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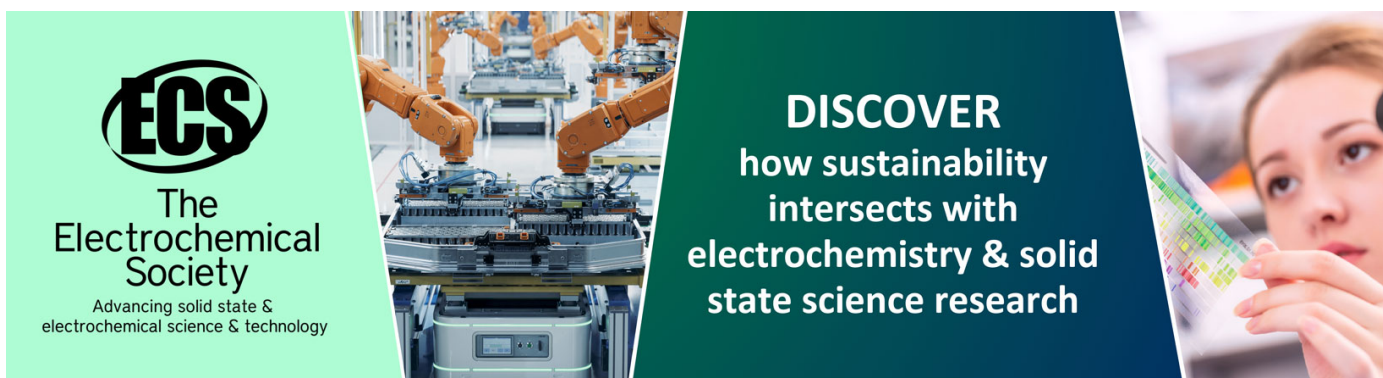
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Development of advanced pyrite passivation strategies towards sustainable management of acid mine drainage

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Abstract. Acid mine drainage (AMD) is one of the most serious environmental problems encountered in mining areas worldwide. When released into the environment without treatment, AMD pollutes the surrounding water bodies and soils with hazardous and toxic elements like arsenic (As), selenium (Se) and heavy metals such as lead (Pb), cadmium (Cd), copper (Cu) and zinc (Zn) that rapidly destroy affected ecosystems. The most commonly used method to treat AMD is chemical neutralization, a technique whereby basic materials like limestone or lime are mixed with AMD to raise its pH and remove most of the contaminants via precipitation. Although effective, this approach requires the continuous supply of chemicals, energy, and manpower, which makes it unsustainable because AMD generation has been documented to continue for a very long time (up to several centuries to millennia). One promising alternative to chemical neutralization is (micro) encapsulation, a technique that directly treats pyrite, the main mineral responsible for AMD formation, and renders it unreactive by encapsulating the mineral with protective coatings. In this study, we introduced two advanced pyrite passivation techniques to limit AMD formation called “carrier-microencapsulation” (CME) and “galvanic microencapsulation” (GME). CME uses a redox-reactive organic carrier to deliver the coating material on the surface of pyrite. Because the carrier only decomposes oxidatively, the primary strength of this technique is its high selectivity for pyrite even in complex systems like mine tailings and pyrite-rich waste rocks. Meanwhile, GME is based on galvanic interactions between pyrite and metals with lower rest potentials so this technique could be applied directly in a ball mill during ore processing or coal cleaning.

1. Introduction

Acid mine drainage (AMD), also called acid rock drainage (ARD), is one of the oldest and most serious environmental problems encountered in many countries around the world. AMD/ARD refers to the very acidic and heavy metal loaded leachate produced in abandoned/closed mine sites [1,2], mining tailings [3] and waste rocks from underground space development [4-7]. Old mining countries



like the US, Japan, Canada, China and Australia, for example, have more than 550 000, 5000, 10 000, 5000 and 52 000 closed/abandoned mines, respectively, a lot of which has already been generating AMD/ARD [8]. If released to the environment without appropriate treatment, AMD/ARD rapidly pollutes river systems, soils and groundwater in affected areas, leading to the destruction of the surrounding ecosystem. Affected people are also not spared, developing many diseases of the cardiovascular organs (heavy metals), kidneys (cadmium and arsenic), nervous system (lead), bladder (arsenic), skin (arsenic) and bones (mercury) [9,10].

Although AMD/ARD is one of the most extensively studied environmental problems in the last few decades, scientifically sound, economically viable and sustainable strategies for its mitigation remains elusive. To date, the most popular and common approach used in AMD/ARD management is chemical neutralization using limestone, lime or other basic substances [8]. It is effective, but only treats the “symptom” of the problem (AMD/ARD) and not the sources (e.g., pyrite and arsenopyrite). Thus, this approach requires the continuous treatment of acidic leachate and disposal of hazardous neutralization sludge until all sulfide minerals in the closed mine or tailings are oxidized. Unfortunately, the oxidation of pyrite, the most abundant sulfide mineral in nature and the main source of AMD/ARD, is a relatively slow process and could continue for several decades or even centuries. For example, a recent study of the authors estimated that AMD generation in the relatively small tailings dam of a closed gold-silver-copper-cobalt-zinc mine in Hokkaido, Japan may continue for at least 1000 years [11]. This means that managing AMD/ARD via chemical neutralization for such a long time is both costly and unsustainable.

The less popular and rarely studied approach is to render the sources of AMD (i.e., pyrite/arsenopyrite) un-reactive via chemical and/or biological treatments. Batch-reactor type experiments using substances like ferric phosphate [2], phospho-silicates [12], phospholipids [13] and iron-8 hydroxy-quinoline [14] to coat pyrite have shown that this passive-type treatment termed loosely as “encapsulation” could effectively suppress pyrite oxidation. Unfortunately, these previous “encapsulation” techniques suffered from two critical flaws: (1) the chemicals/reagents used to coat pyrite were very expensive and impractical for large-scale applications, and (2) these chemicals do not specifically target pyrite in the wastes.

To address these issues, the authors developed two techniques that took advantage of the unique way sulfide minerals like pyrite and arsenopyrite dissolve when in contact with oxygenated water. In contrast to oxide/silicate minerals that dissociate mainly via proton-promoted dissolution, pyrite and arsenopyrite dissolve via an electrochemical mechanism whereby distinct anodic and cathodic reactions occur on mineral surfaces via the movement of electrons through their crystal lattice [8,15,16]. The first technique is called “carrier-microencapsulation” (CME), an approach that utilizes redox-sensitive metal(loid)-organic complexes to deliver the coating material specifically on the surface of sulfide minerals (Figure 1).

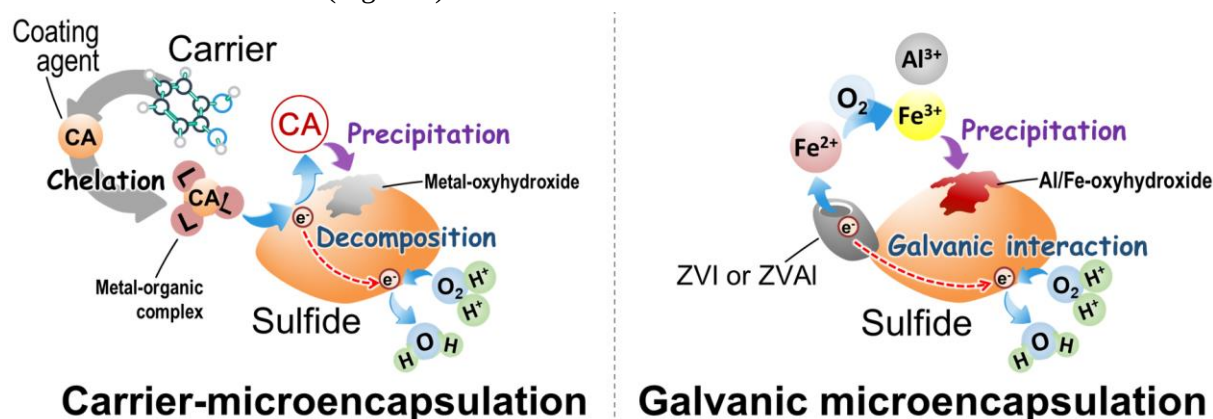


Figure 1. Schematic diagrams of “carrier-microencapsulation” and “galvanic microencapsulation”.

Meanwhile, the second technique is called “galvanic microencapsulation” (GME), which selectively targets sulphide minerals in a complex system via galvanic interactions. Galvanic interactions occur when two conductive or semi-conductive materials having different rest potentials come in close contact with each other. Because of this phenomenon, the material having a lower rest potential becomes the anode and is dissolved while the other material with higher rest potential becomes the cathode and is galvanically protected (Figure 1). In this study, these two novel concepts to passivate sulphide minerals and limit the formation of AMD/ARD are discussed.

2. Carrier-microencapsulation

The concept of CME was first introduced by Satur *et al.* [17] using titanium ion (Ti^{4+}) as coating material and catechol (1,2-dihydroxybenzene, $\text{C}_6\text{H}_4(\text{OH})_2$) as the redox-sensitive carrier. These authors found that catechol could extract Ti^{4+} from anatase and rutile, and their leaching experiments showed that mixing anatase, catechol and pyrite suppressed the generation of acidity and release of dissolved sulfur (S). Unfortunately, these three components were mixed so it was difficult for these authors to identify whether the observed suppressive effects were due to catechol, TiO_2 or Ti-catecholate complex. The extractions of Ti^{4+} from anatase and rutile using catechol were also very low at only around 0.03 and 0.015%, respectively. Furthermore, Satur and coworkers [17] did not evaluate the formation and electrochemical properties of Ti-catecholate complex in their experiments. Park *et al.* [18] recently revisited the Ti-based CME technique, evaluated the redox properties of Ti-catecholate complex, devised a method to synthesize the complex at higher concentrations, and applied CME to prevent the release of toxic arsenic (As) from arsenopyrite. These authors found that Ti-catecholate complex can be easily synthesized by mixing catechol and Ti^{4+} at $\text{pH} < 2$ and then rapidly neutralizing this mixture to $\text{pH} 10$. Using UV-Vis spectroscopy, these authors confirmed that the structure of their synthesized Ti-catecholate complex had the “tris-catecholate” configuration in which three catechol molecules are coordinated with Ti^{4+} (Figure 2a). Using this Ti-catecholate complex, they treated arsenopyrite and suppressed the release of As by over 70% (Figure 2b). These authors also noted that the coating formed on arsenopyrite was a mixture of Ti-O and Ti-C-O phases and proposed a more detailed mechanism of Ti-based CME that involves the following steps: (1) “intermediate” coating formation via the partial oxidation of Ti-catecholate complex adsorbed to arsenopyrite, (2) gradual chemical decomposition of “intermediate” coating and the release of “free” Ti^{4+} , and (3) Ti^{4+} precipitation and coating formation.

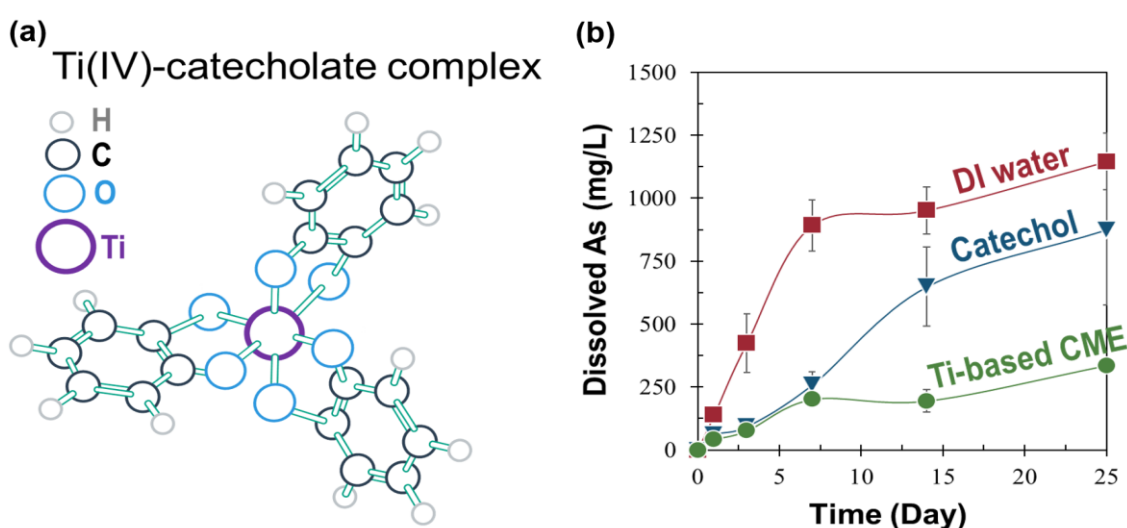


Figure 2. (a) Molecular structure of Ti-catecholate complex, and (b) suppression of arsenic (As) release from arsenopyrite by Ti-based CME [18].

Jha *et al.* [19] expanded the work of Satur *et al.* [17] who used silicon (Si) rather than Ti because the former is more abundant in nature than the latter. These authors also reported that aside from suppressing pyrite oxidation, Si-catecholate complex-treated pyrite became more hydrophilic that aided in its more effective separation from coal during flotation. Yuniati *et al.* [20] also reported the suppression of pyrite oxidation by Si-catecholate complex synthesized using organic-rich waste liquor from the hydrothermal treatment of low-grade coal. These authors also evaluated the stability of coating formed on pyrite and found that the coating was effective even in the presence of *acidithiobacillus ferrooxidans* [20].

Although Ti- and Si-catecholate complexes effectively suppressed pyrite oxidation via CME, the use of these two complexes have drawbacks especially for large-scale applications: (1) Ti-catecholate complex was very stable and at least 14 days of treatment is needed for an effective coating to form, and (2) Si-catecholate complex is difficult to synthesize because this process requires very high concentrations of catechol. To address these issues, Park *et al.* [21] and Li *et al.* [22] proposed the use of aluminum ion (Al^{3+}) and ferric ion (Fe^{3+}) as coating materials, respectively. Park *et al.* [21] reported that 3 days of CME treatment using Al-catecholate complexes was enough to suppress the oxidation of pyrite and arsenopyrite. Depending on the pH, Al^{3+} forms three complexes with catechol – mono ($[\text{Al}(\text{cat})]^+$), bis ($[\text{Al}(\text{cat})_2]^+$) and tris ($[\text{Al}(\text{cat})_3]^+$) [23], and their decomposition occurred sequentially (Figure 3a).

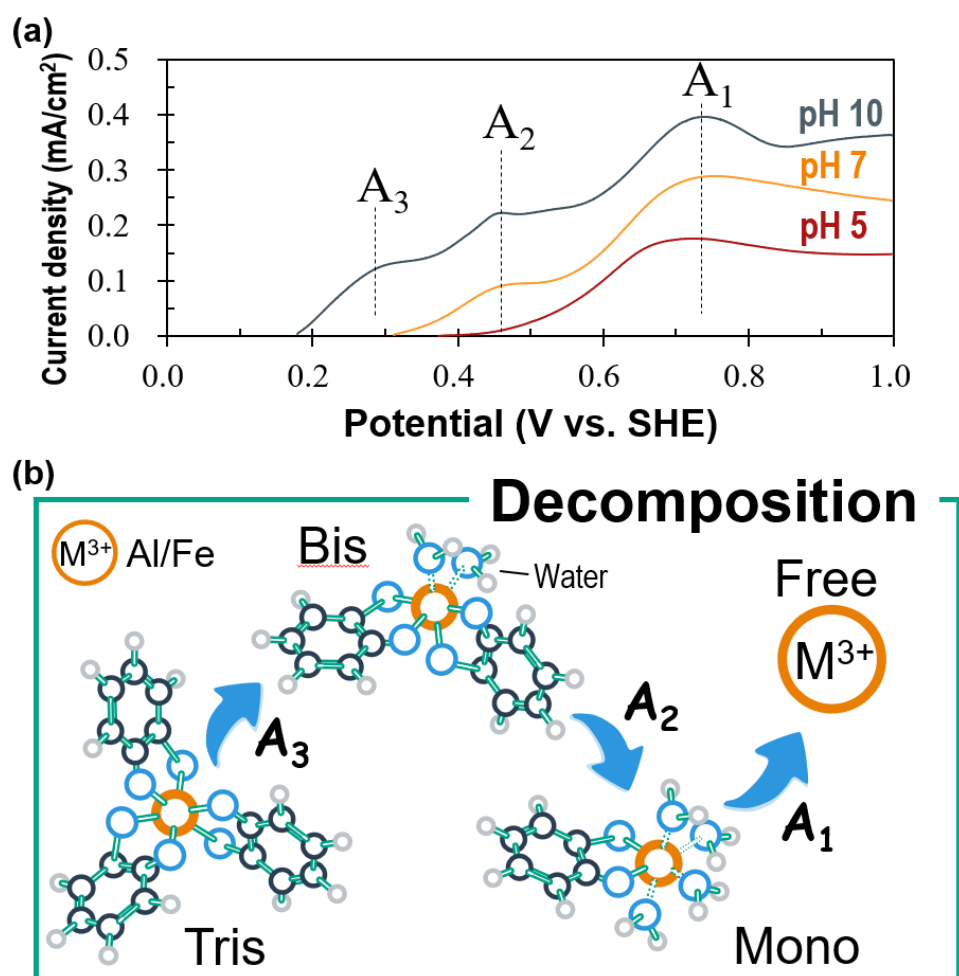


Figure 3. (a) Linear sweep voltammogram of Al-catecholate complexes at pH 5, 7 and 10 [21], and (b) a schematic diagram of the sequential oxidative decomposition of Al-catecholate complexes.

These authors found that among these three complexes, mono-catecholate was the most effective (Figure 4). They explained that the mono-catecholate complex of Al^{3+} was better because it only needed one oxidative decomposition step to release Al^{3+} while bis-catecholate and tris-catecholate complexes required two and three steps, respectively (Figure 3b). Using the mono-catecholate complex of Al^{3+} , Park *et al.* [21] suppressed not only the oxidation of pyrite but also the release of As from arsenopyrite.

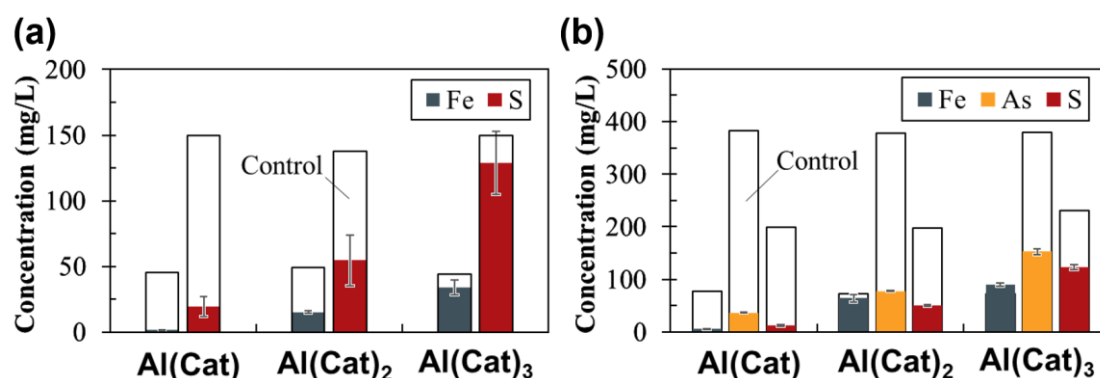


Figure 4. (a) Concentrations of dissolved Fe and S after pyrite treatment for 3 days in Al-catecholate complexes [21], and (b) concentrations of dissolved Fe, As and S after arsenopyrite treatment for 3 days in Al-catecholate complexes [21].

Li *et al.* [22] also reported that Fe^{3+} -catecholate complexes decomposed sequentially similar to those of Al-catecholate complexes. Moreover, these authors found that Fe^{3+} -catecholate complexes suppressed the oxidation of pyrite via two mechanisms (Figure 5): (1) electron donating effects of Fe^{3+} -catecholate complexes, and (2) coating formation.

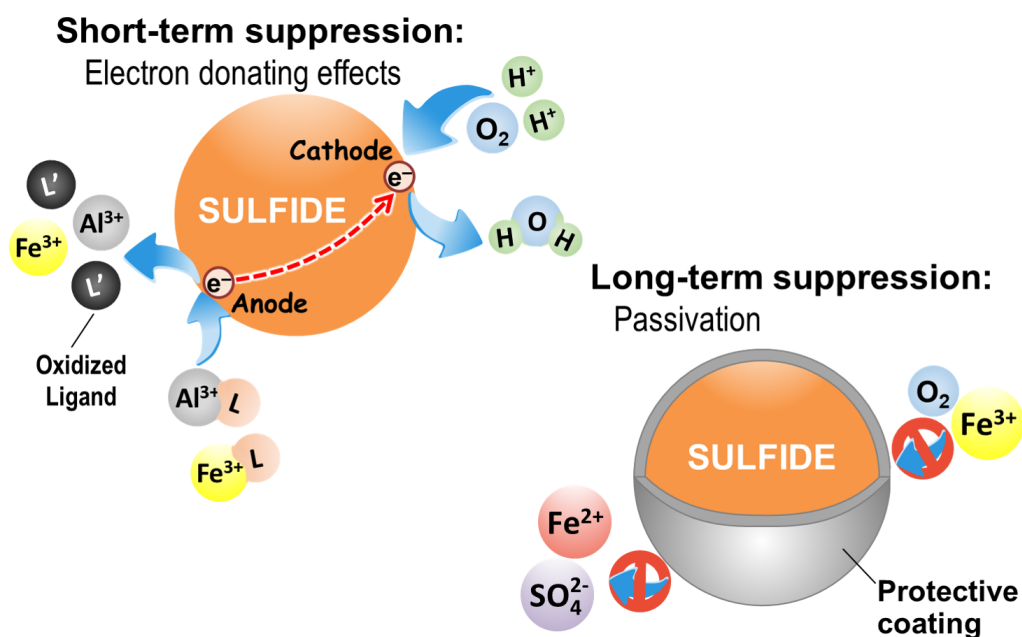


Figure 5. Schematic diagrams of the suppression mechanisms of Al- and Fe-catecholate complexes.

3. Galvanic microencapsulation

Galvanic interaction is a well-known phenomenon in corrosion science and the mineral processing of sulfide ores. For example, Huang and Grano [24] showed that galvanic interactions between pyrite and mild steel media during ball milling strongly affected the surface properties of pyrite and its floatability. This phenomenon is also important in environmental science because a recent study of Chopard *et al.* [25] reported that the release of toxic elements and heavy metals from sulfide-rich wastes was dramatically enhanced due to galvanic effects.

Using the concept of galvanic interactions, Seng *et al.* [26] proposed the use of zero-valent iron (ZVI) and zero-valent aluminum (ZVAI) to galvanically protect pyrite and coat it with Fe- or Al-oxyhydroxide coatings. These authors found that among the two metals, ZVI was better in suppressing pyrite oxidation because the formation of a passivating oxide film on it was more sluggish than that of ZVAI. They also reported that although both metals limited the oxidation of pyrite, the effect was only temporary because coating formation on pyrite was negligible. This is because although galvanic interactions were stronger at $\text{pH} < 5$, Fe- and Al-oxyhydroxides also become less stable under these conditions. To improve their technique, Seng *et al.* [26] combined galvanic interaction and phosphate, which dramatically improved the suppression of pyrite oxidation because of iron phosphate coating formation on the mineral (Figure 6).

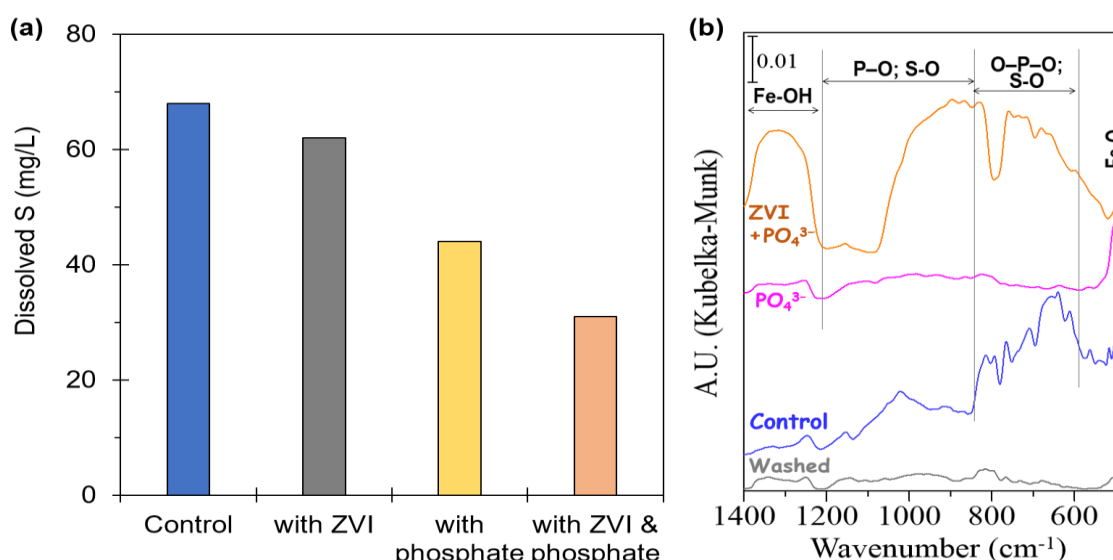


Figure 6. (a) Concentration of dissolved S after pyrite treatment for 7 days in DI water (control), ZVI suspension, phosphate solution and ZVI + phosphate mixture, and (b) diffuse reflectance infrared Fourier transform (DRIFT) spectra of pyrite after 7 days in various solutions/suspensions.

4. Conclusions

This study introduced two advanced passivation techniques to coat sulfide minerals like pyrite and arsenopyrite, suppress their dissolutions and limit the formation of AMD/ARD. “Carrier-microencapsulation” (CME) uses redox-sensitive metal-organic complexes to deliver coating materials on the surface of pyrite and arsenopyrite and target them even in complex systems like tailings and waste rocks containing silicate and alumino-silicate minerals. Meanwhile, “galvanic microencapsulation” (GME) takes advantage of galvanic interactions between materials with different rest potentials to suppress the oxidation of sulfide minerals. Although galvanic interaction alone could only suppress pyrite oxidation temporarily, the addition of phosphate to enhanced coating formation dramatically improved the results. Because steel is commonly used as grinding media in mineral processing, it may be possible to use GME directly in ball mills.

Acknowledgments

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