Low-temperature Conversion of Fe-rich Sludge to KFeS2 Whisker: a New Flocculant Synthesis From Laboratory Scale to Pilot Scale

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Abstract

KFeS\textsubscript{2} is a one-dimensional material and commonly used raw material for synthesising AgFeS\textsubscript{2} and CuFeS\textsubscript{2}. With the solvothermal method, KFeS\textsubscript{2} cluster could be synthesised at 190 °C with chemically pure grade Fe salt as Fe source. Herein, a KFeS\textsubscript{2} whisker was formed in mass production at a low temperature, with waste cold-rolling sludge as Fe source, and exhibited good performance in the removal of Zn/Ni from real electroplating effluent. At laboratory scale, results showed that KFeS\textsubscript{2} was not generated after heating at 50 °C for 24 h; however, after heating at 80 °C for 10 h, KFeS\textsubscript{2} whisker (diameter and length of 0.2 and 0.5–1 mm, respectively) was produced, which grew radially to 1–4 mm after 24 h. This method was applied at pilot scale, where a similar KFeS\textsubscript{2} whisker was also produced with waste cold-rolling sludge as Fe source. At pilot scale, a residual brownish supernatant was observed after the reaction and then completely recycled in the next round for KFeS\textsubscript{2} synthesis. After recycling five times, the produced KFeS\textsubscript{2} whisker did not change. For KFeS\textsubscript{2} drying, freeze-drying and vacuum-drying were applicable, whilst air-drying was not profitable. The prepared KFeS\textsubscript{2} was spontaneously hydrolysed in electroplating wastewater to generate Fe/S-bearing oxyhydroxide colloid for Zn/Ni removal. By adding 1 g of KFeS\textsubscript{2}, the residual levels of Zn/Ni were 0.22 and 0.02 mg/L, met the discharge standard of electroplating wastewater. Undried KFeS\textsubscript{2} showed similar efficiencies of Zn/Ni removal to dried KFeS\textsubscript{2}, whose efficiencies were apparently higher than those with Na\textsubscript{2}S·9H\textsubscript{2}O, polymeric ferric sulfuric, sodium diethyldithiocarbamate and lime. With the method, KFeS\textsubscript{2} whisker was produced at pilot scale without generating any secondary waste and exhibited good performance in the treatment of electroplating wastewater.

Highlights

1. Ferrihydrite-bearing sludge was recycled as KFeS\textsubscript{2} whisker at 80 °C.
2. KFeS\textsubscript{2} whisker was produced at pilot scale.
3. The hydrolysis of KFeS\textsubscript{2} whisker occurred spontaneously at pH 42.
4. The hydrolysed whisker was effective in treating real electroplating effluent.

1 Introduction

KFeS\textsubscript{2} is a fibrous Fe/S-bearing mineral [1] crystallised under high potassium activity and sulphur fugacity [2]. Such conditions are extreme, so it has not been detected in natural rocks. Only its derivate, rasvumite, co-exists with pegmatites in the mafic environment [3]. KFeS\textsubscript{2} is usually synthesised artificially and has a special structure in which one Fe atom is covalent with four sulphur atoms to form a stable tetrahedral (FeS\textsubscript{2})\textsuperscript{n−} bond [4]. The free electrons in large spaces located at edge-sharing (FeS\textsubscript{2})\textsuperscript{n−} chains are neutralised by K\textsuperscript{+} [5] to form a stable Fe-S structure. In the synthesis of KFeS\textsubscript{2}, when cations, e.g. Ag\textsuperscript{+}, Ca\textsuperscript{2+}, Sr\textsuperscript{2+} and Ba\textsuperscript{2+}, are introduced [6, 7], they will embed into the inner lattice via the space channel of
(FeS$_2$)$_n$[6], and K$^+$ is released and escapes, resulting in the replacement reaction between cations and K$^+$. Thus, KFeS$_2$ is an important raw material [8, 9] to produce new ternary metal thioferrate products, including RbFeS$_2$ [10, 11], AgFeS$_2$ [7, 12] and CuFeS$_2$ [12]. Such products are essential photovoltaic materials [13, 14] and a photothermal platform for medical therapy [15, 16], thereby increasing the demand for KFeS$_2$.

The development of a simple method for the synthesis of KFeS$_2$ is urgent for pilot-scale application to increase synthesis yields. In recent years, many methods have been exploited for the synthesis of KFeS$_2$, which can be categorised into two ways: solid-state synthesis and solvothermal method. For the solid phase reaction, iron as raw material was mixed with sulphur and K source (e.g. K$_2$CO$_3$ and K$_2$S$_2$) [10, 17] and then burned in a reducing atmosphere [18]. In the cauterisation process, the oxidation of iron and sulphur occurred, followed by solid conversion to form (FeS$_2$)$_n^-$ structure; K$^+$ was located at edge-sharing (FeS$_2$)$_n^-$ chains to form KFeS$_2$ needle-shaped crystals. For instance, Johnston et al. [17] burned the mixture of K$_2$CO$_3$, sulphur and iron in N$_2$ atmosphere at 900 °C for 4 h and found that needle-shaped KFeS$_2$ crystals were generated. Bronger et al. [18] prepared KFeS$_2$ samples by reacting K$_2$CO$_3$ with iron under a H$_2$S atmosphere at 1000 K for 6 h. After extraction with water and alcohol, well-developed violet needle KFeS$_2$ crystals were generated. Burning occurs in confined spaces and consumes extra energy to maintain high temperatures, resulting in the production of KFeS$_2$ at a low level and high cost. Compared with burning, the solvothermal method showed a clear advantage in lowering the reaction temperature. Insung et al. [9] mixed KNO$_3$, Fe(NO$_3$)$_3$·9H$_2$O and S powder in ethylenediamine solution; after heating at 190°C for 48 h, a black KFeS$_2$ powder was obtained. However, in the presence of deionised water, Fe$_2$O$_3$ was predominant in the product [9]. The extensive use and consumption of organic solvents limit their production on a large scale. To date, the pilot-scale synthesis of KFeS$_2$ has yet to be reported.

For pilot-scale synthesis, reducing the cost of synthesis is crucial. The synthesis costs are high at laboratory scale and mainly come from the use of chemically pure iron salts, organic dissolution and high temperature. Given that rapid hydrolysis and aggregation of Fe$^{3+}$ are needed to form Fe$^{3+}$-bearing flocs in strong alkaline solution, the surface Fe of flocs reacted with OH$^-$ to release Fe(OH)$_4^-$ into the solution [19]. The replacement reaction of Fe(OH)$_4^-$ by HS$^-$ spontaneously happened in the hydrothermal system. This behaviour demonstrated that Fe-rich sludge showed similar performance to Fe salt in strong alkaline solution, which proved the feasibility of using resource-based iron sludge as KFeS$_2$. After the reaction, the supernatant was rich in K$^+$ and HS$^-$ and could be recycled for the next synthesis reaction. The replacement of Fe salt with waste Fe-rich sludge and the recycling of used supernatant showed potential credibility for reduced synthesis costs.

In the conventional route, KFeS$_2$ was commonly used as a chemical intermediate in the synthesis of RbFeS$_2$ [10, 11], AgFeS$_2$ [7, 12] and CuFeS$_2$ [12]. Such conversion was generally performed in alkaline solution. In neutral or weakly alkaline solution, the decomposition of (FeS$_2$)$_n^-$ generated Fe/S-bearing
flocs with numerous hydroxyl groups [20]. Such behaviour of KFeS₂ decomposition was similar to the common flocculants PAC and PFS. However, there have not been reports of KFeS₂ applied in wastewater treatment.

Here, the pilot-scale conversion of waste Fe-rich sludge to KFeS₂ was successfully implemented at a low temperature and atmospheric pressure. The storage of prepared KFeS₂ was also optimised in the range of freeze-drying, vacuum-drying, air-drying and wet storage. The produced KFeS₂ showed superior efficiencies in the removal of Zn/Ni from real electroplating effluent.

2 Materials And Method

2.1 Laboratory-scale experiment for KFeS₂ whisker synthesis

At the laboratory-scale experiment, ferrihydrite was synthesised follow the method of Ding et al. [21]. In brief, 40 g of Fe(NO₃)₃·9H₂O was added to 500 mL of deionised water and then mingled with 330 mL of 1 M KOH with stirring at 120 rpm. After 1 h, a mixed solution was generated and placed for another 2 h. A brownish sediment was produced at the bottom of the solution, gathered and washed by deionised water for three times. The sediment (named as Ferr) was air-dried at 60 °C for subsequent use.

The laboratory-scale conversion of Ferr to KFeS₂ whisker was performed as follows. Firstly, 3 g of Ferr, 3.3078 g of K₂S and 30 mL of 6 M KOH solution were mixed in a beaker with volume of 50ml. Secondly, the beaker was sealed with parafilm, then magnetically stirred at 200 rpm at 50 °C. Thirdly, after 10 h, the beaker was cooled to room temperature and placed at a table for another 2 h. Fourthly, a black deposit was formed at the base of the beaker, gathered and freeze-dried at -80 °C for 24 h. The dried product was named E50-10, where E represents the experimental-scale synthesis, 50 is the heating temperature and 10 is the heating time.

The effect of heating temperature was investigated by changing the heating temperature from 50 °C to 80 °C follow the above-mentioned steps, then the corresponding product was named E80-10. A control experiment was also performed following the above steps, where the heating time was extended from 10 h to 24 h, and the products yielded were named E50-24 and E80-24.

2.2 Pilot-scale production of KFeS₂ whisker

Ferrihydrite-bearing sludge (named as sludge) was collected from the sludge warehouse of Guixi cold-rolling company (Changchun, China). The sludge contained 41.2% Fe, 50.5% water content and less than 10% carbon. A small portion of the sludge was freeze-dried at -80 °C for characterisation.

To produce KFeS₂ whisker, a pilot-scale vessel was made to synthesise KFeS₂ whisker at mass production (Fig. 1). In step 1, approximately 1 kg of sludge, 1.10 kg of K₂S, 3.36 kg of KOH and 10 L of tap water were added to a bucket with a volume of 15 L under stirring at 120 rpm for 1 h to generate a black suspension. In step 2, transferred the suspension sealed vessel, then heated at 80 °C for 24 h.
step 3, the solid sediment and suspension in the vessel were transferred into the suction filter. After filtration, the solid fraction and filter liquor were collected separately. In step 4, the solid fraction (named P80-24) was stored in a bucket, in which a small portion of solid was freeze-dried at -80 °C overnight.

The supernatant generated in step 3 was recycled in the next round as follows (Fig. 1). The total volume of supernatant was adjusted to 10 L with supplementary tap water, followed by adding 1 kg of sludge, 0.22 kg of K₂S and 0.33 kg of KOH under stirring at 120 rpm. After 1 h, a suspension was generated and then treated with the above-mentioned steps. The generated product was named P80-24-1 (1 represents the recycle number of supernatant), whilst the generated supernatant was collected again for further use. The recycle experiment of the supernatant was performed another four times at pilot scale, and the corresponding products were named P80-24-2, P80-24-3, P80-24-4 and P80-24-5.

The drying method of KFeS₂ was also optimised. Two typical drying methods, vacuum-drying at 60 °C and air-drying at 105 °C, were investigated using P80-24 as the targeted KFeS₂ product, in comparison with that with the freeze-drying method.

2.3 Application of KFeS₂ whisker in real electroplating wastewater treatment

Electroplating wastewater was treated with polymeric aluminium chloride and precipitant (e.g. diethyldithiocarbamate) in the wastewater plant of Jitong machinery company (Changchun, China). The effluent discharged from the wastewater plant was collected and used in this study to determine the performance of the synthesised KFeS₂ products. The effluent contained 7.8 mg/L Zn and 0.6 mg/L Ni was at pH 7.42 and then treated as follows. Approximately 0.2 g of P80-24 was mixed with 1000 mL of effluent in a 2000 mL beaker with stirring at 100 rpm for 2 h. Subsequently, the beaker was placed for 2 h to precipitate P80-24, whilst 1 mL of supernatant was sampled for characterisation. Control experiments were carried out by changing the P80-24 dosage from 0.2 g to 0.5, 1, 3, 5 and 10 g. Other products, including the undried P80-24, P80-10, P80-24-1 and P80-24-5, were also used to treat the effluent in accordance with the above-mentioned method and then compared with common reagents, such as Na₂S·9H₂O, polymeric ferric sulfuric, sodium diethyldithiocarbamate and lime.

The zeta potential and hydrodynamic radius of P80-24 were also investigated. Approximately 0.1 g of P80-24 was dispersed in 100 mL of effluent under constant stirring at 150 rpm to form a mixture solution. At a given interval, 5 mL of solution was sampled and then determined by a zeta potentiometer (Nano-ZS, Malvern, UK). The experiment of P80-24 in deionised water was also carried out in accordance with the above method.

3 Results And Discussion

3.1 laboratory-scale synthesis of KFeS₂ whisker

The synthesis of KFeS₂ whisker at low temperature was optimised at lab scale, as shown in Fig. 2. At 50 °C, the product was weakly crystallised and showed a small rod-sharp precursor (Fig. 2 (E50-10)), even
though the heating time was extended from 10 h to 24 h (Fig. 2 (E50-24)). By increasing the temperature from 50 °C to 80 °C, the product E80-10 appeared as sharp whisker particles with 0.2 mm diameter and 0.5–1 mm length, respectively, and indicated representative peaks of KFeS$_2$ (Fig. 2 (E80-10)). After the reaction for 24 h, the product E80-24 showed that the peaks of KFeS$_2$ became sharp (Fig. 2 (E80-24)), and its whisker grew radially to 1–4 mm. This finding demonstrated that 80 °C was an optimal temperature for sharp KFeS$_2$ synthesis.

3.2 Mass production of KFeS$_2$ whisker at pilot scale

Pilot-scale synthesis of KFeS$_2$ was performed at 80 °C for 24 h, and the results are shown in Fig. 3. The sludge was an irregular block (Fig. 3(a) sludge) that showed typical peaks of ferrihydrite and carbon (Fig. 3 (b) sludge). After the reaction, the product P80-24 was a well-formed whisker that showed sharp peaks of KFeS$_2$ (Fig. 3(b) (P80-24)), similar to E80-24 synthesised at lab scale (Fig. 2 (E80-24)). Although impure carbon was mixed with ferrihydrite in the sludge, the XRD peaks of carbon were not recorded after the reaction, revealing that it was covered by KFeS$_2$ whisker and not observed by an XRD diffractometer. The above findings suggested that mass production of KFeS$_2$ whisker was successfully achieved.

3.3 Upcycling of supernatant in KFeS$_2$ synthesis

At pilot scale, the supernatant was recycled as an alkaline solution for KFeS$_2$ synthesis in the next round, and the results are shown in Fig. 4. In the first round, the product P80-24-1 showed sharp peaks of KFeS$_2$ and well-formed whisker (Fig. 4), similar to that without supernatant recycling (Fig. 3 (P80-24)). After recycling for five times, typical KFeS$_2$ whisker was also observed for the product P80-24-5 (Fig. 4 (P80-24-5)), suggesting that the recycling route of supernatant was applicable for KFeS$_2$ synthesis. The supernatant was highly alkaline; its recycling not only reduced KOH consumption and employed sufficient HS$^-$ and S$_2^-$ for KFeS$_2$ synthesis but also avoided the generation of waste alkaline wastewater.

3.4 Optimisation of drying method

The prepared P80-24 was dried in three ways, namely, freeze-drying, air-drying and vacuum-drying. With the freeze-drying method, the product was in the form of KFeS$_2$ whisker (Fig. 3 (P80-24)). In comparison with freeze-drying, the product from vacuum-drying also exhibited well-formed sharp whisker and XRD pattern of KFeS$_2$, even though a small portion of broccoli-sharp aggregates was recorded (Fig. 5(a) vacuum-drying). Such aggregates were generated by the oxidation of structural S in KFeS$_2$ whisker. However, after treatment by air-drying at 105 °C, KFeS$_2$ peaks were also observed (Fig. 5 (air-drying)), but abundant broccoli-sharp aggregates were generated, demonstrating that the oxidation of S was accelerated in air-drying. These results demonstrated that freeze-drying and vacuum-drying were effective for KFeS$_2$ whisker dewatering. To further investigate the storage of KFeS$_2$ whisker, wet P80-24 without dewatering was stored in a sealed bucket for a week, dehydrated and freeze-dried again. The corresponding product was also in the form of a sharp whisker with clear KFeS$_2$ peaks (Fig. S1),
demonstrating that the wet storage of KFeS\(_2\) was a desirable route. The wet sample of P80-24 was also employed in the wastewater treatment as shown in section 3.5.

### 3.5 Application in raw electroplating wastewater treatment

KFeS\(_2\)-bearing products were employed in the treatment of real electroplating effluent, as shown in Fig. 6(a). The effluent had a pH of 7.42 and contained 7.8 mg/L Zn and 0.6 mg/L Ni; it was discharged from the electroplating wastewater plant after treatment with the addition of precipitant and coagulant. In the effluent, Zn/Ni was at high concentrations and should be further removed in accordance with the discharge standard of the electroplating industry [22]. By adding P80-24, Zn/Ni was apparently removed from 0.33 and 0.21 mg/L with 0.2 g, to 0.22 and less than 0.1 mg/L with 1 g and could not be detected with 10 g. This result indicated that P80-24 was effective in removing Zn/Ni. The optimal dosage of P80-24 was 1 g, where approximately 96.6% Zn and 84.4% Ni were removed, whilst the residual Zn/Ni met the discharge standard of electroplating wastewater [22].

P80-24 and the products with recycling supernatant showed similar removal efficiencies of Zn/Ni (Fig. 6(b)), suggesting that the supernatant was recyclable in the preparation of KFeS\(_2\). The removal of Zn/Ni by the products from vacuum-drying and air-drying was also investigated (Fig. 6(b)). The residual Zn/Ni levels were 0.152 and 0.076 mg/L with the product of vacuum-drying and steadily increased to 0.163 and 0.157 mg/L with that of air-drying, demonstrating that air-drying was not desirable in P80-24 drying. The removal performance of undried P80-24 was also investigated, where it had 55% water content; thus, its dosage was 2.22 g after calculation based on the optimal dosage of dried P80-24. By adding wet P80-24, the residual Zn/Ni levels were 0.157 and 0.051 mg/L, which were close to that with dried P80-24; these results revealed that wet P80-24 was efficient in Zn/Ni removal, and the freeze-drying process could be completely omitted. Other common reagents, e.g. Na\(_2\)S·9H\(_2\)O, lime, polymeric ferric sulfuric and sodium diethyldithiocarbamate, were also applied in the removal of Zn/Ni (Fig. 6(c)), but they did not show desirable removal efficiencies in comparison with P80-24. Thus, P80-24 is an applicable reagent in electroplating wastewater treatment.

After use, P80-24 showed that sharp peaks of KFeS\(_2\) disappeared, and only weak peaks of Fe-bearing compound appeared (Fig. 7(a)). Accordingly, a well-formed whisker was not observed, and only irregular blocks were generated (Fig. 7(b)), indicating the decomposition of KFeS\(_2\) in the effluent. P80-24 was also characterised by XPS before and after use as shown in Fig. 8. For the Fe 2p spectra, a typical peak was recorded at the binding energy of 708.4 eV before use, which belonged to structural Fe in (FeS\(_2\))\(_n\)^n- [23] but varied to the binding energy of 710.5 eV after use; this phenomenon was in agreement with the decomposition of KFeS\(_2\) and the formation of Fe/S-bearing compound [24]. For S 2p, four peaks at the binding energies of 160.3, 161.2, 163.2 and 167.4 eV were recorded before use, which were affiliated with structural S in Fe-S bond, S\(^2-\), element S and sulphate, respectively. However, two peaks disappeared after use due to the decomposition of KFeS\(_2\). A new peak at the binding energy of 162.6 eV appeared, along
with the peaks of elemental S and sulphate, which demonstrated the formation of the Fe-S-Zn/Ni bond in the decomposed product of KFeS$_2$ after use.

3.6 Formation and hydrolysis mechanism of KFeS$_2$

KFeS$_2$ whisker had a one-dimensional linear structure, in which an Fe atom was coordinated with four S atoms. It was stable in alkaline solution at pH > 13.6 and commonly formed in strong alkaline solution as follows. Firstly, when Fe$^{3+}$ was added in the alkaline solution, it was rapidly polymerised to form Fe-bearing precipitates in weakly crystallised form. The sludge acquired from the cold-rolling company showed a similar characterisation to the Fe-bearing precipitates; a small portion of carbon was from the dropped emulsion oil [25]. With the addition of KOH and the hydrolysis of K$_2$S, free OH$^-$ was abundantly generated in the solution and then eroded the surface Fe of sludge to generate and release Fe(OH)$_4$ into the solution. Accordingly, the Fe concentration increased in the supernatant. Fig. 9 shows that Fe was 0.045 mg/L at pH 7 and rapidly increased to 5.595 mg/L at pH 15.6, suggesting the dissolution of Fe-bearing precipitates and sludge in strong alkaline solution. Secondly, free SH$^-$ was generated at mass production from the hydrolysis of K$_2$S and then spontaneously replaced OH$^-$ of free Fe(OH)$_4$ to form Fe(OH)$_3$HS$. The replacement reaction continued, where Fe/S-bearing products, e.g. Fe(OH)$_3$HS$^-$(HS)$^-$, were generated. Thirdly, the conjunction reaction between two newly formed Fe/S-bearing products occurred to form (FeS$_2$)$_n$Fe(OH)$_3$HS$^2-$: Such products were sparingly soluble in alkaline solution and precipitated from the solution. Fig. 9 shows that Fe was residual at 0.184 mg/L in the supernatant after the reaction; this residual level was lower than that in pure KOH solution, demonstrating that Fe/S-bearing products were formed and spontaneously precipitated from the solution. The conjunction reaction continued, which accelerated the polymerisation of Fe/S-bearing products, with the generation of linear (FeS$_2$)$_n$ as the final product. Fourthly, in the (FeS$_2$)$_n$ structure, the negative charge was neutralised by free K$^+$, resulting in the formation of one-dimensional KFeS$_2$ whisker.

Impure carbon was not involved in KFeS$_2$ synthesis and did not accumulate in the supernatant. After the reaction, the supernatant was alkaline and rich in HS$^-$, which could serve as a cyclable resource to prepare KFeS$_2$ with supplementary K$_2$S and KOH. Thus, the dosage of K$_2$S and KOH was considerably reduced. Temperature was an important parameter in KFeS$_2$ synthesis. As the temperature rises from 50 °C to 80 °C, both the reaction between OH$^-$ and surface Fe of sludge and the release of Fe(OH)$_4$ to solution accelerated, which employed sufficient Fe(OH)$_4$ for the polymerisation and crystallisation of KFeS$_2$ whisker. Accordingly, high temperature was an important route to reduce the reaction time. For instance, linear KFeS$_2$ particles were generated after hydrothermal treatment at 190 °C for 18 h [9]. The drawback of high-temperature treatment in water was the formation of hematite from the rapid polymerisation of the surface Fe-OH group of sludge [9, 26, 27].

Before the application in wastewater treatment, the storage of KFeS$_2$ was a key step. Wet KFeS$_2$ particles remained stable for a week and showed a similar effect to freeze-dried KFeS$_2$ in the removal of heavy
metals from effluent. Besides wet storage, vacuum-drying could also function as an alternative method for KFeS$_2$ storage, where the dried product showed a similar effect in Zn/Ni removal to freeze-drying. In the air-drying process, the redox reaction between oxygen and structural S of KFeS$_2$ occurred. This phenomenon led to the consumption of KFeS$_2$ and accordingly decreased the Zn/Ni removal efficiency in comparison with the freeze-drying method.

In the effluent, heavy metals were complexed with organics to form stable organic-heavy metal ligands, so that they were refractory to be removed even though the precipitates (e.g. lime and polymeric ferric sulfuric) were added. When KFeS$_2$ was added in the electroplating effluent, it was spontaneously decomposed to generate Fe/S-bearing flocs with numerous Fe-SH and Fe-OH groups [28]. Such flocs were negatively charged (Fig. 11(a)) and had an average hydrodynamic radius of 600 nm (Fig. 11(b)). Subsequently, heavy metals, e.g. Zn and Ni, were coordinated onto the Fe-S/Fe-O groups, resulting in the removal of Zn/Ni from effluent. In comparison with the hydroxyl group, the new -SH group had strong affinity to complex with heavy metals, because S had a bigger atomic radius than O and was more electronegative to from the -S-Me group than O [29]. After heavy metal adsorption, the zeta potential of flocs apparently increased from -50 mV to -35 mV, where its radium considerably increased to 3500 nm, demonstrating the polymerisation of flocs in the adsorption of Zn/Ni. Floc polymerisation continued when stirring was slow and/or stopped, resulting in the generation of heavy metal-bearing sludge.

3.7 Environmental application

The conversion of cold-rolling sludge to KFeS$_2$ was performed at pilot scale, and the product KFeS$_2$ whisker showed superior efficiency in the treatment of real electroplating effluent contain Zn/Ni. The total cost of KFeS$_2$ synthesis was calculated as shown in Table 1. To reutilise 1 ton of sludge with the recycling of supernatant, approximately 0.22 tons of K$_2$S, 0.33 tons of KOH and 0.5 tons of water were consumed, along with the electric power of 18.6 kWh, which amounted to a total cost of US$ 294.9. However, about US$373.3 was spent in the disposal of 1 ton of sludge [30], and this amount can be deducted from the total cost of KFeS$_2$ synthesis. The KFeS$_2$-bearing product was marketable due to its performance in electroplating wastewater treatment, and it cost US$242.9/ton in accordance with the price of polymeric ferric sulphate. Therefore, the recycling of cold-rolling sludge as KFeS$_2$-bearing product was profitable.
Other Fe$^{3+}$-bearing sludge was also produced as solid waste in the steel-making, dye chemical, and mineral industries; it could function as an Fe$^{3+}$-bearing resource to be recycled as KFeS$_2$ whisker. Such recycling not only saved the disposal cost of sludge but also produced new Fe/S-bearing product, thereby exhibiting acceptable application in these industries.

### 4 Conclusion

The conversion of Fe$^{3+}$-bearing sludge to KFeS$_2$ whisker at low temperature was performed successfully. In the lab-scale experiment, ferrihydrite was employed as Fe resource; after treatment at 80 °C for 24 h, well-formed KFeS$_2$ whisker (diameter and length of 0.2 and 4 mm, respectively) was generated. However, KFeS$_2$ was not formed at 50 °C for 10 and/or 24 h. At the lab scale, the cold-rolling sludge was employed as Fe$^{3+}$-bearing resource and directly treated following the lab-scale steps, where KFeS$_2$ whisker was also produced at mass production. The generated supernatant was completely recycled and then supplied with 0.22 kg of K$_2$S, 0.33 kg of KOH and tap water for KFeS$_2$ synthesis in the next round. After supernatant cycling for five times, the product was also in the form of KFeS$_2$ whisker. Freeze-drying and vacuum-drying are desirable routes to dry KFeS$_2$, whilst air-drying was not acceptable due to the oxidation of KFeS$_2$.

The KFeS$_2$ whisker was effective for treating real electroplating effluent. The effluent contained 7.8 mg/L Zn and 0.6 mg/L Ni. After treatment with the addition of 1 g KFeS$_2$ whisker, the residual levels of Zn/Ni
were 0.33 and 0.21 mg/L, which met the discharge standard of the electroplating industry. The wet KFeS$_2$ and the product with supernatant recycling showed similar removal efficiencies of Zn/Ni to KFeS$_2$ whisker with freeze-drying, which exhibited a simple and convenient method for KFeS$_2$ product storage. The Zn/Ni removal efficiencies with KFeS$_2$ whisker were also higher than those with Na$_2$S·9H$_2$O, lime, polymeric ferric sulfuric and sodium diethyldithiocarbamate. Although portions of chemical reagents were consumed in the reaction process, the pilot-scale experiment proved that it was possible to recycle sludge as KFeS$_2$ whisker at mass production. The wet KFeS$_2$ product was marketable and had considerable application in electroplating effluent treatment.

**Declarations**

**Availability of data and materials**

All data generated or analyzed during this study are available from the corresponding author on reasonable request.

**Competing interests**

The authors declare they have no competing interests.

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**Authors' contributions**

Dongxu Liang: Writing - Original Draft. Yu Chen: Writing - Review & Editing. Suiyi Zhu: Conceptualization, Resources, Funding acquisition, Project administration. Yidi Gao: Data Curation, Formal analysis. Tong Sun: Investigation, Validation. Kyonghun Ri: Visualization, Validation. Xinfeng Xie: Conceptualization, Supervision. All authors read and approved the final manuscript.

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