Initial pH and K\(^+\) concentrations jointly determine the types of biogenic ferric hydroxysulfate minerals and their effect on adsorption removal of Cr(VI) in simulated acid mine drainage

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ABSTRACT

It is of practical significance to promote the transformation of Fe in acid mine drainage (AMD) into ferric hydroxysulfate minerals with strong ability to remove heavy metals or metalloids. To investigate the types of biogenic ferric hydroxysulfate minerals generated in AMD by Acidithiobacillus ferrooxidans (A. ferrooxidans), different pH and K\(^+\) concentrations are tested for the formation of precipitates in media containing 160 mmol/L Fe\(^{2+}\). The Cr(VI) removal efficiencies of ferric hydroxysulfate minerals in AMD with different acidities are also compared. Results indicate that the mineralizing abilities of the initial pH levels (pH 3.0 > pH 2.5 > pH 2.0) and K\(^+\) concentrations (53.3 mmol/L > 3.2 mmol/L ≈ 0.8 mmol/L) differ, with cumulative Fe precipitation efficiencies of 58.7%, 58.0%, and 44.2% (K\(^+\) = 53.3 mmol/L) after 96 h of A. ferrooxidans incubation, respectively. X-ray diffraction indicates that K-jarosites are formed in the treatments n(Fe)/n(K) = 0.1 and 3 at pH 2.0–3.0, while only schwertmannite is generated in a system of pH 3.0 and n(Fe)/n(K) = 200. X-ray photoelectron spectroscopy reveals that HCrO\(_4^-\)/C\(_0\) may be adsorbed as an inner-sphere complex on schwertmannite when the AMD pH is 3.0.

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Key words | Acidithiobacillus ferrooxidans, acid mine drainage, Cr(VI), ferric hydroxysulfate minerals, K\(^+\), pH

INTRODUCTION

Acid mine drainage (AMD) is highly acidic and contains a large quantity of Fe (Fe\(^{2+}\) and Fe\(^{3+}\)), heavy metal, metalloid elements (Cravotta & Trahan 1993; Peppas et al. 2000; Sahoo et al. 2010; Wei & Wolfe 2013; Vhahangwele 2016; Wu et al. 2016). Currently, lime neutralization is widely used due to its convenience and speed; however, this method requires a large amount of lime. Furthermore, the products of the neutralization, such as Fe(OH)\(_3\), Fe(OH)\(_2\), and CaSO\(_4\), hinder the reaction by adhering to the lime surface and generating a large amount of waste, which exposes the environment to the risk of secondary pollution (Song et al. 2014; Meschke et al. 2015; Lee et al. 2016).

Acidithiobacillus ferrooxidans (A. ferrooxidans), a common acidophilic Fe-oxidizing bacterium, can efficiently catalyze the oxidation of Fe\(^{2+}\) in AMD to Fe\(^{3+}\) and produce various ferric hydroxysulfate minerals (e.g. schwertmannite (Fe\(_8\)(OH)\(_6\)SO\(_4\)) and jarosite ((K, Na, NH\(_4\), H\(_3\)O)-Fe\(_5\)(SO\(_4\))\(_2\)(OH)\(_6\))) along with the hydrolysis of Fe\(^{3+}\) (Singer & Stumm 1970; Diao et al. 2013; Song et al. 2013; Valente et al. 2013; Zhu et al. 2013). Reactions (1) to (3) present schwertmannite and jarosite formation (Song et al. 2013):

\[
\begin{align*}
4\text{Fe}^{2+} + \text{O}_2 + 4\text{H}^+ &\rightarrow 4\text{Fe}^{3+} + 2\text{H}_2\text{O} \\
8\text{Fe}^{3+} + 14\text{H}_2\text{O} + \text{SO}_4^{2-} &\rightarrow \text{Fe}_8\text{O}_6(\text{OH})_6\text{SO}_4 (\text{schwertmannite}) + 22\text{H}^+ \\
(\text{K, Na, NH}_4, \text{H}_3\text{O})^+ + 3\text{Fe}^{3+} + 2\text{SO}_4^{2-} + 6\text{H}_2\text{O} &\rightarrow (\text{K, Na, NH}_4, \text{H}_3\text{O})\text{Fe}_5(\text{SO}_4)_2(\text{OH})_6(\text{jarosite}) + 6\text{H}^+ 
\end{align*}
\]

Numerous studies have confirmed that these minerals can remove toxic elements in AMD (Wang et al. 2006; Asta et al. 2009; Liao et al. 2011; Mihone et al. 2015; Min...
et al. 2015; Zhang et al. 2016). The specific phases and properties of synthetic ferric hydroxysulfate minerals depend on the contact time, reaction temperature, concentration of Fe$^{2+}$, acidity of the solution, the variety or concentration of monovalent cations, etc. (Dutrizac & Kaiman 1976; Dutrizac 1999; Deng & Zhou 2002). Previous studies showed that schwertmannite formation usually occurs in Fe- and sulfate-rich solutions in a pH range of 2.5–4.5, with lower pH values promoting jarosite precipitation (Schwertmann et al. 1995; Yu et al. 1999; Kawano & Tomita 2001). In addition, the monovalent nature of the cations (e.g. K$^+$, NH$_4^+$, or Na$^+$) and their initial concentration impact the types of ferric hydroxysulfate minerals produced (Majzlan & Myneni 2005; Gramp et al. 2008; Bai et al. 2012). For instance, Bigham et al. (1996) demonstrated that schwertmannite, formed through the bio-oxidation of Fe$^{2+}$ by A. ferrooxidans, was the only mineral phase at pH 3.0. Liao et al. (2009) observed that the formed ferric hydroxysulfate minerals were a mixture of Na-jarosite and schwertmannite at an initial pH of 3.5, while pH in the range of 1.6–3.4 produced only pure schwertmannite. Moreover, Wang et al. (2007) found that a mixed product of NH$_4$-jarosite and schwertmannite was precipitated when the NH$_4^+$ concentration was between 11.5 and 85.4 mmol/L, while only schwertmannite was produced when the NH$_4^+$ concentration was less than 10 mmol/L, and only NH$_4$-jarosite was formed when the concentration of NH$_4^+$ was as high as 165 mmol/L. Finally, Gramp et al. (2008) found that NH$_4$-jarosite, Na-jarosite, and K-jarosite were not present in an A. ferrooxidans culture solution until the concentrations of NH$_4^+$, Na$^+$, and K$^+$ were above 160, 100, and 4 mmol/L, respectively.

According to literature data, initial pH and the monovalent nature of cations were crucial factors determining the formation of ferric hydroxysulfate minerals in Fe- and sulfate-rich solutions (Bigham et al. 1996; Wang et al. 2007; Gramp et al. 2008; Liao et al. 2009). It was verified that the ferric hydroxysulfate minerals obtained in the pH range of 2.0–2.6 were pure schwertmannite when the Na$^+$ concentration range was between 80 and 160 mmol/L in the medium containing 160 mmol/L Fe$^{2+}$. If the concentration of Na$^+$ was as high as 520 mmol/L, Na-jarosite began to form and the characteristic diffraction peak in X-ray diffraction (XRD) analysis became stronger with increasing Na$^+$ concentration (Song et al. 2018a). Under similar conditions, when the initial NH$_4^+$ concentration was 80 mmol/L at pH 2.6, the ferric hydroxysulfate minerals obtained were pure schwertmannite; when the NH$_4^+$ concentration exceeded 160 mmol/L and the pH was below 2.3, NH$_4$-jarosite began to form in this system (Song et al. 2018b). Bai et al. (2012) reported that the capacity to promote jarosite formation was in the order K$^+$ > NH$_4^+$ > Na$^+$, and the capacity of K$^+$ is about 75 and 200 times greater than those of NH$_4^+$ and Na$^+$, respectively. This indicated a difference in the ability of these three ionic species to catalyze the transformation of Fe into ferric hydroxysulfate minerals. Nevertheless, it is still unclear how the initial pH and K$^+$ concentration jointly impact the mineralogy of the ferric hydroxysulfate mineral precipitates in A. ferrooxidans culture solutions.

Therefore, the objectives of this study were to analyze the influences of initial pH and K$^+$ concentration in a 160 mmol/L Fe$^{2+}$ medium inoculated with A. ferrooxidans on the formation of biogenic ferric hydroxysulfate minerals. The Cr(VI) adsorption removal efficiencies of ferric hydroxysulfate minerals under different pH conditions were also compared. The presented results may provide an essential theoretical basis to elucidate the transformation of Fe to ferric hydroxysulfate minerals and the removal of toxic elements in an acid sulfate environment.

MATERIALS AND METHODS

Preparation of A. ferrooxidans LX5 cell suspensions

Acidithiobacillus ferrooxidans LX5 (CGMCC No. 0727), obtained from China General Microbiological Culture Collection Center, was grown in 9 K medium (Silverman & Lundgren 1959). A. ferrooxidans LX5 numbers were determined to be $3 \times 10^6$ CFU/mL by using the double-layer plate method prior to the following synthesis experiments (Wang & Zhou 2005).

Influence of initial pH and K$^+$ concentrations on the biosynthesis of ferric hydroxysulfate minerals mediated by A. ferrooxidans LX5

The experiments on Fe$^{2+}$ oxidation and Fe$^{3+}$ hydroxysulfate precipitate formation with A. ferrooxidans LX5 were conducted in 36 Erlenmeyer flasks (500 mL). Briefly, after the addition of 160 mmol/L (8,960 mg/L) Fe$^{2+}$ (added as FeSO$_4$·7H$_2$O) and K$^+$ (added as K$_2$SO$_4$), the A. ferrooxidans LX5 cells were added to each Erlenmeyer flask, resulting in a bacterial density of $5 \times 10^7$ CFU/mL. The n(Fe)/n(K) (molar ratio) was designed to be 0.1, 3, 50, and 200 through the alteration of the initial K$^+$ concentration. Initial solution pH was adjusted to 3.0, 2.5, and 2.0 at each n(Fe)/n(K) level with 10 mol/L H$_2$SO$_4$ to fix the final volume of 250 mL. The
Initial solution pH effect on Cr(VI) adsorption by ferric hydroxysulfate mineral

Treatment of the synthetic AMD with pH 3.0 and n(Fe)/n(K) = 200 afforded schwertmannite. To compare the Cr(VI) adsorption removal efficiency of the schwertmannite under different pH conditions, experiments were conducted by adding 0.05 g synthesized schwertmannite to 250 mL Erlenmeyer flasks, each containing 100 mL of solution initially containing 10 mg/L Cr(VI) (prepared from K$_2$Cr$_2$O$_7$). The suspension pH was adjusted to the desired values, ranging from 1.0 to 5.0 by adding 1 mol/L HNO$_3$. The pH was set to 7.0 in the control. All Erlenmeyer flasks were shaken in a reciprocating shaker at 28 °C and 180 rev/min. After shaking for 4 h (Chen & Zhou 2006; Liao et al. 2011), the solutions in different systems were filtered through 0.22 μm membranes and Cr(VI) concentrations in the liquid phases were examined.

Analytical procedures

The solution pH was measured using pHS-3C. The Fe$^{2+}$ and total Fe concentrations were determined using the 1,10-phenanthroline method according to the standard method (APHA 2012). The mineral phase and morphology of the precipitate were determined by XRD (Bruker D8A25) and field-emission scanning electron microscopy (FE-SEM, SU8010) (Liu et al. 2015). The specific surface area of the precipitate was determined using the multi-point Brunauer-Emmett-Teller method (BET, TriStar II 3020) (Manna & Ghosh 2007). The Cr(VI) concentration was determined by inductively coupled plasma-atomic emission spectrometer (ICP-AES) (Houngaloune et al. 2014). The chemical analysis of Cr species was performed using X-ray photoelectron spectroscopy (XPS, VG-Multilab 2000) (Huang et al. 2012). The chemical composition of the dried precipitates was determined by X-ray fluorescence (XRF) spectrometry (Minipal 4, The Netherlands). Experimental data were analyzed using SAS 9.2 software. The data shown in the figures are presented as the mean values with standard deviations to show their reproducibility and reliability.

RESULTS AND DISCUSSION

Changes of pH during the biogenic formation of ferric hydroxysulfate minerals

It has previously been demonstrated that when the solution pH > 5, the oxidation rate of Fe$^{2+}$ was positively correlated with pH. With one unit increment for pH, the oxidation rate of Fe$^{2+}$ would increase by a factor of 100 (Singer & Stumm 1970). However, when pH < 3.5, the oxidation rate of Fe$^{2+}$ was independent of pH with a low oxidation rate constant of 10$^{-3.5}$/d (Umita 1996). In an acidic environment, A. ferrooxidans could increase the oxidation rate of Fe$^{3+}$ 10$^{3}$-10$^{6}$ times (Bosecker 1997).

Reactions (1)–(3) clearly show that the oxidation of Fe$^{2+}$, mediated by A. ferrooxidans to form minerals, involves a two-step acid effect process. The first step is the acid-depleting bio-oxidation of Fe$^{2+}$, while the second step is the acid-producing hydrolysis of Fe$^{3+}$ to form minerals. Therefore, the degree of oxidation of Fe$^{2+}$ and the degree of mineralization of Fe$^{3+}$ could be roughly determined from the evolution of the reaction system pH. The dynamic changes of pH in solution with different initial pH and K$^+$ concentrations (Figure 1) show that the pH sharply increased during the first 24 h and then slightly decreased over the period of 24–96 h of the incubation. For instance, the solution pH sharply increased from the initial 3.0, 2.5, or 2.0 to 3.1, 2.9, or 2.6 in 24 h and then decreased slightly to 2.6, 2.5, or 2.2 at 96 h for the treatment of n(Fe)/n(K) = 3, respectively. In addition, in solutions with high K$^+$ concentrations (except for n(Fe)/n(K) = 0.1), the trend of pH decrease is more sensitive to increase in K$^+$ concentration. According to Reactions (2) and (3), 1 mol/L of Fe$^{3+}$ can generate 2.75 mol/L of H$^+$ during schwertmannite bio-synthesis through Fe$^{3+}$ hydrolysis; however, only 2.0 mol/L of H$^+$ can be obtained during the process of K-jarosite bio-synthesis. The results of this study indirectly indicate that a suitable concentration of K$^+$ can precipitate more Fe$^{3+}$ by the formation of K-jarosite, thus releasing more H$^+$ in the system.
Changes of Fe\(^{2+}\) concentrations during the biogenic formation of ferric hydroxysulfate minerals

The influence of initial pH and K\(^+\) concentrations on the oxidation of Fe\(^{2+}\) by *A. ferrooxidans* is given in Figure 2. The Fe\(^{2+}\) oxidation rates varied greatly at different initial K\(^+\) concentrations in solution. For n(Fe)/n(K) ratios ranging between 3 and 200, no difference in Fe\(^{2+}\) oxidation was observed for the different treatment processes. However, when the K\(^+\) concentration was further raised such that the n(Fe)/n(K) ratio was 0.1, the biological oxidation activity of *A. ferrooxidans* was inhibited. Csonka (1989) reported that the capacity of organisms to respond to fluctuations in their osmotic environments is an important physiological process that determines their ability to thrive in a variety of habitats. This possibly occurs because the high-concentration salt causes a change in the osmotic pressure of the microbial cells, influencing the bio-oxidation activity of Fe\(^{2+}\) (Wu 2007). These results are in good agreement with those reported by Wang *et al.* (2015), who also found no effect on the activity of *A. ferrooxidans* within the 81.6–326.5 mmol/L concentration range of Na\(^+\), with the growth curves of *A. ferrooxidans* being essentially identical. Yet, when the concentration of Na\(^+\) was increased to 653 mmol/L, the growth of *A. ferrooxidans* was inhibited. These results confirm that the concentration of monovalent cations exhibits considerable influence on the biological oxidation of Fe\(^{2+}\) in AMD. In addition, the Fe\(^{2+}\) oxidation rates in solution varied little when the initial pH was in the range of 2.0–3.0. The result observed in this research was similar to those reported by Nemati *et al.* (1998), who concluded that *A. ferrooxidans* can obtain energy for growth from the oxidation of Fe\(^{2+}\) to Fe\(^{3+}\) and often grows within the pH range 1.5–6.0, with an optimum pH between 2.0 and 2.5. The Fe\(^{2+}\) oxidation rate in the present work is comparable to many field determinations of Fe\(^{2+}\) oxidation rates in acid sulfate environments (España *et al.* 2005; Wang & Zhou 2012).

Changes of total Fe precipitation efficiency during the biogenic formation of ferric hydroxysulfate minerals

Figure 3 compares the time-dependent trend of total Fe precipitation efficiency in the different treatment processes. Both Figures 2 and 3 indicate that the total Fe precipitation efficiency can be improved if the concentration of K\(^+\) is maintained within an appropriate range that does not inhibit the oxidation activity of *A. ferrooxidans*. For instance, the variation trend in the total Fe precipitation efficiency was almost identical at n(Fe)/n(K) ratios of 200 and 50 when
the initial pH levels of solutions were constant. This indicates that the ferric hydroxysulfate minerals’ formation ability was poor when the K\(^+\) concentration remained within this range. When the concentration of K\(^+\) was raised to 53.3 mmol/L [n(Fe)/n(K) = 3], the total Fe precipitation efficiency increased to 58.7\% at 96 h. Within the period of 24–72 h, the biological oxidation rate of Fe\(^{2+}\) was very high and Fe\(^{3+}\) ions were supplied rapidly. This changes the driving force of ferric hydroxysulfate mineral formation in the environment and accelerates their formation to some extent (Sasaki & Konno 2000; Regenspurg et al. 2004). Because the biological oxidation activity of A. ferrooxidans was inhibited when the K\(^+\) concentration was 1,600 mmol/L [n(Fe)/n(K) = 0.1], Fe\(^{3+}\) was absent during ferric hydroxysulfate mineral formation. However, the presence of K\(^+\) in the solution was still helpful for the synthesis of ferric hydroxysulfate minerals from the low concentration of Fe\(^{3+}\). These results were in good accordance with Kashkay & Borovskaya (1975) and Wang et al. (1985), who demonstrated that K\(^+\) readily enters ferric hydroxysulfate minerals in the K\(^+\)-Fe\(^{3+}\)-SO\(_4\)\(^2-\) medium. Furthermore, the initial pH exhibited different mineralizing abilities, specifically, pH 3.0 > pH 2.5 > pH 2.0. According to Reactions (2) and (3), hydrolysis of Fe\(^{3+}\) to form ferric hydroxysulfate minerals is an acid-producing process, therefore, introducing more H\(^+\) can inhibit the total Fe precipitation because the addition of a product to the chemical equilibrium does not favor the ferric hydroxysulfate minerals’ bio-synthesis.

Changes in mineral phases during biogenic formation of ferric hydroxysulfate minerals

XRD spectra of the obtained ferric hydroxysulfate minerals were recorded, and the results are presented in Figure 4. Compared to the standard schwertmannite and K-jarosite spectra (JCPDS 2002), the afforded spectra indicated that the K\(^+\) concentrations exhibited a major influence on the variety of biogenic ferric hydroxysulfate minerals. Thus, a rise in K\(^+\) concentration was beneficial for the biosynthesis of K-jarosite. For instance, the treatments at n(Fe)/n(K) = 0.1 and 3 afforded K-jarosites when the solution pH was 2.0–3.0. At n(Fe)/n(K) = 200, only schwertmannite was generated at pH 3.0. These results are consistent with those reported previously by Gramp et al. (2008). For other treatment processes, a mixture of schwertmannite and K-jarosite was generated. According to the experimental results, the pH differed in terms of their K-jarosite-forming ability, specifically, pH 2.0 > pH 2.5 > pH 3.0. Bai et al. (2012) reported that only schwertmannite was observed when n(Fe)/n(K) was 200 at the same Fe\(^{2+}\) concentration as this study, but they ignored the influence of initial pH. Obviously, at a fixed K\(^+\) concentration, lower initial pH was not conducive to the formation of schwertmannite. However, Liao et al. (2009) found that the formed ferric hydroxysulfate minerals were a mixture of Na-jarosite and schwertmannite at an initial pH of 3.5, while only pure schwertmannite was obtained at pH 1.6–3.4. Wang et al. (2007) also reported that when the NH\(_4\) concentration was less than 10 mmol/L, the product was pure schwertmannite at initial pH 2.0. Analysis shows that the minerals phase may be influenced by these differences in the relative mineralizing ability of various monovalent cations. Bai et al. (2012) observed that the capacity in promoting jarosite formation was K\(^+\) > NH\(_4\)\(^+\) > Na\(^+\), and the capacity of K\(^+\) is about 75 and 200 times greater than NH\(_4\)\(^+\) and Na\(^+\), respectively. Clearly, both the initial pH and K\(^+\) concentration play critical roles in determining the types of ferric hydroxysulfate minerals produced.

Effect of initial pH on Cr(VI) adsorption removal efficiency by ferric hydroxysulfate mineral

Wei (2001) has investigated the basic physical and chemical properties of AMD in China’s major mining areas and
found that there were differences between the properties of AMD; especially, the pH value was within a wider range of 1.7–5.0. Cr(VI) is carcinogenic and teratogenic, which poses a serious threat to human health. In addition, Cr(VI) is strongly oxidizing under acidic conditions, which will accelerate the oxidation process of pyrite and lead to the release of heavy metals and increase water pollution. Therefore, it is important to use appropriate methods to remove Cr(VI) from AMD. To compare the biogenic schwertmannite removal efficiency of Cr(VI) present in AMD with different pH values, we selected schwertmannite synthesized under the mineralization system of initial pH 3.0 and n(Fe)/n(K) = 200 as the adsorbent, according to XRD analysis. Based on the determination of the elemental composition, the schwertmannite could be expressed as the chemical formula Fe$_3$O$_6$(OH)$_{4.65}$(SO$_4$)$_{1.57}$. Although the Fe/S ratio of schwertmannite typically ranges between 4.6 and 8.0 (Bigham et al. 1990), the results in our study were consistent with those observed by Yu et al. (1999), who reported an Fe/S ratio of 4.3-4.6 for schwertmannite formed in natural stream water polluted by AMD. The SEM image (Figure 5(a)) shows that the schwertmannite particle surface was slightly coarse with a specific surface area of 8.65 m$^2$/g. We noted that the specific surface area of schwertmannite in this study was much lower than that reported by Bigham et al. (1990), but consistent with Wang et al. (2007) who reported 10.3 m$^2$/g of specific surface area for schwertmannite. The relatively low specific surface area could be attributed to the fact that adsorbed SO$_4^{2-}$ at low pH and high SO$_4^{2-}$ concentration facilitated aggregation of the particles while drying and thereby reduced the surface area available for the N$_2$ gas adsorption in the BET measurement (Jönsson et al. 2005).

![Figure 4](https://iwaponline.com/wst/article-pdf/78/10/2183/516494/wst078102183.pdf)

Figure 4 | XRD patterns of precipitates formed through Fe$^{3+}$ oxidation by A. ferrooxidans.
The removal of Cr(VI) in AMD with pH ranging from 1.0 to 5.0 through adsorption onto biogenic schwertmannite is shown in Figure 5(b). A lower pH was not beneficial to the adsorption of Cr(VI) in the solution, and the adsorption capacity of Cr(VI) at pH 2.0 was only 4.2 mg/g. However, Cr(VI) adsorption by biogenic schwertmannite increases sharply when solution pH exceeds 3.0, and the adsorption capacity of Cr(VI) at pH 5.0 was 16.3 mg/g. In contrast, the amount of Cr(VI) adsorbed by schwertmannite reached a maximum (19.0 mg/g) in the control treatment (pH 7.0). Given that Cr(VI) is influenced by the acidity or alkalinity of the solution, the transformation processes between various forms are as follows:

\[
\begin{align*}
Cr_2O_2^{2-} + H_2O & \leftrightarrow 2HCrO_4^- \quad \text{pK}_1 = 2.2 \\
HCrO_4^- & \leftrightarrow CrO_4^{2-} + H^+ \quad \text{pK}_2 = 5.9
\end{align*}
\]

When solution pH is below 2.2, along with the increase in solution acidity, the predominant Cr(VI) species is neutral H_2Cr_2O_7, which is not conducive to adsorption on schwertmannite. In the pH range from 2.2 to 5.9, HCrO_4^- can be complexed with Fe^{3+} in the schwertmannite structure. When solution pH is above 5.9, CrO_4^{2-} can be exchanged with SO_4^{2-} not only in the surface structure of schwertmannite, but also through ligand exchange into the internal structure of the mineral, producing Cr(VI) removal efficiency (Bigham et al. 1990; Regenspurg & Peiffer 2005). The results in the present study are in good agreement with those obtained from theoretical analyses. However, although the adsorption capacity of Cr(VI) was more than 10.0 mg/g in the pH range from 3.0 to 5.0, XPS analysis revealed no significant peak intensity of HCrO_4^- (Figure 6). The possible reason for the lack of HCrO_4^- in the XPS spectra is that HCrO_4^- was exchanged with SO_4^{2-} in the schwertmannite tunnel structure and complexed with Fe^{3+}, while XPS can only detect the surface physicochemical characteristics of a material.

**CONCLUSIONS**

The effects of initial pH and K^+ concentrations in FeSO_4 medium inoculated with *A. ferrooxidans* on the formation of biogenic ferric hydroxysulfate minerals were investigated in the present study. The mineralizing abilities of the initial pH (pH 3.0 > pH 2.5 > pH 2.0) and K^+ concentrations (53.3 mmol/L > 3.2 mmol/L ≈ 0.8 mmol/L) differ, with cumulative Fe precipitation efficiencies of 58.7%, 58.0%, and 44.2% (K^+ = 53.3 mmol/L), and 58.7%, 29.9%, and
29.6% (pH 3.0) after 96 h of A. ferrooxidans incubation, respectively. XRD indicated that the crystallinity of K-jarosite increased with decreasing initial pH and increasing K⁺ concentration in the medium. It was concluded that both the initial pH and K⁺ concentration played a critical role in determining the types of ferric hydroxysulfate minerals obtained. The Cr(VI) adsorption capacity in synthetic AMD was increased with pH increasing from 1.0 to 5.0 by using biogenic schwertmannite. XPS analysis revealed that Cr(VI) may have been adsorbed as an inner-sphere complex on schwertmannite when the synthetic AMD pH was 3.0. This study makes a significant contribution to the literature because it provides essential parameter support for the process optimization of the biosynthesis of ferric hydroxysulfate minerals facilitated by A. ferrooxidans and their effective application in the treatment of AMD.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

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