

Article

# The Effect of Quartz on the Flotation of Fine Wolframite with Octyl Hydroxamic Acid

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**Abstract:** The influence of quartz on the flotation of fine wolframite using octyl hydroxamic acid (OHA) as the collector was investigated by micro-flotation tests, inductively coupled plasma (ICP) measurements, adsorption experiments, zeta potential, and Fourier transform infrared spectroscopy (FT-IR) analysis. Micro-flotation tests showed that a large difference in floatability existed between fine wolframite and quartz in the pH range of 7.0 to 10.0. However, in a synthetic mixture, the flotation separation of fine wolframite from quartz became more difficult as the particle size of the latter decreased. When a dissolved solution of wolframite was used as the flotation medium, quartz floatability improved significantly. Zeta potentials of quartz particles shifted positively in the dissolved solution of wolframite compared to distilled water, especially at a pH level of 7.0–10.0, which was attributed to the metal ions dissolved from the wolframite being adsorbed onto the quartz surface. The surface activation of quartz led to an increase in the OHA adsorption and made the surface hydrophobic. FT-IR analysis further demonstrated that OHA could adsorb onto the activated quartz surface through a dominantly chemical process.

**Keywords:** quartz; wolframite; flotation; octyl hydroxamic acid

## 1. Introduction

Wolframite, the same-phase compounds of  $\text{FeWO}_4$  and  $\text{MnWO}_4$  tungstates crystallizing in a monoclinic structure, mainly occurs in high-temperature hydrothermal quartz veins and is the primary source of tungsten products. China is rich in tungsten reserves and produces the most tungsten in the world, but high-grade wolframite ores that are easily separated are decreasing each year as the industry demand increases. Therefore, the use of slimes produced by the comminution process, due to the brittle nature of wolframite, is urgently needed [1,2]. Froth flotation, in contrast with gravity and magnetic separation, is a surface chemistry-based process and takes advantage of the floatability difference between various minerals. Froth flotation is regarded as the most effective method for the separation and use of slimes and finely disseminated particles [3,4].

Anionic surfactants, such as fatty acids, phosphonic acid, sarcosine acid, and hydroxamic acid, are usually used as collectors for fine wolframite flotation. Previous studies indicate that these anionic collectors can interact with metal ions on the wolframite surface and increase the mineral hydrophobicity [5–8]. Quartz is the major gangue mineral associated with fine wolframite in the flotation concentrate. Si and O atoms occupy the entirety of the surface of quartz, but those atoms are not active sites for the adsorption of anionic surfactants. Additionally, quartz is a naturally hydrophilic oxide. It seems inconceivable that a relatively high content of quartz would be floated, affecting the grade and recovery of the wolframite concentrate [9]. In theory, the suspension containing

wolframite and quartz is a stable dispersion system because of their negatively charged surfaces, and quartz would not be floated due to heterocoagulation in alkaline conditions. In wolframite slimes, the naturally hydrophilic quartz is comprised of liberated particles, and the floated quartz is not due to under-liberated interlocked wolframite minerals.

The probable flotation mechanism, by which quartz is activated by the metal ions dissolved from mineral surfaces, has attracted increasing interest. Due to the slight dissolution of metallic oxides, unavoidable metal ions can activate quartz and significantly affect its flotation behavior with anionic collectors, which results in the unexpected presence of quartz in flotation concentrates [10,11]. Fornasiero and Ralston's work showed that quartz could be activated by  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  ions at a pH level of 7.0–10.0. The stable species adsorbed on the mineral surface, such as copper and nickel hydroxides, improved the floatability of quartz using xanthate as the collector [12]. The island-like precipitate structures of  $\text{Pb}^{2+}$  ions on the quartz surface have been observed, and the hydrophobic species, in the form of lead amyl xanthate, was determined to improve the floatability of quartz [9]. The surface of quartz, with sodium oleate, switched from polar to non-polar in the presence of  $\text{Fe}^{3+}$  ions, which adsorbed onto the mineral surface and resulted in an increase in sodium oleate adsorption [13]. Fuerstenau confirmed that  $\text{Fe}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Ca}^{2+}$  ions could also activate quartz and improve its floatability [14].

Wolframite is a salt-type mineral, and metal ions on the wolframite surface commonly dissolve in suspension during the flotation process [15]. As a consequence, the objective of this study was to investigate the flotation behavior of quartz and its influence on the flotation of fine wolframite using an anionic octyl hydroxamic acid (OHA) collector. The flotation mechanism of quartz in a suspension of fine wolframite was analyzed through inductively coupled plasma (ICP) tests, zeta-potential measurements, and Fourier transform infrared spectroscopy (FT-IR) analysis.

## 2. Materials and Methods

### 2.1. Materials

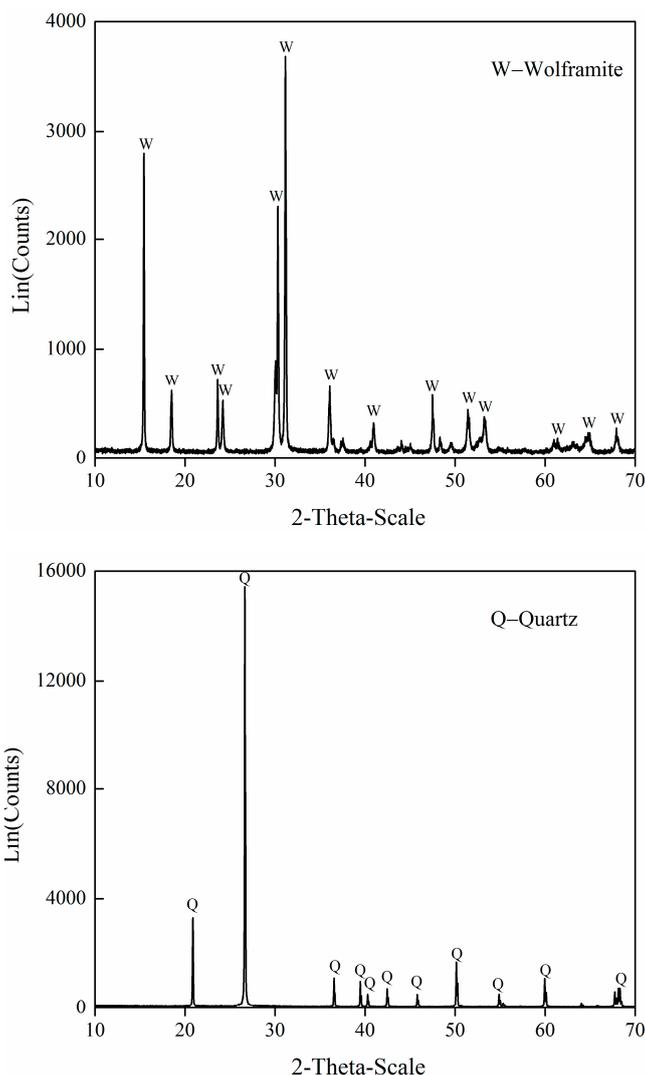
The pure samples of wolframite and quartz minerals were obtained from Yaogangxian, Hunan Province, China. The chemical composition of wolframite given in Table 1 shows that its purity was greater than 97%. XRD analysis of wolframite and quartz (see Figure 1) also confirm that the samples had little impurities.

The samples were crushed and ground using an agate mortar. Products were then sieved to obtain different size fractions, and  $-20\ \mu\text{m}$  fraction was elutriated to attain a particle size of  $-10\ \mu\text{m}$ . The prepared fine wolframite ( $-10\ \mu\text{m}$ ) had 90% passing at  $10.95\ \mu\text{m}$ , and quartz ( $-10\ \mu\text{m}$ ) had 90% passing at  $12.00\ \mu\text{m}$ . Five size fractions of quartz, namely,  $-74 + 55\ \mu\text{m}$ ,  $-55 + 38\ \mu\text{m}$ ,  $-38 + 20\ \mu\text{m}$ ,  $-20 + 10\ \mu\text{m}$ , and  $-10\ \mu\text{m}$ , were collected for experiments. The quartz samples were washed with 2 M hydrochloric acid for 24 h to remove metal ions that might be present on the surface. After this period, the samples were washed with distilled water to a neutral pH, dried, and preserved for subsequent use.

Octyl hydroxamic acid (OHA) as the anionic collector was prepared in the laboratory. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) used for pH adjustments were of analytical grade. Distilled water was utilized for all experiments. The dissolved solution of wolframite was prepared for analyzing the flotation mechanism of quartz. A 2.0 g fine wolframite sample was conditioned with 40 mL of distilled water and stirred for 30 min at  $25\ ^\circ\text{C}$ . The suspension was centrifuged at 9000 rpm for 10 min, and the liquid supernatant was collected for experiments.

**Table 1.** Chemical compositions of wolframite sample (Mass fraction, %).

$\text{WO}_3$	$\text{MnO}$	$\text{Fe}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{SO}_3$	Others
74.18	8.98	14.30	0.23	0.67	0.56	1.08



**Figure 1.** XRD diffraction patterns of wolframite and quartz.

## 2.2. Micro-Flotation Experiments

Micro-flotation experiments were conducted in a mechanical agitation flotation machine (XFG-II, Jilin Exploring Machinery Plant, Changchun, China). Pure mineral samples (2.0 g) were placed in a Plexiglas cell, and 40 mL of distilled water was then added. The mineral suspension was adjusted to the desired pH value by HCl or NaOH solutions for 2 min, and the collector was then added and mixed for 3 min. The micro-flotation was scraped out every 10 s for a total of 5 min. The floated and sank particles were weighed and assayed after drying separately, and the flotation recovery was calculated. Three measurements in the microflotation experiments were carried out, and their averages were taken as the results.

## 2.3. Flotation Experiments of Artificially Mixed Minerals

The artificially mixed minerals were combined with 0.67 g of pure wolframite ( $-10\ \mu\text{m}$ ) and 1.33 g of pure quartz of five different particle sizes, and the  $\text{WO}_3$  grade of mixed minerals was around 24.72%. The flotation experiments of artificially mixed minerals were performed in a Plexiglas flotation cell. Each test was carried out with 2.0 g of artificially mixed minerals and 40 mL of distilled water. The suspension was adjusted to a pH of 8.5–9.0 with dilute hydrochloric acid or a sodium hydroxide solution and agitated for 2 min. Then, the collector was added to the suspension and conditioned

for 3 min. The flotation was carried out for 5 min. The concentrates and tailings were filtered, dried, weighted, sampled, and assayed for  $\text{WO}_3$  grade. The flotation recovery of wolframite concentrates was calculated based on the yield and  $\text{WO}_3$  grade. Three measurements of flotation experiments under the same conditions were obtained, and their averages were taken as the results of the artificially mixed mineral flotation.

#### 2.4. ICP-AES Tests

The concentrations of metal ions dissolved from wolframite surfaces were measured using inductively coupled plasma-atomic emission spectroscopy (ICP-AES, PS-6, Baird, Bedford, MA, USA). A 2.0 g wolframite sample was conditioned with 40 mL of distilled water solutions at a desired pH value and stirred for 30 min at 25 °C. The samples were centrifuged at 9000 rpm for 10 min, and then ion concentrations of the supernatant were measured by ICP-AES.

#### 2.5. Adsorption Measurements

A 1.0 g,  $-10\ \mu\text{m}$  quartz sample was conditioned with 40 mL of OHA solution at a pH of 8.5–9.0 and stirred for 20 min at 25 °C. The suspension was then centrifuged at 9000 r/min for 10 min, and the supernatant was monitored by UV–Vis spectrophotometer (UV1901PC, Aoxi, China). OHA concentration was measured using UV absorbance at the wavelength of 507 nm based on the ferric hydroxamate method [16,17]. The adsorption amount of OHA on quartz surfaces in distilled water and the dissolved solution of wolframite was calculated from the difference between the initial and final concentrations, which was assumed to adsorb onto the quartz surface.

#### 2.6. Zeta-Potential Measurements

Zeta-potential measurements of quartz were performed in a  $1 \times 10^{-2}\ \text{mol}\cdot\text{L}^{-1}$  KCl background electrolyte solution using a Zeta Plus meter (Brookhaven Instruments, Upton, NY, USA). A 30 mg quartz sample ( $-5\ \mu\text{m}$ ) was mixed with 40 mL of distilled water or dissolved solution of wolframite. The pH value of the prepared suspension was adjusted by HCl or NaOH solutions for 3 min. Next, the suspension was conditioned for another 5 min with the addition of OHA. To ensure precise zeta potential determination, three measurements were conducted, and their average was calculated for the final value.

#### 2.7. FT-IR Spectra Analysis

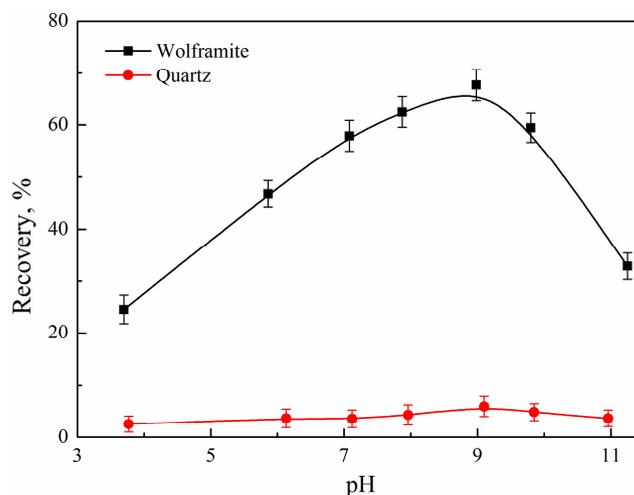
To prepare the samples for FT-IR analysis, a 2.0 g quartz sample ( $-5\ \mu\text{m}$ ) was mixed with 40 mL of aqueous solution with/without OHA at a pH of 9.0 and stirred for 20 min. Finally, the samples were filtered, washed three times using distilled water with the same pH value, then dried in a vacuum oven at 50 °C prior to FT-IR analysis. The FT-IR spectra were recorded in the range  $400\text{--}4000\ \text{cm}^{-1}$  to characterize the interaction between OHA and quartz through an FT-IR spectrometer (Nicolet 740, Thermo Fisher Scientific, Waltham, MA, USA). Approximately 1 mg of desired quartz sample was mixed with 100 mg of spectroscopic grade KBr and pressed into a pellet to record the spectrum.

### 3. Results and Discussion

#### 3.1. Micro-Flotation of Fine Wolframite and Quartz

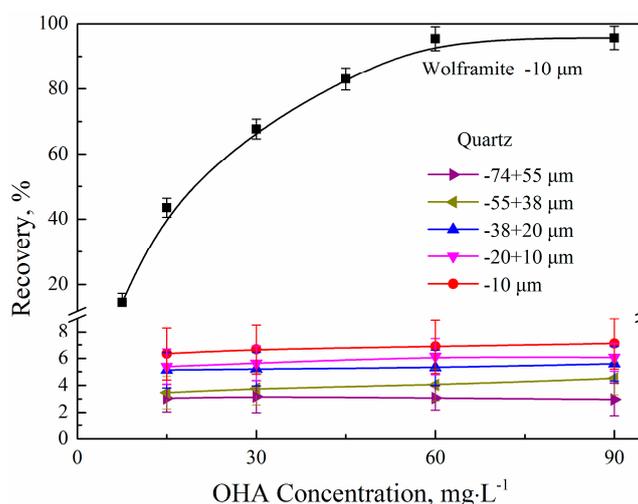
The effect of pH value on the flotation behavior of  $-10\ \mu\text{m}$  wolframite and quartz, with an OHA concentration of  $30\ \text{mg}\cdot\text{L}^{-1}$ , is presented in Figure 2. The flotation recovery of fine wolframite increased with a pH value in the range from 4.0 to 9.0 and, beyond a pH of 9.0, decreased until pH reached approximately 11.0. The maximum recovery of fine wolframite, at 67.7%, was achieved at a pH of 9.0. Fine wolframite showed excellent floatability in a wide range of pH values, from 7.0 to 10.0. A previous study [18] indicated that the coadsorption process first occurs between OHA and wolframite, in the form of ferrous and manganous hydroxamate precipitates, and that the OHA molecule is then

physically adsorbed onto the first chemisorbed layer, which results in the firm adsorption of OHA, improving the wolframite floatability. Yet, the flotation recovery of fine quartz was far lower than that of fine wolframite in the researched pH range, suggesting the weak floatability of quartz with OHA.



**Figure 2.** The effect of pH value on the flotation behavior of  $-10\ \mu\text{m}$  wolframite and quartz ( $C_{\text{OHA}} = 30\ \text{mg}\cdot\text{L}^{-1}$ ).

Figure 3 shows the flotation recovery of  $-10\ \mu\text{m}$  wolframite and quartz of different size classes, as a function of initial OHA concentration, at a pH of 8.5–9.0. The recovery of fine wolframite increased rapidly with an increase in OHA concentration and reached a high level platform when the collector concentration was more than  $60\ \text{mg}\cdot\text{L}^{-1}$ . The recovery of fine wolframite was above 95% at an OHA concentration of  $60\ \text{mg}\cdot\text{L}^{-1}$ . Figure 3 also shows that the recovery of quartz of different size fractions was below 8%, even at high OHA concentrations, indicating that quartz cannot be floated when OHA is used as a collector.

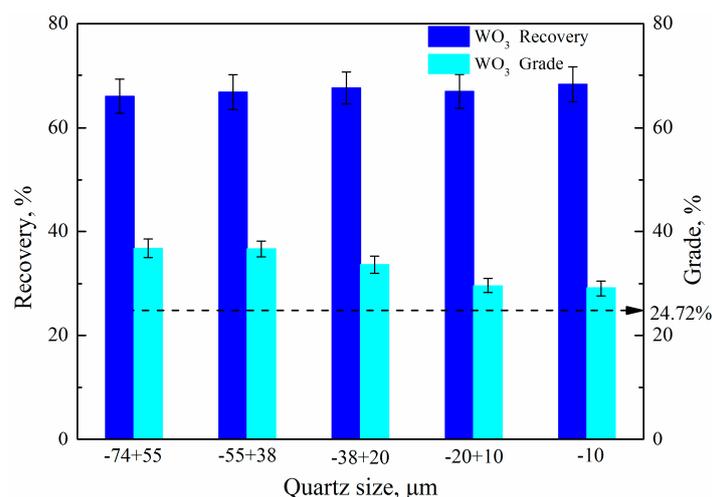


**Figure 3.** The effect of octyl hydroxamic acid (OHA) concentration on the flotation behavior of  $-10\ \mu\text{m}$  wolframite and quartz of different size fractions (pH = 8.5–9.0).

### 3.2. Flotation of Artificially Mixed Minerals

As the above flotation results indicate,  $-10\ \mu\text{m}$  wolframite with OHA exhibited excellent floatability and selectivity to quartz at a pH of 9.0. To investigate the separation efficiency of fine wolframite from quartz gangue, flotation experiments of artificially mixed minerals were conducted,

and the results are shown in Figure 4. All recoveries of fine wolframite were within the range of 66%–68%. No differences were observed when wolframite was mixed with the quartz of five different size fractions. Nevertheless, the particle size of quartz had an impact on the concentrate grade of fine wolframite, which decreased with the reduction in quartz particle size. When fine wolframite was mixed with  $-10\ \mu\text{m}$  quartz, the  $\text{WO}_3$  grade of the concentrate only improved by 4.28%, from 24.72% to 29.00%. The flotation recovery remained the same for both the artificially mixed minerals and the pure minerals, while a high grade of wolframite concentrate was not achieved at the same pH value and OHA concentration, suggesting a failure in the flotation separation of fine wolframite from quartz.



**Figure 4.** Flotation separation of fine wolframite in artificially mixed minerals ( $C_{\text{OHA}} = 30\ \text{mg}\cdot\text{L}^{-1}$ ,  $\text{pH} = 8.5\text{--}9.0$ ).

### 3.3. Flotation and OHA Adsorption in the Dissolved Solution of Wolframite

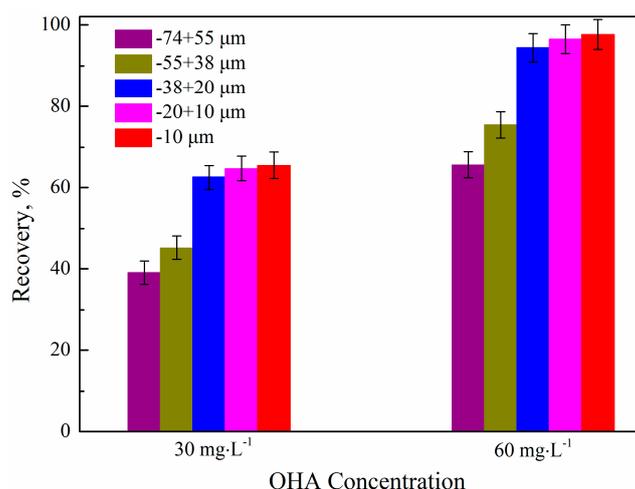
Wolframite is a salt mineral and is easily dissolved in water. The dissolved metal ions will inevitably affect the flotation behavior of quartz. Therefore, the amount of metal ions dissolved from the wolframite surface was measured at a pH of 8.0 to 10.0, in which better floatability of fine wolframite was achieved. The results are listed in Table 2.  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  ions were found to slightly dissolve from wolframite surface, and their amounts were about  $10^{-5}$  orders of magnitude. These metal ions could not be ignored in the flotation of quartz mixed with wolframite.

**Table 2.** The amount of metal ions dissolved from wolframite surfaces.

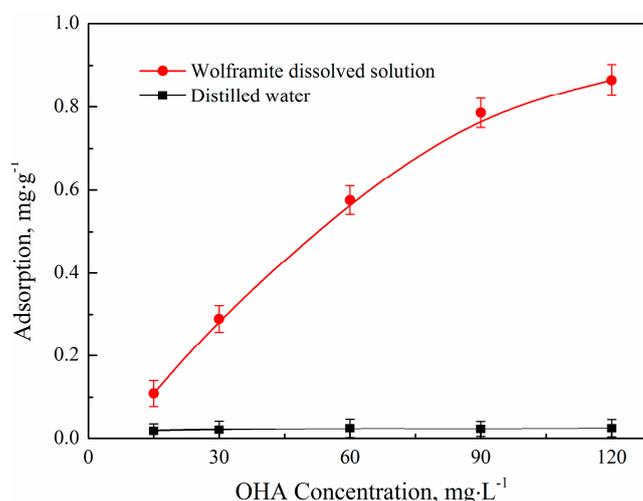
Solution pH	$\text{Fe}^{2+}$ ( $\times 10^{-5}\ \text{mol}\cdot\text{L}^{-1}$ )	$\text{Mn}^{2+}$ ( $\times 10^{-5}\ \text{mol}\cdot\text{L}^{-1}$ )
8.02	0.36	3.69
8.99	0.60	1.58
10.25	0.86	0.66

The flotation recovery of quartz of different size fractions, using the dissolved solution of wolframite as a flotation medium, is presented in Figure 5. The results show that the recovery of quartz of five different size fractions increased with collector concentration and decreasing particle size. When OHA concentration was  $30\ \text{mg}\cdot\text{L}^{-1}$ , the recoveries of  $-74 + 55\ \mu\text{m}$ ,  $-55 + 38\ \mu\text{m}$ ,  $-38 + 20\ \mu\text{m}$ ,  $-20 + 10\ \mu\text{m}$ , and  $-10\ \mu\text{m}$  fractions increased by 35.90%, 41.51%, 57.32%, 57.90%, and 58.11%, respectively, compared to quartz in distilled water. We also found that the flotation recovery of quartz increased rapidly with OHA initial concentration, and the recovery of  $-38\ \mu\text{m}$  quartz was close to that of  $-10\ \mu\text{m}$  wolframite (Figure 5).

Figure 6 shows the adsorption behavior of OHA on quartz surfaces as a function of collector concentration. The results in Figure 6 indicate that significant differences existed in the adsorption behavior of OHA on quartz surfaces treated in the dissolved solution of wolframite compared to distilled water. OHA scarcely adsorbed onto the quartz surface in distilled water. Nevertheless, the adsorption of OHA on quartz increased with the rise in collector initial concentration at a pH of 8.5–9.0 in the dissolved solution of wolframite, which agreed with the flotation behavior of quartz shown in Figures 3 and 5. These results suggest that metal ions dissolved from wolframite surface would activate the quartz surface and improve the adsorption of OHA. Quartz, with induced hydrophobization, was floated out along with fine wolframite, which led to a decrease in the grade of wolframite concentrate.



**Figure 5.** Flotation recovery of quartz of different size fractions in the dissolved solution of wolframite (pH = 8.5–9.0).



**Figure 6.** Effect of collector concentration on the OHA adsorption on  $-10\ \mu\text{m}$  quartz surface (pH = 8.5–9.0).

### 3.4. Zeta Potentials

To investigate the quartz activation mechanism by metal ions in the dissolved solution of wolframite, zeta potentials data were used to interpret the trend in flotation performance and the modification of quartz surface by metal ions and OHA. Zeta potentials of quartz, as a function of pH under distilled water and the dissolved solution of wolframite, with or without OHA ( $30\ \text{mg}\cdot\text{L}^{-1}$ ), are depicted in Figure 7. In distilled water, the point of zero charge (PZC) of quartz has been reported to

have a pH of around 2.0 [19]. Zeta potentials of quartz were all negative in the measured pH range in this study, and the values became more negative with increasing pH. With the addition of OHA, zeta potentials had an insignificant shift, indicating that OHA did not change the surface charge of quartz.

In the dissolved solution of wolframite, zeta potentials of quartz were still negative in the measured pH range, but the surface charge of quartz became less negative compared to quartz in distilled water, especially within the pH range of 7.0–10.0. Therefore, we confirmed that the surface property of quartz could be modified by metal ions dissolved from wolframite. Figure 8 shows the distributions of  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  species as a function of pH, under ion concentrations of  $10^{-5} \text{ mol}\cdot\text{L}^{-1}$ , which were calculated according to the stability constants and solubility products [14,20]. The system was unsaturated concerning any insoluble or precipitated species at all pH values. The correlation of metal ion species distributions with zeta potential results indicates that the positively charged  $\text{Fe}^{2+}/\text{Mn}^{2+}$  and  $\text{Fe}(\text{OH})^+/\text{Mn}(\text{OH})^+$  species were the dominant species when pH value was below 10.0, resulting in a positive shift of the zeta potential due to electrostatic attraction. At  $\text{pH} > 10.0$ ,  $\text{Fe}(\text{OH})_3^-/\text{Mn}(\text{OH})_3^-$  and  $\text{Fe}(\text{OH})_4^{2-}/\text{Mn}(\text{OH})_4^{2-}$  species increased, and the zeta potentials of quartz dropped. Meanwhile, within the pH range of 6.0–9.0, the concentration of  $\text{Fe}(\text{OH})^+/\text{Mn}(\text{OH})^+$  species became significant. The zeta potential of quartz increased sharply due to the specific adsorption via  $\text{Fe}^{2+}/\text{Mn}^{2+}$  hydroxyl compounds coating onto the quartz surface. The electrokinetic behavior of quartz in the dissolved solution of wolframite was attributed to metal ions being adsorbed onto the negatively charged surface of quartz [9,11].

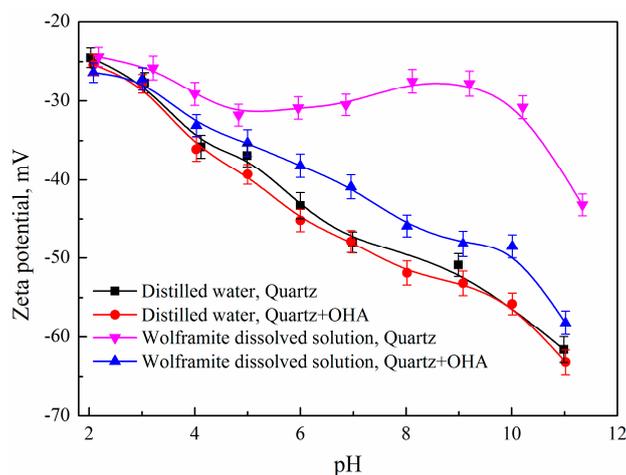


Figure 7. Relationship between zeta potentials of quartz and pH value ( $C_{\text{OHA}} = 30 \text{ mg}\cdot\text{L}^{-1}$ ).

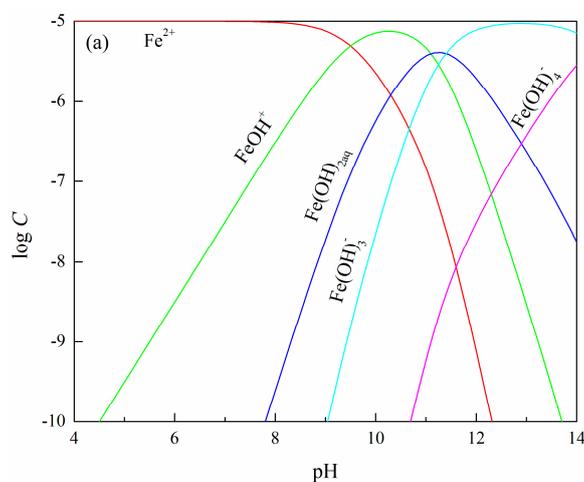
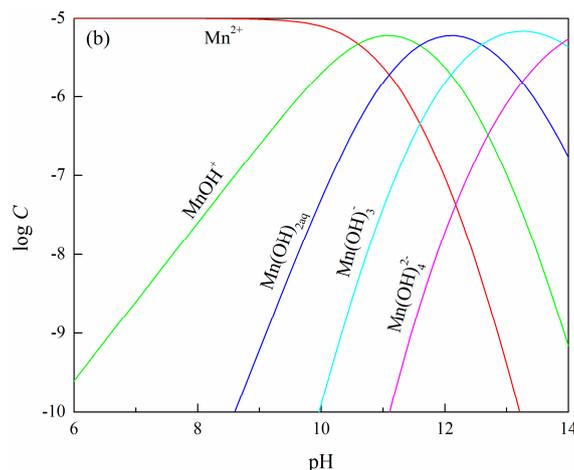


Figure 8. Cont.



**Figure 8.** Species distribution diagrams of metal ions: (a)  $\text{Fe}^{2+}$ ; (b)  $\text{Mn}^{2+}$ ;  $C_{\text{Fe}/\text{Mn}} = 1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ .

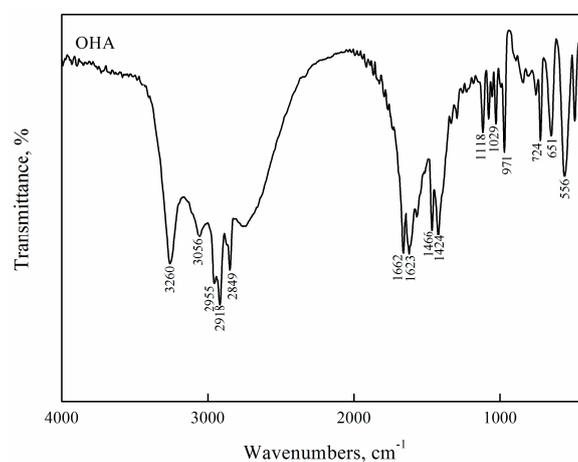
After that, in the presence of OHA, the negative charge of quartz significantly decreased in alkaline conditions. At a pH of 9.0, the zeta potential of quartz decreased by  $-20.4 \text{ mV}$ , from  $-27.8 \text{ mV}$  to  $-48.2 \text{ mV}$ . When quartz was treated with OHA in the dissolved solution of wolframite, the extent of variation of zeta potentials was more obvious than that in distilled water, which was ascribed to the increase in OHA adsorption on quartz surfaces (see Figure 6). These results indicate that metal ions dissolved from wolframite could activate the surface of quartz and further stimulate the interaction between OHA and activated quartz. OHA is an anionic collector, and the activated quartz emerged with a negative charge. The presence of OHA made quartz more negatively charged in the dissolved solution of wolframite, suggesting that specific adsorption of OHA on the activated-quartz surface might be involved [13].

### 3.5. FT-IR Spectra Analysis

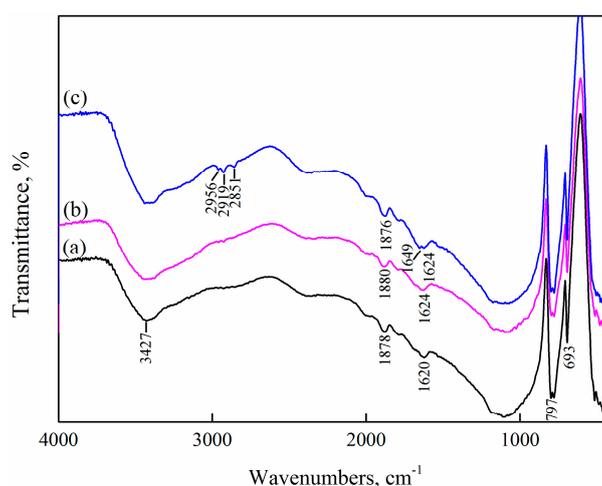
The adsorption mechanism of OHA with quartz in the dissolved solution of wolframite was investigated by FT-IR spectroscopy. FT-IR spectra of OHA and quartz conditioned with OHA at a pH of 9.0, with distilled water or dissolved wolframite solution, are shown in Figures 9 and 10. In the OHA spectrum (Figure 9), the peak at  $3260 \text{ cm}^{-1}$  was associated with the overlapping peak of the N-H stretching vibration and the O-H stretching vibration. The peaks at  $2955 \text{ cm}^{-1}$ ,  $2918 \text{ cm}^{-1}$ ,  $2849 \text{ cm}^{-1}$ , and  $724 \text{ cm}^{-1}$  referred to stretching vibrations and bending vibrations of  $-\text{CH}_3/-\text{CH}_2-$  groups. Additionally, the peaks at  $1662 \text{ cm}^{-1}$  and  $1623 \text{ cm}^{-1}$  correspond to the characteristic peaks of the C=O stretching vibration and the C=N stretching vibration, respectively [21,22]. In the quartz spectrum (Figure 10a), the peaks at  $3427 \text{ cm}^{-1}$  and  $1620 \text{ cm}^{-1}$  belonged to the stretching vibration of  $-\text{OH}$  and the bending vibration of  $-\text{OH}$  from Si-OH silanol groups, respectively. The characteristic peaks ranging from  $900$  to  $1200 \text{ cm}^{-1}$ , and around  $797 \text{ cm}^{-1}$  and  $693 \text{ cm}^{-1}$  were attributed to the symmetrical stretching and bending vibrations of Si-O bonds [23,24].

As shown in Figure 10b, when quartz was treated with OHA in distilled water, no peak was observed in the quartz spectrum. However, the FT-IR spectrum for quartz treated with OHA in the dissolved solution of wolframite (see Figure 10c) had new peaks at around  $2956 \text{ cm}^{-1}$ ,  $2919 \text{ cm}^{-1}$ ,  $2851 \text{ cm}^{-1}$ , and  $1649 \text{ cm}^{-1}$ , of which the peak at  $2956 \text{ cm}^{-1}$  was attributed to the asymmetrical stretching vibrations of  $-\text{CH}_3$ , and the peaks at  $2919 \text{ cm}^{-1}$  and  $2851 \text{ cm}^{-1}$  were related to the asymmetrical and symmetrical stretching vibrations of  $-\text{CH}_2-$ . The new peak at  $1649 \text{ cm}^{-1}$ , with an offset of  $13 \text{ cm}^{-1}$ , was attributed to the stretching vibrations of C=O in the OHA molecule, which could be attributed to the iron and manganese hydroxamate precipitates [25]. These changes indicate that a chemisorption process was occurring during the interaction of OHA onto the quartz surface in the dissolved solution of wolframite. The chelating group of OHA was able to bond with metal ions

coated onto the quartz surface and formed stable  $\text{Fe}^{2+}/\text{Mn}^{2+}$  chelate compounds, which was similar to the interaction between wolframite and OHA previously documented [6,26]. Comparing the spectra of quartz in the dissolved solution of wolframite to distilled water, the metal–OHA complexes occurred on the quartz surface. This result shows that  $\text{Fe}^{2+}/\text{Mn}^{2+}$  ions dissolved from wolframite were able to specifically adsorb onto the quartz surface and interact with OHA.



**Figure 9.** FT-IR spectrum of OHA.



**Figure 10.** FT-IR spectra of quartz at a pH of 9.0: (a) Quartz; (b) Quartz with OHA in distilled water; (c) Quartz with OHA in the dissolved solution of wolframite.

### 3.6. Flotation Mechanism of Quartz

Quartz is comprised of an infinite three-dimensional framework of silica–oxygen tetrahedra. When a quartz crystal is crushed, the fracture orientation occurs in the Si–O bond direction. Broken Si–O bonds create reactive sites on which water molecules can chemisorb to cover the surface with hydroxyl groups. These surface hydroxyl groups adsorb/dissociate hydrogen ions, depending on the pH value [27]. The chemical reactions are illustrated in Scheme 1. At a pH of 7.0–10.0 for the flotation of wolframite with OHA, the quartz surface consists mainly of silanol groups (Si–OH) and silicic acid groups (Si–O<sup>−</sup>), which are naturally hydrophilic in water and do not respond to flotation even with the addition of an ionic collector.

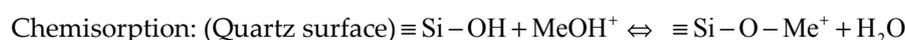
$\text{Fe}^{2+}/\text{Mn}^{2+}$  ions could dissolve from wolframite surfaces and modify the surface property of quartz, as shown in Table 2 and Figure 7.  $\text{Fe}^{2+}/\text{Mn}^{2+}$  and  $\text{Fe}(\text{OH})^+/\text{Mn}(\text{OH})^+$  species were the dominant species responsible for the positive shift of zeta potentials. These species might

adsorb onto quartz surfaces via two potential approaches. The positively charged  $\text{Fe}^{2+}/\text{Mn}^{2+}$  and  $\text{Fe}(\text{OH})^+/\text{Mn}(\text{OH})^+$  species adsorbed onto the negatively charged surfaces of quartz through electrostatic attraction. Moreover, the dehydration reaction occurred in the coating process of  $\text{Fe}(\text{OH})^+/\text{Mn}(\text{OH})^+$  species with silanol groups ( $\text{Si}-\text{OH}$ ), which was expected to form metal ion-containing complexes on the surface of quartz [9,27]. The involved interactions of  $\text{Fe}^{2+}/\text{Mn}^{2+}$  ions with quartz surfaces are listed in Scheme 2.

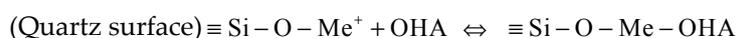
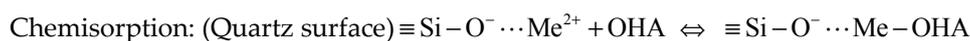
The results of adsorption and flotation experiments indicate that the activation of  $\text{Fe}^{2+}/\text{Mn}^{2+}$  ions dissolved from wolframite surfaces increased OHA adsorption on quartz surfaces, thereby improving its floatability. With the addition of OHA, the zeta potentials of activated quartz shifted to more negative charges, which implied that the attractive force between OHA and quartz was larger than their electrostatic repulsion force. Therefore, OHA might chemisorb on activated quartz surfaces through a covalent bond, which is consistent with the results revealed by FT-IR analysis. The oxygen atoms from carbonyl ( $\text{C}=\text{O}$ ) and hydroxyl ( $\text{N}-\text{OH}$ ) of OHA had a high affinity to bonding with the adsorbed  $\text{Fe}^{2+}/\text{Mn}^{2+}$  ions on quartz surfaces, and formed stable iron and manganese hydroxamate complexes [6,25]. The potential interactions are presented in Scheme 3. It was believed that, during the flotation of wolframite, the dissolved  $\text{Fe}^{2+}/\text{Mn}^{2+}$  ions and OHA reacted with the quartz surface in sequence, which made the quartz hydrophobic. A two-step sequential adsorption mechanism for the modification of quartz surfaces with metal ions and OHA is depicted in Figure 11.



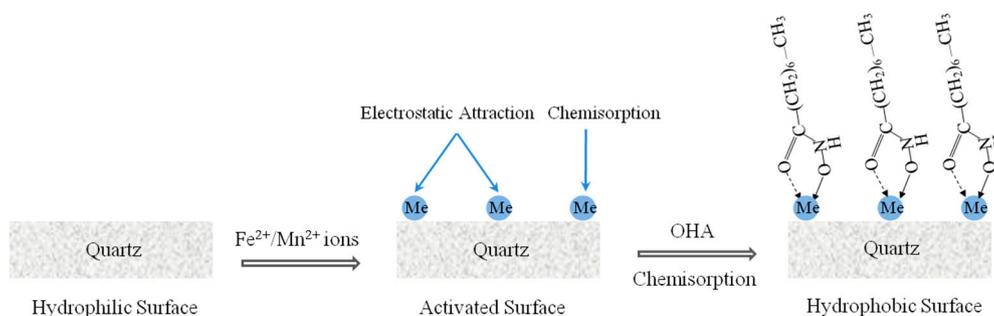
**Scheme 1.** The hydrolysis of silanol groups on quartz surfaces.



**Scheme 2.** The adsorption of  $\text{Fe}^{2+}/\text{Mn}^{2+}$  ions onto quartz surfaces.



**Scheme 3.** The adsorption of OHA onto activated quartz surfaces.



**Figure 11.** Proposed adsorption model of OHA on a quartz surface in the dissolved solution of wolframite.

#### 4. Conclusions

This study systematically investigated the involvement of quartz in the flotation of fine wolframite using octyl hydroxamic acid as a collector. Micro-flotation tests showed that wolframite resulted in better floatability than quartz. However, the floatability of quartz was increased in the dissolved solution of wolframite, and the flotation recovery of  $\sim 38 \mu\text{m}$  quartz was close to that of fine wolframite. The flotation separation between fine wolframite and quartz did not work, and the grade of wolframite concentrate decreased as the size of the quartz particles reduced. The ICP and zeta potential results suggest that metal ions dissolved from wolframite changed the surface charge of quartz, especially at a pH of 7.0–10.0, and activated quartz surfaces for inducing OHA adsorption. The FT-IR analysis indicates that the chemisorption process was responsible for the adsorption of OHA onto the activated quartz surface. OHA reacted with the adsorbed  $\text{Fe}^{2+}/\text{Mn}^{2+}$  ions on the quartz surface and formed stable iron and manganese hydroxamate complexes. These results confirm that quartz can be activated and floated with OHA in the flotation of fine wolframite, which results in a decrease in the grade of wolframite concentrate.

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

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