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Study on the activation mechanism of lead ions in wolframite flotation using benzyl hydroxamic acid as the collector

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ABSTRACT

The activation mechanism of Pb(II) on the flotation of wolframite was systematically investigated. Micro-flotation test results showed that Pb(II) effectively improved the flotation of wolframite in the presence of benzyl hydroxamic acid (BHA). Maximum floatability of wolframite was achieved at approximately pH 8.5. Adsorption of the hydrolyzed species of Pb(II) occurred at this pH value, which provided more activated sites on the wolframite surface. As such, BHA-Pb complexes were formed on the wolframite surface, which increased the BHA adsorption. In addition, BHA-Pb complexes were also formed in solution, which replaced the Fe and interacted with the Mn on the wolframite surface. These findings were proved by the results of zeta-potential measurements, adsorption measurements, solution chemistry calculations, Fourier transform infrared spectroscopy (FT-IR) analysis, and X-ray photoelectron spectroscopy (XPS) characterization.

1. Introduction

Tungsten is an important rare metal (Chen et al., 2018; Liu et al., 2016a), which has been used in communication technology, electronics, aerospace development, medicine, health care, etc., due to its specific physical and chemical properties such as high hardness, high melting point, and corrosion resistance (Bar et al., 2000; Feng et al., 2015; Ilhan et al., 2013; Yan et al., 2017). Scheelite and wolframite are the two main resources of tungsten metal (Chen et al., 2017a, 2017b; Meng et al., 2015). Generally, wolframite is recovered by gravity separation methods when the particle size is sufficiently large (Ai et al., 2017; Pradip, 1996). However, with the exploitation of high-grade wolframite resources, low-grade wolframite ores are considered for tungsten-mineral beneficiation. In the low-grade ores, tungsten minerals are usually finely dispersed, and thus enhanced gravity separators should be used to achieve satisfactory beneficiation performance (Mohammadnejad et al., 2018). Alternatively, froth flotation can also be utilized to treat the finely dispersed, low-grade wolframite ores since it has a relatively small lower particle size limit (around 10 μm; Trahar and Warren, 1976).

Froth flotation is an effective method for the separation of fine valuable minerals from gangue minerals. Collector selection is critical for the efficient separation. To achieve efficient separation, many investigations have been performed regarding wolframite flotation using different collectors. Meng et al. (2015) assessed the flotation performance of wolframite in the presence of octyl hydroxamic acid and investigated the interaction of octyl hydroxamic acid (OHA) with wolframite by solution component measurements and surface chemistry analysis, indicating that OHA replaced WO_2^{2-} ions and interacted with Mn/Fe sites at wolframite surface. Deng et al. (2015) found that N-(6-(hydroxyamino)-6-oxohexyl) octanamide (NHOO) presented a good separation performance in wolframite bench-scale flotation tests, suggesting that NHOO might adsorb on wolframite surface mainly through hydrogen bonding and electrostatic attraction by its amide $-C(=O)H_2N^{+}-$ group at pH below 6.7 or coordination bonding by its hydroxamic $-C(=O)NHO^{-}$ group at pH above 9.4. In the pH range 6.7–9.3, NHOO might exist as zwitterion species which was formed through intramolecular electrostatic attraction between its positive amide and negative hydroxamic groups. Yang et al. (2016) discovered that the mixed benzyl hydroxamic acid/sodium oleate (BHA/NaOl) collector caused a higher floatability for wolframite than the individual BHA and NaOl collectors, which was attributed to the interaction of BHA with the Fe sites and NaOl with the Mn sites on wolframite surfaces. Zhu and Sun (1980) studied the interaction of benzyl arsenic acid with wolframite. Furthermore, some other collectors (e.g., 8-hydroxyl quinoline and aminodimethyl phosphate) were also utilized for wolframite

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flotation (Tian et al., 2002; Zhu and Wu, 1990). However, the above-mentioned reagents in flotation plants will cause a series of issues, such as high operation cost (for instance, when using BHA), high toxicity, and low selectivity for the separation.

Currently, the most commonly used collector in the industrial practice of wolframite flotation is BHA. Wolframite floatability is low when using solely BHA due to the low amount of active sites on wolframite surfaces, which limits the collector adsorption (Dai and Zhang, 1995; Yang and Ai, 2016). The solvation free energy of iron and manganese ions on wolframite surfaces are much higher than that of the tungstate radicle ions. As such, preferential dissolution of the iron and manganese ions occurred in water, which resulted in negative charges on wolframite surfaces and thus preventing the collector adsorption (Wang and Hu, 1988). Therefore, an activator, lead nitrate, is normally used for wolframite flotation in the real ore systems (Guan et al., 2006; Qi, 2014). Regarding lead ion activation, Feng et al. (2017) studied the activation mechanism of lead ions in cassiterite flotation using salicylhydroxamic acid as collector. Li et al. (2016) also reported the interaction of lead ions with rutile/water interfaces. In addition, lead ions were also used as an activator for hemimorphite, ilmenite, and rare earth flotation (Liu et al., 2016b; Meng et al., 2018; Xia et al., 2015). However, very little research has been conducted concerning the activation mechanism of lead ions in the flotation of wolframite when BHA was used as collector.

In this study, the effects of Pb(II) on the flotation of wolframite when using BHA as the collector were investigated. The interaction mechanisms among lead ions, BHA, and the wolframite surfaces were discussed. This was accomplished using the findings from micro-flotation tests, zeta-potential measurements, adsorption measurements, Fourier transform infrared spectroscopy (FT-IR) analysis, and X-ray photoelectron spectroscopy (XPS) characterization.

2. Material and methods

2.1. Mineral samples and reagents

The wolframite samples were obtained from Xingluokeng, Fujian province, China. The chuck samples were crushed manually and relatively high-grade samples were handpicked by naked eye observation. The samples were dry ground and screened. The −74 + 37 µm fraction was used for micro-flotation tests and adsorption measurements. The −37 µm fraction was further ground to −5 µm (d_{90}) for zeta potential measurements, FT-IR analysis, and XPS characterization. Multi-element analysis of wolframite samples using Inductively Coupled Plasma Optical Emission Spectrometry (Teledyne Leeman Labs, USA) indicated that the contents of Fe, Mn and W were 10.5%, 6.2%, and 60.7%, respectively. In addition, the purity of the wolframite samples was confirmed by X-ray diffraction (XRD) analysis and the pattern is presented in Fig. 1. It can be observed from Fig. 1 that the sample purity is high, which is qualified to be used for the experiments.

BHA of more than 85% purity was used as the collector, which was synthesized (using benzoic acid and hydroxylamine (Zhu and Zhu, 2011) by Chemistry and Chemical Engineering, Central South University. Analytical-grade lead nitrate ($Pb(NO_3)_2$) purchased from Tianjin Kermil Chemical Reagents Development Centre (Tianjin, China) was used as the source of lead ions. Analytical-grade sodium hydroxide (NaOH) and hydrochloric acid (HCl) were utilized as pH modifiers in the experiments. Distilled water with a resistivity of 18.2 MΩ·cm was used for all the tests.

2.2. Micro-flotation tests

The flotation tests were performed using an XFGC-1600 machine (manufactured by Jilin Exploration Machinery Factory, China). Pure mineral particles (2 g) and deionized water (40 ml) were mixed in the plexiglass cell. The pH of the pulp was adjusted by NaOH and/or HCl solution and the slurry was conditioned for 2 min, after which Pb(II) ions (when required) and BHA were added subsequently and conditioned for 3 min, respectively. The slurry pH values that reported in this study were measured and recorded right before the flotation step, which was conducted for a period of 4 min. Both the floated and unfloated products were collected, filtered, and dried. The recovery was calculated based on the dry weights of the floated and unfloated products.

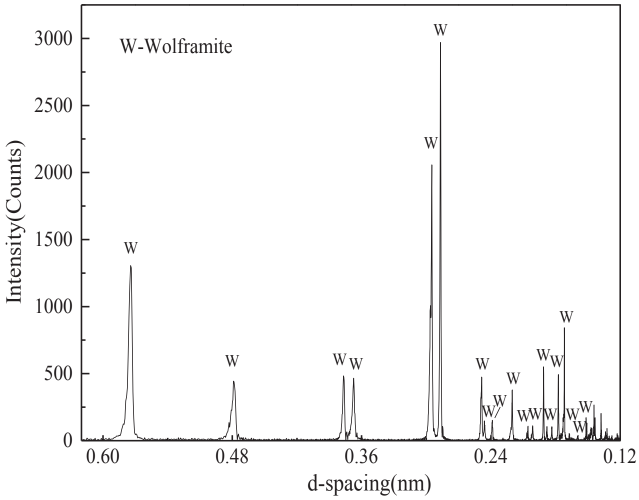

Fig. 1. XRD pattern of the pure wolframite sample.

2.3. Adsorption tests

For each test, 1 g material was conditioned in BHA solution of desired concentration both in the absence and presence of Pb(II). The total volume was 40 ml and the pH value was adjusted using HCl and/or NaOH solution. The slurry was conditioned for 20 min to ensure that adsorption equilibrium was achieved. The equilibrium concentration of BHA in the solution was measured by a Ultraviolet–Visible (UV–VIS) spectrophotometer (Thermo Fisher Scientific, USA) and the value was calculated from the calibration curve of BHA, which was developed using a series of BHA solution of known concentrations (absorbance at 228 nm). The amount of adsorption was calculated using the initial and residual concentration of BHA in the solution.

2.4. Zeta potential measurements

Zeta potential measurements were performed using a Malvern Instrument Nano-ZS90 analyzer (Malvern Panalytical, England). The −5 µm (d_{90}) sample of 40 mg was mixed with 80 ml 1×10^{-3} mol/L KNO_3 background electrolyte solution. The system was magnetically stirred for 6 min to thoroughly disperse the samples. The slurry pH was adjusted using NaOH and/or HCl solution, after which the reagents (e.g., BHA) of desired concentrations were added into the system. After conditioning, the slurry was settled for 10 min and the pH value was recorded. The supernatant was collected for zeta potential measurements. In this study, zeta potential of each sample was measured three times and an average was reported as the final value. The standard deviation was calculated, which was presented as an error bar in the plots.

2.5. FT-IR spectroscopy analysis

To characterize the nature of the interaction between the reagents and the mineral surfaces, FT-IR spectra analysis was performed using a Nicolet 6700 FT-IR spectrometer (Thermo Fisher Scientific, USA). Approximately 1 mg solid sample was mixed with 100 mg spectroscopic grade KBr. The wave-number range of the spectra was 400–4000 cm^{-1}. A suspension was prepared by adding 2.0 g of the −5 μm (d_{90}) pure mineral particles to 40 ml deionized water with and without the reagents at a desired pH, which was conditioned for 5 min. Subsequently, the solid samples were washed two times using distilled water with the same pH and allowed to dry (in a vacuum drying oven) prior to FT-IR analyses.

2.6. XPS characterization

The XPS characterization was performed by ESCALAB 250Xi (Thermo Fisher Scientific, USA), using a K-Alpha 1063 equipped with a monochromatic Al X-ray source. The analyzed sample was first gone through a survey scan to distinguish chemical components, followed by high-resolution scans on certain elements. The spectra and surface atomic ratios were obtained and calculated using the MultiPak Spectrum software. All spectra were calibrated using the carbon 1s spectral peak at 284.8 eV since carbon is ubiquitous in XPS characterization.

3. Results and discussion

3.1. Micro-flotation test results

Micro-flotation tests were conducted on the pure mineral to investigate the effects of Pb(II) on wolframite floatability. As shown in Fig. 2, the wolframite floatability with solely BHA collector was low. A maximum recovery of approximately 26% was obtained at pH around 8.5 when adding 5.8×10^{-4} mol/L (corresponding to 1.6 kg/ton) BHA, indicating that interaction of BHA with wolframite was weak. In the presence of 1×10^{-4} mol/L Pb(II) and 5.8×10^{-4} mol/L BHA, the wolframite recovery increased gradually with the elevation in the slurry pH and reached a maximum value (about 75%) at pH 8.5. When the pH exceeded 9.0, a noticeable decrease in the wolframite recovery occurred.

Fig. 3 shows the effect of lead ion concentration on the flotation of wolframite at pH 8.5 in the presence of 5.8×10^{-4} mol/L BHA collector. As shown in Fig. 3, the flotation recovery of wolframite initially increased significantly with the increase in lead ion concentration and reached a maximum (about 85%) at 2×10^{-4} mol/L Pb(II). When the lead ion concentration was above 2×10^{-4} mol/L, the flotation recovery of wolframite maintained constant.

The wolframite flotation recovery as a function of BHA concentration with and without Pb(II) at pH 8.5 is shown in Fig. 4. The recovery gradually increased with the increase in BHA concentration and maintained constant when BHA concentration was above 5.8×10^{-4} mol/L. In this case, only 30% of the wolframite were recovered. In the presence of Pb(II), maximum recovery of wolframite occurred at 6.2×10^{-4} mol/L BHA and the recovery was approximately 90%.

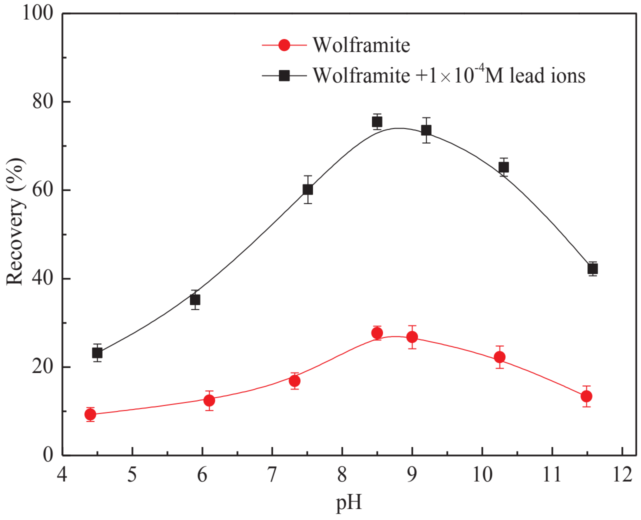

Fig. 2. Effect of pH on the floatability of wolframite using 5.8×10^{-4} mol/L BHA with and without Pb(II).

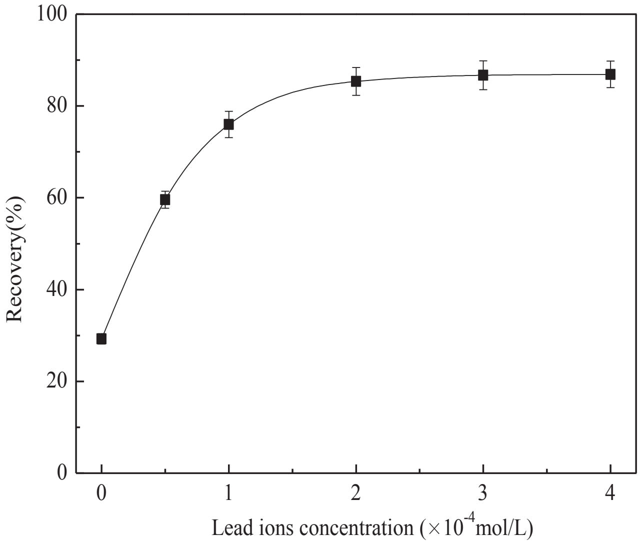

Fig. 3. Effect of Pb(II) concentration on the flotation of wolframite at pH 8.5 with 5.8×10^{-4} mol/L BHA.

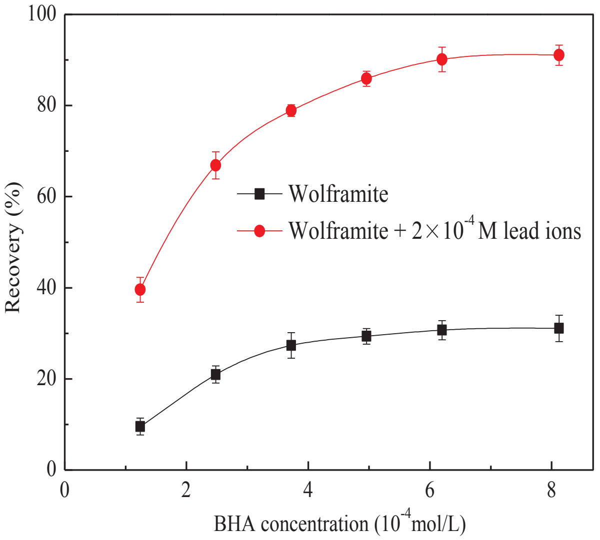

Fig. 4. Effect of BHA concentration on the flotation of wolframite at pH 8.5 with and without Pb(II).

3.2. Adsorption test results

The amount of BHA adsorbed onto the wolframite surfaces was measured as a function of pH in the absence and presence of Pb(II). The results are shown in Fig. 5. It can be seen from the figure that the adsorption amount of BHA on the wolframite surfaces firstly increased and then decreased with the elevation in pH. The maximum adsorption occurred at approximately pH 8.5 for both with and without Pb(II). However, much more BHA collector was absorbed on the wolframite surfaces in the presence of Pb(II) relative to the system in the absence of Pb(II). The finding indicates that Pb(II) enhanced the amount of BHA

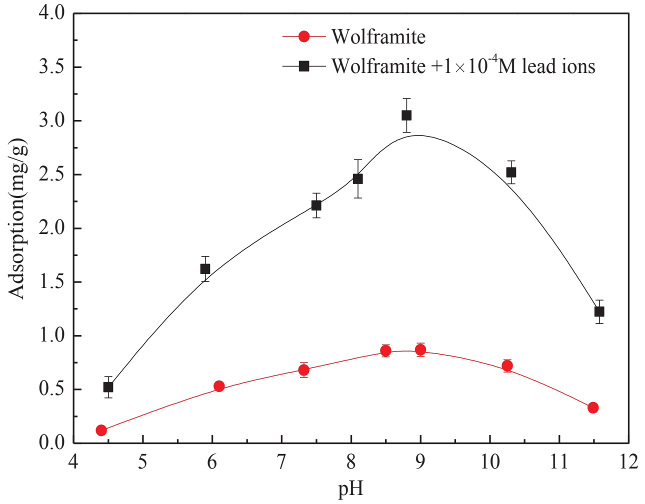

Fig. 5. BHA adsorption on wolframite surface as a function of pH with and without Pb(II)ions.

adsorbed on the wolframite surfaces and thus improving the wolframite floatability.

3.3. Zeta potential measurements

Electro-kinetic tests were performed on the wolframite sample to assess the adsorption of Pb(II) and BHA on its surfaces. As shown in Fig. 6, the wolframite surface charges were negative across the entire pH range, which agrees with a previous investigation (Meng et al., 2015). As such, more negative species existed on the wolframite surfaces. In the presence of Pb(II), zeta potential of wolframite was changed to positive when pH was below 9.8, while it was maintained negative for higher pH. This electro-kinetic characteristic was attributed to the adsorption/precipitation of lead species onto the negatively charged wolframite surfaces. After being treated with BHA, the zeta potential of wolframite was decreased by 9 mV while that of the lead ion-activated wolframite was decreased by 35 mV at pH around 8.5, indicating that the interaction between BHA and the lead ion-activated wolframite was stronger than the interaction between BHA and the non-activated wolframite.

The speciation diagrams of Pb(II) ions and BHA as a function of pH are presented in Fig. 7. It can be seen from Fig. 7(a) that the positively charged Pb^{2+} and $PbOH^{+}$ species dominate in the pH ranges of < 7.8 and 7.8–8.8, while at pH > 8.8, the main species of lead ions is $Pb(OH)_{2(s)}$ precipitate (Somasundaran and Wang, 2006; Wang and Hu, 1988). In the case of BHA (Fig. 7(b)), the dissociation equilibrium constant (p*K*a) of BHA is 8.2, when pH < p*K*a, BHA mainly exists as neutral molecules (HB) whereas BHA is predominantly in the form of BHA anions (B^{-}) at pH > p*K*a (Xu et al., 2017). The positively charged lead cations and the hydrolyzed species are expected to be adsorbed onto the negatively-charged wolframite surfaces by electrostatic attraction and/or hydrogen bonding. This agrees with the fact that the wolframite surface charges become positive at pH < 9.5 (Fig. 6) after conditioning with 2×10^{-4} mol/L Pb(II). Fuerstenau and Palmer (1976) indicated that the specific adsorption of metal cations onto a mineral surface occurs at a pH where the metal cation is in a monohydroxy state, suggesting that monohydroxy species are the surface active species.

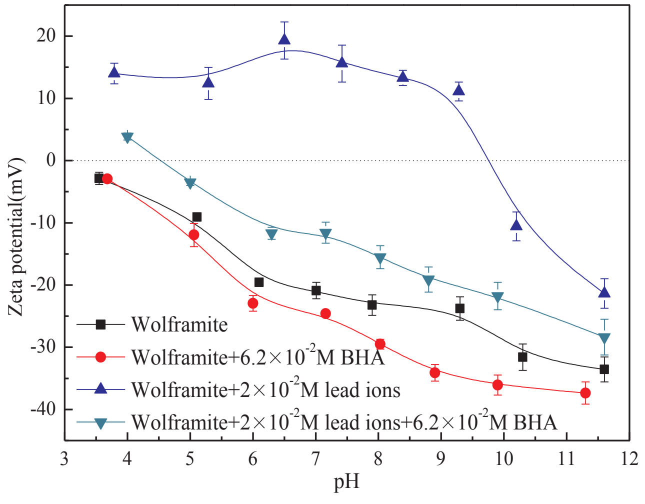

Fig. 6. The effect of pH on the zeta potential of wolframite.

The flotation recovery of wolframite reached a maximum at approximately pH 8.5, which may be due to the interaction between $PbOH^{+}$ and benzyl hydroxamate species. The maximum concentration of $PbOH^{+}$ occurred at a pH that is close to where the maximum recovery was obtained (around pH 8.5), which also agrees with the conclusion. At higher pH, OH^{-} might compete with the collector to complex with the lead species and thus preventing the BHA adsorption, which is consistent with the micro-flotation test results (Fig. 2).

3.4. FT-IR analysis

FR-IR analysis was performed on the wolframite samples conditioned using different reagents to investigate the surface functional group changes and the adsorption mechanisms. Fig. 8 shows the FT-IR spectra of BHA and wolframite. In the FT-IR spectrum of BHA, the peak at 3298 cm^{-1} can be attributed to the overlap stretching vibrations of N-H and O-H groups. The peak at around 3070 cm^{-1} can be assigned to N-H stretching vibration. The characteristic bands at 1575 cm^{-1}, 1490 cm^{-1}, and 1453 cm^{-1} belong to the benzene ring vibration (Gao et al., 2014). The peaks at 1074 cm^{-1}, 1040 cm^{-1}, and 1023 cm^{-1} can be attributed to the stretching vibration of N—O group. The peaks at 1648 cm^{-1} and 1162 cm^{-1} are assigned to the C═N and the C—N stretching vibration of the hydroxamate. The peaks of C—H out-of-plane bending vibrations of benzene rings occurred at 690 cm^{-1} and 540 cm^{-1}, respectively. In the case of wolframite, several characteristic peaks are observed at 866 cm^{-1}, 809 cm^{-1}, 616 cm^{-1}, 518 cm^{-1}, and 460 cm^{-1}, respectively (Ye, 2000).

Fig. 9 presents the FT-IR spectra of wolframite treated with BHA in the absence and presence of Pb(II) ions, when wolframite was treated by BHA alone, several new peaks appeared at 1636 cm^{-1}, 1561 cm^{-1}, and 1384 cm^{-1}, which correspond to the peaks at 1646 cm^{-1}, 1575 cm^{-1} and 1323 cm^{-1}, respectively, in the spectrum of BHA. The corresponding peaks were shifted by 10 cm^{-1}, 14 cm^{-1}, and 61 cm^{-1}, respectively, probably indicating that a chemical interaction occurred between BHA and wolframite and Fe/Mn-BHA chelates probably formed on the mineral surfaces.

After the wolframite was conditioned with Pb(II) ions and BHA, new peaks appeared at 1598 cm^{-1}, 1484 cm^{-1}, and 1151 cm^{-1} relative to the spectrum of wolframite treated by BHA alone. New bands 1598 cm^{-1} and 1484 cm^{-1} may be attributable to the characteristic bands of benzene rings caused by the Pb(II) addition. The peak at 1153 cm^{-1} can be assigned to the lead hydroxamate precipitates on the wolframite surfaces. In addition, 1022 cm^{-1} and 691 cm^{-1} peaks also appeared on the mineral surfaces, which can be attributed to the stretching vibration of N—O group and C—H out-of-plane bending vibration of benzene rings, respectively, suggesting the adsorption of BHA on the wolframite surfaces in the presence of Pb(II).

3.5. XPS analysis

The above results of the FT-IR analysis indicated that Pb(II)

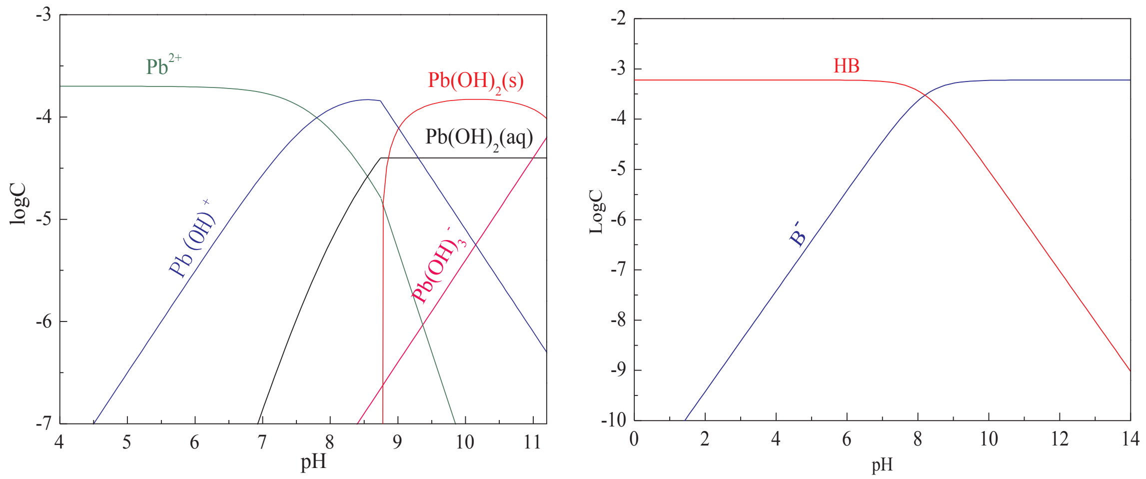

Fig. 7. Species distribution diagrams of (a) 2 × 10^{-4} mol/L lead ions and (b) 6.2 × 10^{-4} mol/L BHA as a function of pH.

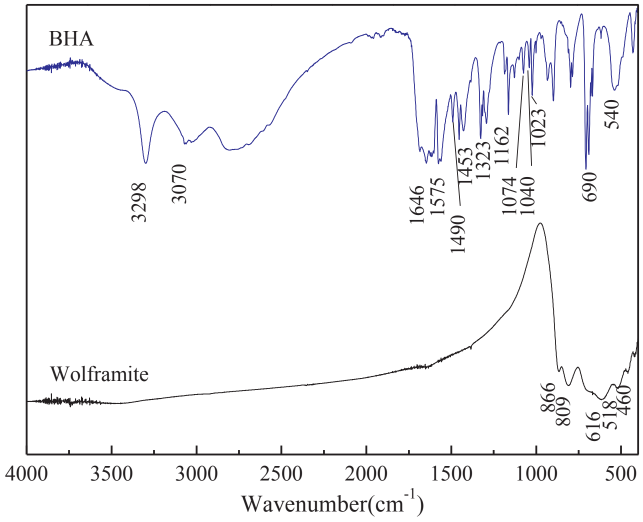

Fig. 8. FT-IR spectra of BHA and wolframite.

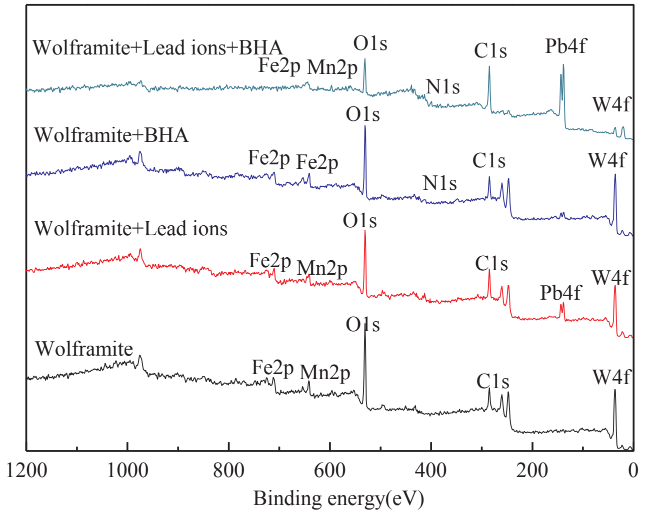

Fig. 10. XPS full-spectrum scanning of wolframite before and after lead ions and BHA treatment.

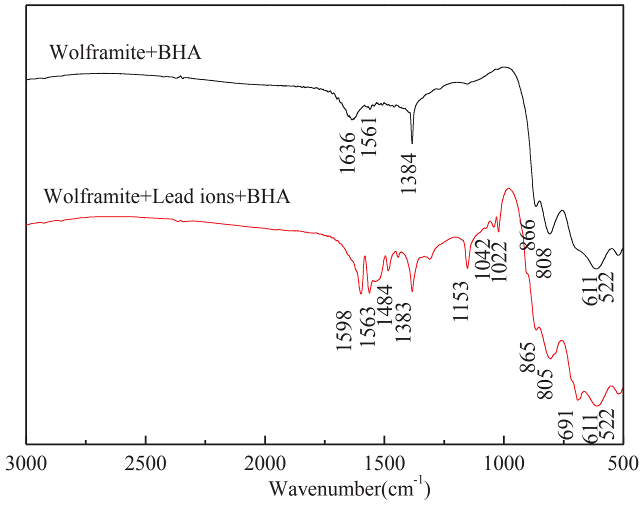

Fig. 9. FT-IR spectra of wolframite treated by BHA and by lead ions plus BHA.

significantly enhanced the interaction of BHA with the wolframite surfaces at approximately pH 8.5. To further explore the activation mechanisms of BHA interaction with the lead ion-activated wolframite, XPS analysis of the wolframite samples conditioned with different reagents was conducted. The XPS full-spectrum scanning results of wolframite before and after Pb(II) and BHA treatment are shown in Fig. 10. The binding energies and relative contents of the elements on the wolframite surfaces treated using different chemicals are given in Tables 1 and 2, respectively.

As shown in Table 1, several peaks of bare wolframite are observed at 284.8(C1s), 530.42(O1s), 35.51 eV(W4f), 640.80 eV(Mn2p), and 710.24 eV(Fe2p). C(1 s) peak can be attributed to the wolframite surface contamination by hydrocarbons. After treated by BHA, a new peak appears at 400.67 eV, which is attributed to N(1s). The binding energy of Fe(2p) and Mn(2p) was shifted by −0.34 eV and 0.03 eV, respectively, indicating that chemical interaction occurred between the Fe sites and the BHA on the wolframite surfaces. After treated with Pb(II) ions alone, a new peak of Pb(4f) is observed at 138.68 eV, and the binding energy of W(4f) shifted by −0.21 eV, indicating that chemical interaction occurred between the Pb(II) species and the W atoms on the wolframite surface. After wolframite was conditioned with Pb(II) and BHA, the binding energy of Pb(4f) and N(1s) shifted by +0.21 eV and −0.51 eV, respectively. These two pronounced changes in the binding energies of Pb(4f) and N(1s) suggested that strong chemical interaction occurred between the BHA and the Pb atoms on the wolframite surface.

As shown in Table 2, when the wolframite mineral was treated by BHA and Pb(II) separately, the relative contents of N(1s) and Pb(4f) on the wolframite surface were 2.92% and 1.23%, respectively. However,

Table 1
Binding energies of elements on the wolframite surface.

Sample	Binding energy (eV)						
	C1s	O1s	W4f	Mn2p	Fe2p	Pb4f	N1s
Wolframite	284.8	530.42	35.51	640.80	710.24	–	–
Wolframite + BHA	284.8	530.29	35.39	640.77	709.90	–	400.67
Wolframite + Pb(II)	284.8	530.33	35.30	640.90	710.32	138.68	–
Wolframite + Pb(II) + BHA	284.8	530.96	35.60	640.67	710.17	138.47	399.16

Table 2
Relative content of elements on the wolframite surface.

Sample	Relative content (%)						
	C1s	O1s	W4f	Mn2p	Fe2p	Pb4f	N1s
Wolframite	34.75	47.11	7.62	3.61	6.91	–	–
Wolframite + BHA	31.97	46.09	8.08	4.65	6.29	–	2.92
Wolframite + Pb(II)	40.48	41.60	7.10	3.90	5.70	1.23	–
Wolframite + Pb(II) + BHA	61.31	21.59	1.40	3.57	1.69	4.12	5.95

after the wolframite mineral was treated with Pb(II) and BHA simultaneously, the relative contents of Pb(4f) and N(1s) increased to 4.12% and 5.95%, respectively, indicating more BHA-Pb complex was absorbed on the wolframite surfaces (Han et al., 2018; Tian et al., 2017). The content of Fe(2p) was decreased from 6.91% to 6.29% and 5.70% after the wolframite was conditioned with BHA and Pb(II), respectively. The content was further decreased to 1.69% when the wolframite was conditioned with both Pb(II) and BHA. It might be due to that BHA-Pb complexes more likely replaced the Fe on the wolframite surfaces. The binding energy of Fe(2p) of the wolframite was solely decreased by 0.07 eV (710.24 eV to 710.17 eV) after conditioning with BHA and Pb(II) (Table 1). As such, the Fe left on the wolframite surfaces after the addition of BHA and Pb(II) did not interact with the reagents.

The binding energy changes of Mn(2p) were 0.03 eV and 0.1 eV when the wolframite was conditioned with solely BHA and Pb(II), respectively, indicating the interactions were weak. However, after treated by Pb(II) plus BHA, the binding energies of Mn(2p) shifted by -0.23 eV relative to the wolframite treated with solely Pb(II). This might be due to the interaction of BHA-Pb complex with the Mn sites on the wolframite surfaces since the relative contents of Mn(2p) on the wolframite surfaces maintained nearly constant.

The relative contents of W(4f) and O(1s) decreased to 1.40% and 21.59%, respectively. This probably indicates that a large amount of WO_4^{2-} dissociated from the mineral surfaces and the residual W sites were not interactive with the metal ions on wolframite surface because of the binding energies of W(4f) shifted by only -0.09 eV relative to the bare wolframite (Table 1).

Based on the above experimental results and discussion, Pb(II) ions significant increased the floatability of wolframite when BHA was used as collector. A potential schematic illustration of the activation and adsorption model is presented in Fig. 11. A part of lead species firstly adsorbed onto the wolframite surface and provided more activated site for BHA absorption. Then BHA-Pb chelates were formed on the wolframite surface and a part of Pb(II) ions interacted with BHA in solution which replaced Fe on the wolframite surface. A part of BHA-Pb also interacted with Mn site on the wolframite surface, hence more BHA-Pb existed on wolframite surface, which explained the significantly enhanced floatability. The activation mechanisms of Pb(II) when using hydroxamate collectors have been investigated for several different minerals, e.g., cassiterite, ilmenite, and scheelite (Han et al., 2018; Meng et al., 2018; Feng et al., 2017). Two well-accepted mechanisms have been proposed: (1) adsorption of lead species on the minerals surfaces, which provides more active sites for the hydroxamate collectors adsorption; (2) adsorption of the lead-hydroxamate complexes that formed in solution. It can be found that the activation mechanisms of lead species for wolframite flotation are more complicated. The surface species (mainly Fe) on the wolframite surfaces was also exchanged by the BHA-Pb complexes, which will deepen researchers' understanding regarding this topic.

As one of the most poisonous heavy metals, lead pollution mainly originating from mining, smelting, waste incineration, industrial uses, coal burning and leaded gasoline has been threatening public health in China for many years (Chen and Hu, 2010; Cohen and Amon, 2012). Lead toxicity disrupts the functions of digestive systems, nervous system, respiratory system, reproductive system, etc., and it also prevents enzymes from performing their normal activities (Wani et al., 2015). To the authors' knowledge, the environmental issues of using the Pb(II) as an activator in the flotation system have rarely been reported in literature. However, systematic environmental tests are suggested to be performed before industrial application of the lead activation flotation method. For example, to study the solid waste disposal impacts, characterization of the mobility of Pb(II) from the flotation solid waste material using methods such as TCLP (toxicity characteristic leaching procedure) is suggested to be conducted in lab-scale in future (Liu et al., 2015).

4. Conclusions

Effects of Pb(II) on wolframite flotation were systematically studied and the interaction mechanisms were discussed. Micro-flotation test results showed that Pb(II) increased the floatability of wolframite significantly when using BHA as collector and the recovery was increased from about 30% to 90% at pH 8.5. Adsorption measurements indicated that the adsorption of BHA on the wolframite surfaces was increased after adding Pb(II). The zeta potential measurements indicated that the wolframite surface charges were changed to positive at $pH < 8.5$ in the presence of Pb(II). At pH 8.5 the predominant hydroxyl complex $Pb(OH)^+$ was absorbed onto the wolframite surfaces and provided more activated sites for BHA absorption. FT-IR analysis demonstrated that chemical interactions occurred between BHA and the lead ion-activated wolframite surface. XPS characterization showed that different interaction mechanisms existed between BHA and wolframite in the absence and presence of Pb(II). In the former case, BHA mainly interact with the Fe sits on the wolframite surfaces. In the presence of Pb(II), the interaction is more complicated. Lead species was firstly adsorbed onto the wolframite surfaces and then interacted with BHA. In addition, the BHA-Pb complexes were also formed in solution, which were able to replace the Fe and interacted with the Mn sites on the surfaces.

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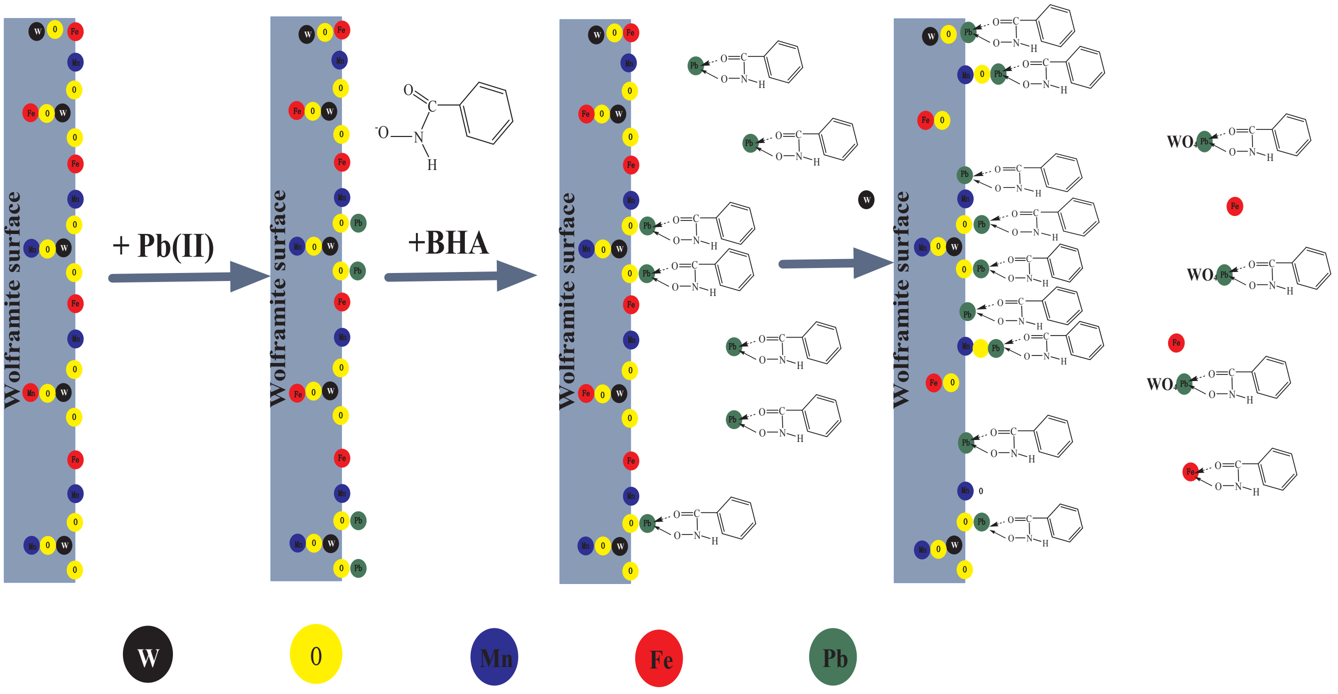

Fig. 11. Schematic illustration for lead ions activation and BHA adsorption on the wolframite surface.

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