and SHA on the surface of ilmenite indicated that the lead ions adsorbed preferentially on the mineral surface enhanced the adsorption of SHA. Moreover, the free lead ions in the solution might form a complex with SHA to adsorb on the ilmenite surface. This adsorption mechanism was similar to that of Pb(II)/BHA for ilmenite flotation [18]. Notably, in order to avoid detection errors of the surface elements content, three tests were conducted for the atomic concentration of the mineral surface, and the remaining two results (Table S1) attached to the attachment were consistent with the trend in Table 2.

Table 2. Relative atomic concentrations of elements on ilmenite surfaces.

Samples	Element (%)					
	C(1s)	Ti(2p)	Fe(2p)	O(1s)	Pb(4f)	N(1s)
Ilmenite	45.00	11.44	6.33	37.23	-	-
Ilmenite + SHA	45.77	10.27	6.03	37.31	-	0.62
Ilmenite + Pb ²⁺	44.81	10.21	5.96	37.59	1.43	-
Ilmenite + Pb ²⁺ + SHA	46.13	8.25	4.05	37.96	2.4	1.21

In order to further detect the detailed information about the chemical status of surface species, high-resolution XPS spectra were characterized in Figure 9. Figure 9a shows the high-resolution XPS Fe2p3/2 spectra of ilmenite, before and after conditioning with Pb²⁺ and SHA. In these spectra, the peaks occurring at around 710.8 eV and 713.7 eV were respectively assigned to ferrous species and ferric species [30,31]. After Pb²⁺ activation, the Fe2p3/2 binding energy of ferrous and ferric species shifted for −0.6 and −0.5 eV, respectively, suggesting that the Pb species can interact with the ilmenite surface and change the chemical circumstance of Fe species. Moreover, when the ilmenite was treated in the order of lead nitrate and SHA, the binding energies for ferrous and ferric species were further negatively shifted 0.1 eV and 0.4 eV, suggesting the chemical reaction of SHA with Fe sites. Titanium species on the surface of ilmenite had similar results with iron species on the chemical environment change caused by the adsorption of flotation reagents, as demonstrated in Figure 9b. The binding energies of 458.1 eV for Ti2p3/2 spectra peaks were observed at the high-resolution XPS spectra of pure ilmenite [28]. After the addition of Pb²⁺ and the treatment of Pb²⁺ and SHA, the binding energy of Ti2p3/2 was negatively shifted to 457.5 eV and 457.1 eV, respectively, revealing that Pb²⁺ and SHA might bond with Ti species of ilmenite surfaces.

As presented in Figure 8, the Pb4f7/2 XPS spectra could not be fitted with its characteristic peak, because of the low peak intensity of ilmenite samples without Pb²⁺ treatment. Figure 9c shows the Pb4f7/2 spectra of Pb²⁺-activated ilmenite, before and after SHA treatment. The Pb4f7/2 XPS spectra of the ilmenite surfaces that were treated with Pb ions were fitted with a binding energy of 138.5 eV, and this peak belonged to PbO species [30]. After treatment with Pb ions and SHA, the binding energies of Pb4f7/2 shifted to 138.7 eV, indicating the interaction of SHA with the lead species adsorbed on the mineral surface.

The O1s high-resolution XPS spectra of the ilmenite surfaces that were treated with different flotation reagents were recorded in Figure 9d. Table 3 presents the detailed values of the binding energies, chemical states, and species distribution in the O1s spectra for mineral samples conditioned with different flotation reagents. The O1s spectrum of the pure ilmenite includes three diverse characteristic peaks with binding energies, at approximately 530.3, 531.7, and 532.3 eV. The spectral peak centered at approximately 530.3 eV was attributed to Ti–O species, 531.7 eV was assigned to Fe–O species, and 532.3 eV was ascribed to H–O species on the ilmenite surface [32–34]. After Pb-treatment and Pb-SHA-treatment, the spectrum peak of Ti–O was negatively shifted to 530.1 eV and 529.9 eV, respectively. This suggests that lead species would interact with active titanium sites to form new Ti–O–Pb sites on the ilmenite surface, subsequently promoting the SHA adsorption. As for Fe–O bond on ilmenite surfaces, its relative intensity increased from 11.67% of pure ilmenite to 15.42% of

lead-activated ilmenite, and then to 30.4% of lead-SHA-treated ilmenite, while that of H–O bonds decreased from 44.96% to 28.28%, and further to 19.44%. These results illustrated that Pb^{2+} would interact with active iron sites to form new Fe–O–Pb sites; meanwhile, SHA replaced OH^- ions to bond with these new active metal sites, improving the floatability of ilmenite.

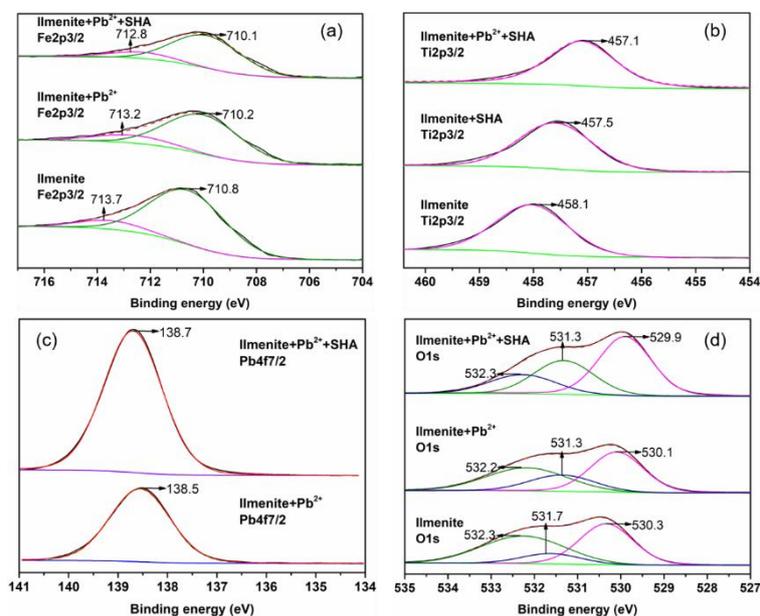


Figure 9. High-resolution XPS spectra of ilmenite, before and after Pb^{2+} and SHA treatment (a: $\text{Fe}2p_{3/2}$; b: $\text{Ti}2p_{3/2}$; c: $\text{Pb}4f_{7/2}$; d: $\text{O}1s$).

Table 3. $\text{O}1s$ parameters on ilmenite surfaces treated with different flotation reagents.

Sample	Binding Energy (eV)	Assignment	Area Ratio (%)
Ilmenite	530.3	Ti–O	43.37
	531.7	Fe–O	11.67
	532.3	H–O	44.96
Ilmenite+ Pb^{2+}	530.1	Ti–O	56.30
	531.3	Fe–O	15.42
	532.2	H–O	28.28
Ilmenite+ Pb^{2+} +SHA	529.9	Ti–O	50.16
	531.3	Fe–O	30.40
	532.3	H–O	19.44

In summary, the potential adsorption mechanism of SHA on the lead(II)-activated ilmenite surface (Figure 10) could be presumed as follows: when Pb^{2+} was added to the ilmenite suspension, a portion of lead species was adsorbed with the Ti–O and Fe–O sites to form new Fe/Ti–O–Pb sites, and thus SHA simultaneously chelated with Ti/Fe–O and Fe/Ti–O–Pb sites. Moreover, some of the lead ions remaining in the slurry solution possibly formed the Pb–SHA complexes to adsorb on the mineral surface, thereby increasing the floatability of ilmenite. Notably, the chelation of the phenolic hydroxyl group with the C=O group was not considered for the simplification of the adsorption model in Figure 10.

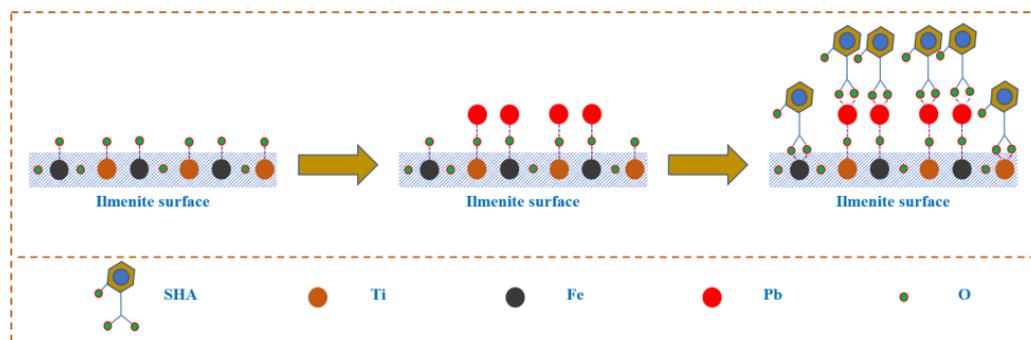


Figure 10. Schematic of the adsorption model SHA on the ilmenite surface after Pb^{2+} activation.

4. Conclusions

SHA is a highly efficient flotation collector that can achieve better floatability of ilmenite than BHA in the pH range of 6–8. Lead ions can also greatly activate the flotation behavior of SHA to ilmenite, which was investigated using flotation tests, adsorption and zeta potential measurements, FTIR, and XPS analysis. The flotation and adsorption tests show that lead ions can significantly increase the adsorbed amounts of SHA on the mineral surface. This condition benefits ilmenite flotation, especially at pH 6.0–8.0. The obtained zeta potential measurements indicate that, in the optimum pH range for ilmenite flotation, the main species adsorbed on ilmenite are $\text{Pb}(\text{OH})^+$ and Pb^{2+} . These species act as active sites and cause positive surface potential shift, thereby enabling negatively charged SHA to be chelated on the mineral surface easily. FTIR and XPS analyses indicate that lead species increase the chemical adsorption of SHA on the surface of ilmenite.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2075-163X/10/6/567/s1>, Table S1: Relative atomic concentrations of elements on ilmenite surfaces.

Author Contributions: Conceptualization, P.C. and C.Z.; Methodology, P.C.; Software, W.S.; Validation, J.Z.; Formal analysis, C.Z.; Investigation, H.L. and W.Z.; Resources, W.C.; Data curation, X.R.; Writing—original draft preparation, H.L. and W.Z.; Writing—review and editing, X.L. and H.L.; Supervision, S.W.; Project administration, P.C.; Funding acquisition, P.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Hunan Provincial Natural Science Foundation for the youth, China (2018JJ3665), National Key R&D Program of China (2019YFC1803501), China Postdoctoral Science Foundation (2019M650188), National Key Scientific Research Project (2018YFC1901601 and 2018YFC1901602) and Science and Technology Planning Project of Guangdong Province of China (Grant No. 2017B030314046).

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

References

- Chen, D.-S.; Zhao, L.-S.; Qi, T.; Hu, G.-P.; Zhao, H.-X.; Li, J.; Wang, L.-N. Desilication from titanium–vanadium slag by alkaline leaching. *Trans. Nonferrous Met. Soc. China* **2013**, *23*, 3076–3082. [CrossRef]
- Samal, S.; Mohapatra, B.K.; Mukherjee, P.S.; Chatterjee, S.K. Integrated xrd, epma and xrf study of ilmenite and titania slag used in pigment production. *J. Alloys Compd.* **2009**, *474*, 484–489. [CrossRef]
- Kothari, N.C. Recent developments in processing ilmenite for titanium. *Int. J. Miner. Process.* **1974**, *1*, 287–305. [CrossRef]
- Chen, P.; Zhai, J.; Sun, W.; Hu, Y.; Yin, Z. The activation mechanism of lead ions in the flotation of ilmenite using sodium oleate as a collector. *Miner. Eng.* **2017**, *111*, 100–107. [CrossRef]
- Fan, X.; Rowson, N.A. The effect of $\text{pb}(\text{no } 3) 2$ on ilmenite flotation. *Miner. Eng.* **2000**, *13*, 205–215. [CrossRef]
- Fan, X.; Waters, K.E.; Rowson, N.A.; Parker, D.J. Modification of ilmenite surface chemistry for enhancing surfactants adsorption and bubble attachment. *J. Colloid Interface Sci.* **2009**, *329*, 167–172. [CrossRef]
- Li, F.; Zhong, H.; Zhao, G.; Wang, S.; Liu, G. Adsorption of α -hydroxyoctyl phosphonic acid to ilmenite/water interface and its application in flotation. *Colloids Surf. A Physicochem. Eng. Asp.* **2016**, *490*, 67–73. [CrossRef]

8. Xu, H.; Zhong, H.; Tang, Q.; Wang, S.; Zhao, G.; Liu, G. A novel collector 2-ethyl-2-hexenoic hydroxamic acid: Flotation performance and adsorption mechanism to ilmenite. *Appl. Surf. Sci.* **2015**, *353*, 882–889. [[CrossRef](#)]
9. Tian, J.; Xu, L.; Yang, Y.; Liu, J.; Zeng, X.; Deng, W. Selective flotation separation of ilmenite from titanite using mixed anionic/cationic collectors. *Int. J. Miner. Process.* **2017**, *166*, 102–107. [[CrossRef](#)]
10. Liu, X.; Xie, J.; Huang, G.; Li, C. Low-temperature performance of cationic collector undecyl propyl ether amine for ilmenite flotation. *Miner. Eng.* **2017**, *114*, 50–56. [[CrossRef](#)]
11. Xu, L.; Tian, J.; Wu, H.; Lu, Z.; Yang, Y.; Sun, W.; Hu, Y. Effect of Pb^{2+} ions on ilmenite flotation and adsorption of benzohydroxamic acid as a collector. *Appl. Surf. Sci.* **2017**, *425*, 796–802. [[CrossRef](#)]
12. Mehdilo, A.; Irannajad, M.; Rezai, B. Effect of chemical composition and crystal chemistry on the zeta potential of ilmenite. *Colloids Surf. A Physicochem. Eng. Asp.* **2013**, *428*, 111–119. [[CrossRef](#)]
13. Nuri, O.S.; Mehdilo, A.; Irannajad, M. Influence of microwave irradiation on ilmenite surface properties. *Appl. Surf. Sci.* **2014**, *311*, 27–32. [[CrossRef](#)]
14. Mehdilo, A.; Irannajad, M.; Rezai, B. Effect of crystal chemistry and surface properties on ilmenite flotation behavior. *Int. J. Miner. Process.* **2015**, *137*, 71–81. [[CrossRef](#)]
15. Irannajad, M.; Mehdilo, A.; Salmani Nuri, O. Influence of microwave irradiation on ilmenite flotation behavior in the presence of different gangue minerals. *Sep. Purif. Technol.* **2014**, *132*, 401–412. [[CrossRef](#)]
16. Kupka, N.; Rudolph, M. Froth flotation of scheelite—A review. *Int. J. Min. Sci. Technol.* **2018**, *28*, 373–384. [[CrossRef](#)]
17. Tian, M.; Gao, Z.; Sun, W.; Han, H.; Sun, L.; Hu, Y. Activation role of lead ions in benzohydroxamic acid flotation of oxide minerals: New perspective and new practice. *J. Colloid Interface Sci.* **2018**, *529*, 150–160. [[CrossRef](#)]
18. Fang, S.; Xu, L.; Wu, H.; Tian, J.; Lu, Z.; Sun, W.; Hu, Y. Adsorption of $Pb(II)$ /benzohydroxamic acid collector complexes for ilmenite flotation. *Miner. Eng.* **2018**, *126*, 16–23. [[CrossRef](#)]
19. Feng, Q.; Zhao, W.; Wen, S.; Cao, Q. Activation mechanism of lead ions in cassiterite flotation with salicylhydroxamic acid as collector. *Sep. Purif. Technol.* **2017**, *178*, 193–199. [[CrossRef](#)]
20. Marion, C.; Jordens, A.; Li, R.; Rudolph, M.; Waters, K.E. An evaluation of hydroxamate collectors for malachite flotation. *Sep. Purif. Technol.* **2017**, *183*, 258–269. [[CrossRef](#)]
21. Li, H.; Mu, S.; Weng, X.; Zhao, Y.; Song, S. Rutile flotation with Pb^{2+} ions as activator: Adsorption of Pb^{2+} at rutile/water interface. *Colloids Surf. A Physicochem. Eng. Asp.* **2016**, *506*, 431–437. [[CrossRef](#)]
22. Meng, Q.; Yuan, Z.; Yu, L.; Xu, Y.; Du, Y. Study on the activation mechanism of lead ions in the flotation of ilmenite using benzyl hydroxamic acid as collector. *J. Ind. Eng. Chem.* **2018**, *62*, 209–216. [[CrossRef](#)]
23. Feng, Q.-C.; Wen, S.-M.; Zhao, W.-J.; Cao, Q.-B.; Lü, C. A novel method for improving cerussite sulfidization. *Int. J. Miner. Metall. Mater.* **2016**, *23*, 609–617. [[CrossRef](#)]
24. Nogales-Bueno, J.; Baca-Bocanegra, B.; Rooney, A.; Hernández-Hierro, J.M.; Byrne, H.J.; Heredia, F.J. Study of phenolic extractability in grape seeds by means of ATR-FTIR and Raman spectroscopy. *Food Chem.* **2017**, *232*, 602–609. [[CrossRef](#)] [[PubMed](#)]
25. Maiti, K.S. Ultrafast n-h vibrational dynamics of hydrogen-bonded cyclic amide reveal by 2DIR spectroscopy. *Chem. Phys.* **2018**, *515*, 509–512. [[CrossRef](#)]
26. Rintoul, L.; Micallef, A.S.; Bottle, S.E. The vibrational group frequency of the n-o stretching band of nitroxide stable free radicals. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2008**, *70*, 713–717. [[CrossRef](#)]
27. Fernandes, M.R.C.; Huang, X.; Abbenhuis, H.C.L.; Hensen, E.J.M. Lignin oxidation with an organic peroxide and subsequent aromatic ring opening. *Int. J. Biol. Macromol.* **2019**, *123*, 1044–1051. [[CrossRef](#)]
28. Meng, Q.; Feng, Q.; Shi, Q.; Ou, L. Studies on interaction mechanism of fine wolframite with octyl hydroxamic acid. *Miner. Eng.* **2015**, *79*, 133–138. [[CrossRef](#)]
29. Li, F.; Zhong, H.; Wang, S.; Liu, G. The activation mechanism of $Cu(II)$ to ilmenite and subsequent flotation response to α -hydroxyoctyl phosphinic acid. *J. Ind. Eng. Chem.* **2016**, *37*, 123–130. [[CrossRef](#)]
30. Chen, P.; Zhai, J.; Sun, W.; Hu, Y.; Yin, Z.; Lai, X. Adsorption mechanism of lead ions at ilmenite/water interface and its influence on ilmenite flotability. *J. Ind. Eng. Chem.* **2017**, *53*, 285–293. [[CrossRef](#)]
31. Yamashita, T.; Hayes, P. Analysis of XPS spectra of Fe^{2+} and Fe^{3+} ions in oxide materials. *Appl. Surf. Sci.* **2008**, *254*, 2441–2449. [[CrossRef](#)]
32. Soccol, D.; Martens, J.; Claessens, S.; Fransaer, J. Effect of carbon modification of particles on their incorporation rate during electrodeposition. *J. Electrochem. Soc.* **2011**, *158*, D515–D523. [[CrossRef](#)]

33. Ouerd, A.; Alemany-Dumont, C.; Berthomé, G.G.; Normand, B.; Szunerits, S. Reactivity of titanium in physiological medium. *J. Electrochem. Soc.* **2007**, *154*, C593–C601. [[CrossRef](#)]
34. Daou, T.J.; Begin-Colin, S.; Grenèche, J.M.; Thomas, F.; Derory, A.; Bernhardt, P.; Legaré, P.; Pourroy, G. Phosphate adsorption properties of magnetite-based nanoparticles. *Chem. Mater.* **2007**, *19*, 4494–4505. [[CrossRef](#)]



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