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Biodegradable acids for pyrite depression and green flotation separation – an overview

Ali Asimi Neisiani^a and Saeed Chehreh Chelgani^b

^aDepartment of Mining and Metallurgical Engineering, Yazd University, Yazd, Iran; ^bMinerals and Metallurgical Engineering, Swedish School of Mines, Department of Civil, Environmental and Natural Resources Engineering, Luleå University of Technology, Luleå, Sweden

ABSTRACT

Exponential increasing demands for base metals have made meaningful processing of their quite low-grade (>1%) resources. Froth flotation is the most important physicochemical pretreatment technique for processing low-grade sulfide ores. In other words, flotation separation can effectively upgrade finely liberated base metal sulfides based on their surface properties. Various sulfide surface characters can be modified by flotation surfactants (collectors, activators, depressants, pH regulators, frothers, etc.). However, these reagents are mostly toxic. Therefore, using biodegradable flotation reagents would be essential for a green transition of ore treatment plants, while flotation circuits deal with massive volumes of water and materials. Pyrite, the most abundant sulfide mineral, is frequently associated with valuable minerals as a troublesome gangue. It causes severe technical and environmental difficulties. Thus, pyrite should be removed early in the beneficiation process to minimize its problematic issues. Recently, conventional inorganic pyrite depressants (such as cyanide, lime, and sulfur-oxy compounds) have been successfully assisted or even replaced with eco-friendly and green reagents (including polysaccharide-based substances and biodegradable acids). Yet, no comprehensive review is specified on the biodegradable acid depression reagents (such as tannic, lactic, humic acids, etc.) for pyrite removal through flotation separation. This study has comprehensively reviewed the previously conducted investigations in this area and provides suggestions for future assessments and developments. This robust review has systematically explored depression performance, various adsorption mechanisms, and aspects of these reagents on pyrite surfaces. Furthermore, factors affecting their efficiency were analyzed, and gaps within each area were highlighted.

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Introduction

Froth flotation as a physicochemical pretreatment technique is the most common and effective beneficiation method to enrich low-grade metal minerals. It assists in selectively separating valuable minerals from their non-valuable associated minerals (gangue phases) based on their surface properties [1–3]. In flotation beneficiation, by using different surfactants (reagents: collectors, activators, depressants, pH regulators, frothers, etc.), the surface characteristics of various minerals would be modified (making hydrophobic or hydrophilic), and they can selectively be separated based on their floatability [4,5,6]. Since the grade of valuable metals from their primary resources has markedly decreased, and their demands have significantly increased, flotation separation deals with a tremendous

amount of water and materials through the upgrading process. Thus, flotation reagents' toxicity could be considered a substantial environmental challenge for processing plants (especially for pyrite (Figure 1) rejection) [7].

Pyrite is the most abundant iron-bearing sulfide mineral. It is frequently observed in: massive hydrothermal deposits, veins and replacements, igneous rocks, and sedimentary beds. Pyrite can be occasionally hosted in precious elements such as gold; thus, it sometimes recovers and concentrates [8,9,10–13]. Its various accompanying types of ore deposits (including: nonferrous base metals, precious metals, coal, and rare earth elements) impose technical difficulties and environmental problems during beneficiation processes [14–18,19,20]. The reaction of pyrite with atmospheric

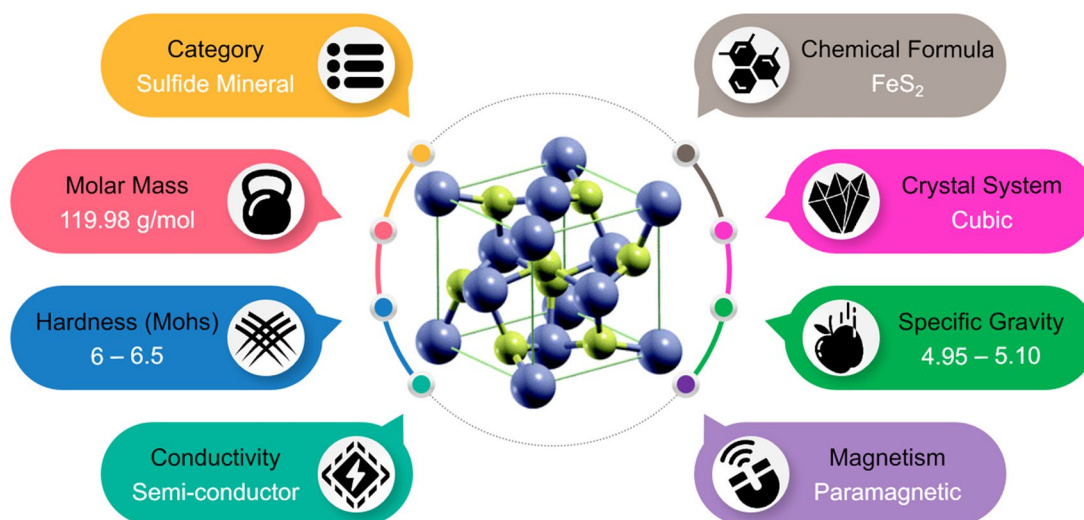
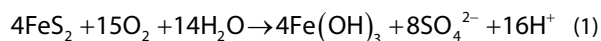


Figure 1. Physical and chemical characteristics of pyrite mineral.

oxygen and moisture leads to acid mine drainage (AMD) (Equation (1)). AMD can acidify the adjacent aqueous zones and streams. Also, it can increase the concentration of hazardous heavy metals and metalloids [21–23].



Moreover, the presence of pyrite in the base metal concentrates leads to a reduction in grade and quality as well as a rise in iron and sulfur content, leading to more smelting expenses [24,25]. Pyrite can potentially contain heavy metals, such as arsenic, and cause harmful dust and fumes through thermal processes, such as smelting [26–29]. Coal deposits may also have a high pyrite content, which is essential to remove. Otherwise, burning coal produces SO_2 and releases it into the atmosphere [28–32], and results in an acid rain disaster [30,31]. Furthermore, in beneficiating base metals' concentration by hydrometallurgical methods, pyrite can contaminate the solution with iron ions as a troublesome impurity [32]. Thus, removing the pyrite content is a crucial pretreatment step in the beneficiation process of many ore deposits [33].

Flotation separation has been widely used to selectively remove pyrite early in the beneficiation process (before hydro- or pyrometallurgical operations) [34,35]. Due to the natural hydrophobicity of pyrite particles, depressants play a significant role in deactivating the pyrite surface and separating it from other valuable hydrophobic minerals [36,37]. Conventional depression reagents used to deactivate pyrite surface are cyanide, lime, and sulfur-oxy species [34,35,38–44]. Even though these inorganic depressants have been highly

influential, their usage can lead to high costs and environmental concerns [45,46]. For example, sodium cyanide (as the most toxic chemical among mentioned reagents for pyrite depression) can be quite harmful to humans and the environment. The precipitated cyanide in the tailing dams could be a source of underground water pollution and an immense hazard to the environment in the case of dam damage or collapse [47]. Therefore, nonbiodegradable, toxic flotation reagents may accumulate in plant and animal species through the bioaccumulation process. Therefore, biodegradable reagents for pyrite depression have gained substantial attention. Since froth flotation is the most important mineral enrichment method and reagents play a remarkable role in making the process selective, flotation reagent properties would have an essential impact on nature. Reducing consumption or replacing environmentally harmful substances with eco-friendly ones would be a significant practical step in moving toward green transition and sustainable development [48].

The inhibitory effect of polysaccharide-based depressants (such as starch, dextrin, chitosan, guar gum, locust bean gum, etc.) as biodegradable reagents on pyrite surface has been partially investigated [49–51]. Polysaccharide-based depressants have shown satisfactory performance for the depression of pyrite in various flotation systems. However, due to the continuous decrease in the grade and quality of various ore deposits and the increased environmental restrictions, it would be beneficial to introduce other eco-friendly depressants to replace or assist inorganic depression. Thus, recently several investigations have been conducted on the depression behavior of various

biodegradable acid-based substances (such as lactic acid, tannic acid, etc.) on pyrite floatability. However, there is still a need-to-be-filled gap in the existence of a robust review article to comprehensively explore various adsorption aspects and facilitate an understanding of pyrite surface interactions with these green depressants. As a unique approach, the present review has effectively scrutinized the performance of biodegradable acids used as green depressants to separate pyrite from valuable minerals through the flotation technique. Numerous parameters that need to be considered for their applications have been discussed and assessed. Adsorption mechanisms and gaps within each area were analyzed and highlighted.

Main challenges for pyrite depression

Natural floatability-high collector adsorption affinity

Pyrite is a naturally hydrophobic mineral that can be floated without adding any collecting agent (collectors which make surface hydrophobic) under specific conditions. Additionally, its high affinity to xanthates (the most common collectors for sulfide minerals) causes it to be recovered in the froth zone, reducing the quality and grade of the valuable minerals (chalcopyrite “CuFeS₂,” sphalerite “ZnS,” galena “PbS,” etc.) [52,36]. It has been reported that the process of xanthate adsorption onto the pyrite surface occurs through four main steps, including (1) oxidation of pyrite surface, (2) adsorption of xanthate ions onto pyrite surface, which leads to ferric xanthates formation, (3) oxidation of xanthate ions to di-xanthogen, (4) xanthate collector adsorption through interaction between ferric xanthates (on pyrite) and di-xanthogen [53].

Electrochemical-potential

As many other metallic sulfides, pyrite is a semiconductor mineral. This leads to occurring various electrochemical reactions during flotation separation when pyrite is in the system [54–58]. The rate of pyrite oxidation is the function of several parameters, including: pH, electrochemical potential, the type and dosage of oxidant, particle size, temperature, and stirring speed [59–64]. It has been reported that the electrochemical potential of the slurry/particle interface is the most significant parameter that affects flotation systems containing pyrite [65,66]. The electrochemical-potential controls for the formation of surface species are enhancing pyrite floatability (such as polysulfides, elemental sulfur, and xanthate), and also surface species

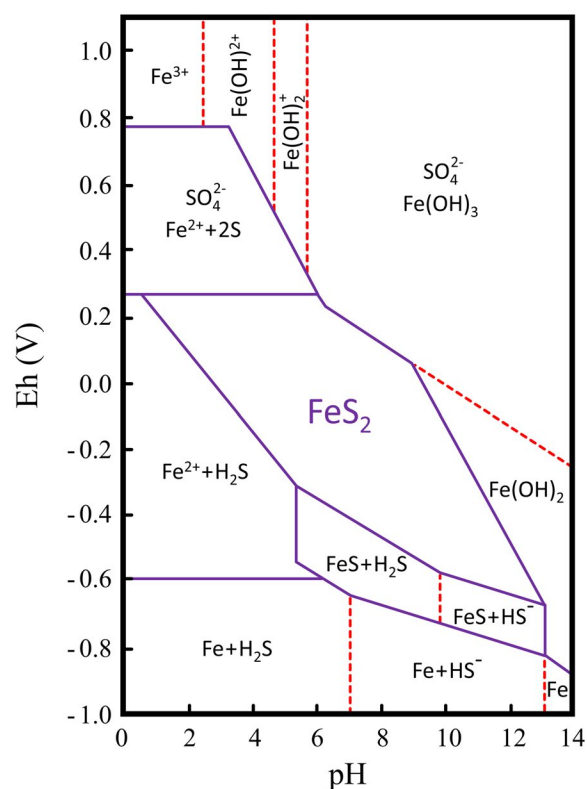


Figure 2. Eh-pH diagram for FeS₂-H₂O system at 25°C and 10⁻⁵ M dissolved species [63].

are depressing the pyrite surface (such as ferric oxide/hydroxide and sulfate) [36]. These species are the products of the electrochemical oxidation of pyrite in aqueous solutions (Figure 2). It is also worth mentioning that various pyrite samples are different in surface morphology, Fe/S ratio, and crystal structure, resulting in a different electrochemical reactivity [8,67].

Activation of pyrite

Pyrite without activation could be easily depressed at high pH levels. In general, the floatability of pyrite is highly pH-dependent, and it would be depressed by increasing pH (pH > 9) [68]. However, the selective separation of pyrite in flotation systems is challenging because of its unintended activation. The activation can occur when metallic cations, more specifically Cu²⁺ and Pb²⁺, are in the flotation solution (come from associated copper and lead sulfides) [69–72,36,37,73,74]. Cu²⁺ ions can electrochemically activate the pyrite surface. This process comprises one step in which copper cations quickly adsorb on the reactive sulfur sites of the pyrite surface. During the copper adsorption, cupric ion (Cu²⁺) reduces to cuprous (Cu⁺). In this reaction, Cu(I)-sulfide compounds and elemental sulfur are formed (Figure 3) [75,38,76,77]. Unlike copper activation, in the process of

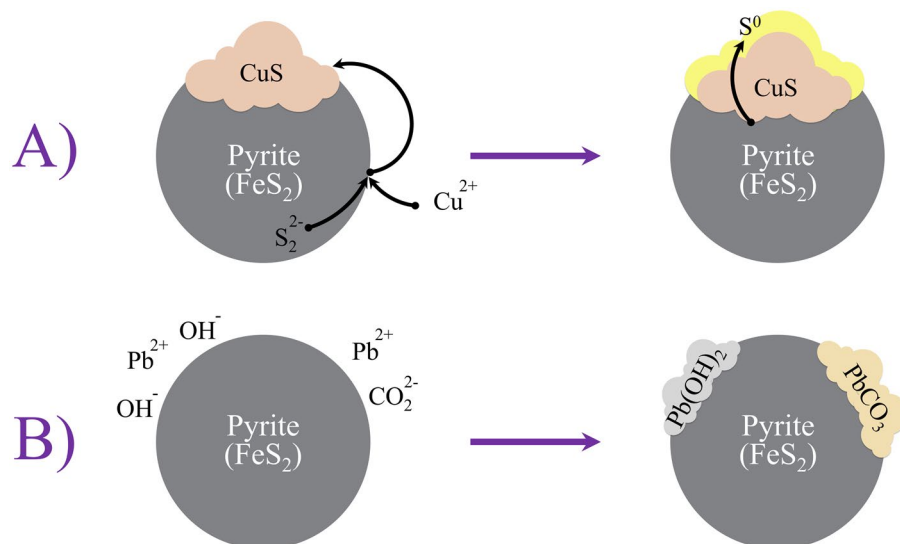


Figure 3. Pyrite activation in the presence of (A) Cu²⁺ and (B) Pb²⁺ cations [75].

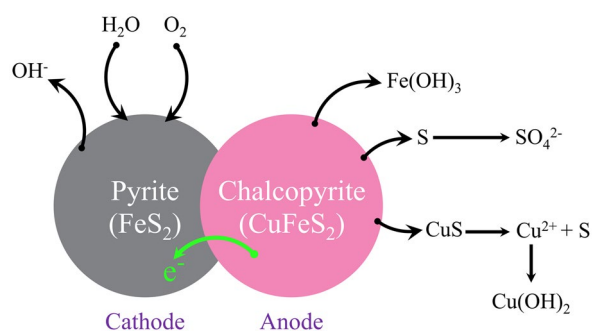


Figure 4. Galvanization process between pyrite (cathode) and chalcopyrite (anode) [72].

pyrite activation by lead cations, an electrochemical reaction does not occur. Some Pb-containing compounds (hydroxides or carbonates) precipitate on the pyrite surface during the lead activation process. The precipitation of these species is highly pH-dependent [78]. Since these substances precipitated on the pyrite surface during the undesirable activation process have a strong affinity for xanthate ions, this phenomenon can disturb the pyrite depression system [37,69,79].

Galvanization

The simultaneous presence of species with different rest potentials in the flotation system can cause galvanization. This electrochemical interaction may also occur between minerals and the grinding media [72,80–82]. One of the most traditional flotation processes is the separation of pyrite (which has to be depressed) from chalcopyrite. In this system, pyrite that possesses more rest potential than chalcopyrite

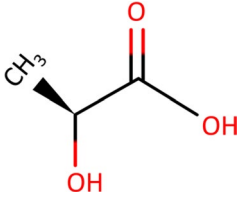
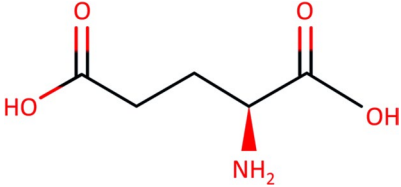
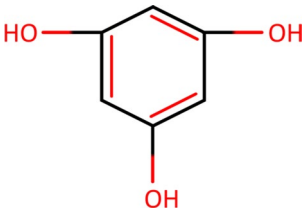
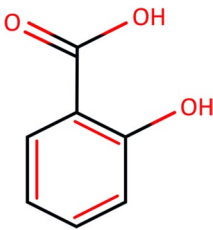
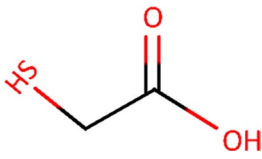
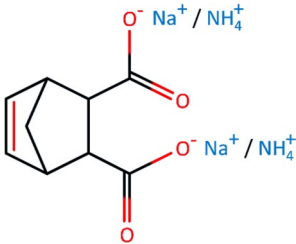
plays a cathodic role in electrochemical reaction (Figure 4). Therefore, pyrite is galvanically protected, and chalcopyrite (anode) is oxidized [72,83,84]. It has been proven that when these minerals are galvanically coupled, the floatability of pyrite could be promoted, but chalcopyrite recovery would be reduced [72].

Biodegradable acids

Biodegradable acids (BAs) (Table 1) are comparatively weak acidic compounds that do not completely dissociate in water [85,86]. BAs are widely distributed in nature as they can generate from: animals, plants, fungi, yeasts, and bacteria. They contain one or more carboxylic acid groups, which could be covalently linked into amides, esters, and peptides [87]. The strength of BAs depends on the functionalities, such as carboxyl (–COOH), sulfonic (–SO₃⁻), hydroxyl (–OH), etc. [85,88]. With the focus on green processes and the restrictions imposed on mining activities, these naturally occurring and eco-friendly chemicals have received more attention than before. Several investigations have been conducted to use them as pyrite depressants during flotation (Table 2).

These studies indicated that pyrite's isoelectric point (iep) could be varied in a wide pH range. This variation depends on the oxidation rate of the pyrite surface and has been reported from pH 2 (non-oxidized pyrite) to 7 (fully oxidized pyrite) [99]. Reagents impact on the pyrite's electrical surface charge (Table 3). It was found that LA and SA (Table 2) can adsorb on the pyrite surface through simultaneous physical and chemical mechanisms and increase the iep on the pyrite surface [89,93]. However,

Table 1. Biodegradable acids were used as a flotation reagent for depressing pyrite.

Organic depressant	Chemical formula	Functional group	Molecular structure
Lactic acid	$C_3H_6O_3$	$-COOH-OH$	
Polyglutamic acid	$C_5H_7NO_4$	$-COOH-NH_2$	
Pyrogalllic acid	$C_6H_6O_3$	Benzene ring-OH	
Salicylic acid	$C_7H_6O_3$	Benzene ring-COOH-OH	
Thioglycolic acid	$C_2H_4O_2S$	$-COOH-SH$	
Humic acid's salts	$C_9H_8Na_2O_4$ $C_9H_{16}N_2O_4$	Benzene ring-COOH	

other organic depressants (PGA, PA, NaHu, PCA, and TA) significantly decrease pyrite iep [90–92,94,97,98]. Zeta potential measurements revealed that the presence of Ca^{2+} ions (originated from lime dissolution) decreases the negative charge on the pyrite surface [91].

Lactic acid

As a monocarboxylic organic acid ($C_3H_6O_3$), lactic acid (LA) is a widely used chemical substance with various

applications (such as acidity regulator, food preservative, fragrance, anti-microbial agent, etc.). Since LA production can be performed through a biotechnological process (using herbal wastes and residues), it can be considered a renewable and environmentally friendly chemical substance [100]. It was reported that LA addition considerably affected the number of sulfur species on the pyrite surface, which is beneficial for mineral depression [101,102]. Han et al. [89] utilized LA as an effective depressant for separating pyrite from

Table 2. Application of biodegradable acids as green depression reagents in pyrite flotation.

Associated minerals	Pyrite depressant	Depressant dosage	pH	Collector	Particle size	Metallurgical responses	Ref.
Chalcopyrite	LA	20 mg/L	8	Sodium Butyl Xanthate	−74 μm + 38 μm	Pyrite Recovery: 25.01% Chalcopyrite Recovery: ~95%	[89]
Chalcopyrite	LA	200 mg/L	8	Sodium Butyl Xanthate	−74 μm + 38 μm	Pyrite Recovery: 11.05% Chalcopyrite Recovery: 97.06%	[89]
Chalcopyrite	PGA	35 mg/L	9	Sodium Butyl Xanthate	−74 μm + 38 μm	Pyrite Recovery: <20% Chalcopyrite Recovery: >85%	[90]
Chalcopyrite	PGA + Lime	15 mg/L PGA + 200 mg/L Lime	9	Sodium Butyl Xanthate	−74 μm + 38 μm	Pyrite Recovery: <20% Chalcopyrite Recovery: >80%	[91]
Chalcopyrite	PA	200 mg/L	8	Sodium Butyl Xanthate	−74 μm + 38 μm	Pyrite Recovery: ~3% Chalcopyrite Recovery: >90%	[92]
–	PA	100 g/t	–	Butyl Xanthate	−74 μm	Pyrite Recovery: ~10%	[10]
Chalcopyrite	SA	200 mg/L	8	Sodium Butyl Xanthate	−74 μm + 38 μm	Pyrite Recovery: ~3% Chalcopyrite Recovery: >95%	[93]
–	TGA	1000 g/Ton	–	Butyl Xanthate	−74 μm	Pyrite Recovery: ~10%	[10]
Chalcopyrite	NaHu + CaO	52 g/t NaHu + 1300 g/t CaO	10	Butyl Xanthate	−90 μm + 60 μm	Cu Grade: 24% S Content: 32.45% Cu Recovery: 97.26%	[94]
Sphalerite	NaHu + CaO	30 g/t NaHu + 850 g/t CaO	11.5	Butyl Xanthate	−74 μm + 38 μm	Zn Grade: 46.01% Zn Recovery: 90.11%	[95]
Chalcopyrite	NH ₄ Hu + CaO	1678 g/t NaHu + 2000 g/t CaO	10.29	Iso-Butyl Ethionine (Z200) + Sodium n-Butyl Xanthate	d ₈₅ : 74 μm	Cu Grade: 19.92% S Content: 29.72% Cu Recovery: 84.32%	[96]
Chalcopyrite	TA	20 mg/L	8	Sodium Butyl Xanthate	−74 μm + 38 μm	Pyrite Recovery: ~30% Chalcopyrite Recovery: >90%	[97]
Chalcopyrite	TA	200 mg/L	8	Sodium Butyl Xanthate	−74 μm + 38 μm	Pyrite Recovery: ~5% Chalcopyrite Recovery: >90%	[97]
Chalcopyrite	PCA	60 mg/L	8.16	Sodium Butyl Xanthate	−74 μm + 38 μm	Pyrite Recovery: 1.29% Chalcopyrite Recovery: 90.88%	[98]

LA: lactic acid; PGA: polyglutamic acid; PA: pyrogalllic acid; SA: salicylic acid; TGA: thioglycollic acid; NaHu: sodium humate; NH₄Hu: ammonium humate; TA: tannic acid; PCA: polypropylene carboxylic acid.

chalcopyrite in froth flotation (pH 8) when sodium butyl xanthate (SBX) was used as a collector. LA showed a satisfactory depression impact on pyrite particles, while chalcopyrite floatability was not affected (Figure 5). Adsorption analyses revealed that LA reduced the adsorption amount of SBX on the surface of pyrite particles with negligible effect on the chalcopyrite mineral. Zeta potential and Infrared spectroscopy (IR) analyses demonstrated that the LA adsorption onto the pyrite surface occurred through chemical and physical mechanisms. LA adsorption on the pyrite surface formed a considerable quantity of hydrophilic compounds, increasing the pyrite hydrophilicity. Time-of-Flight secondary ion mass spectrometry (TOF-SIMS) and X-ray photoelectron spectroscopy (XPS) outcomes showed that LA significantly interacted with iron sites located on the surface of pyrite. This led to hydrophilic iron hydroxide forming on the pyrite surface [89]. XPS analysis can distinguish the elemental components and chemical states of produced species of mineral-reagent reaction [103]. The XPS results

revealed that the pretreated surface of pyrite has a higher Fe concentration (13.40%) than the fresh sample (7.18%). The rise in iron sites on the surface of pyrite led to enhancing the formation of hydrophilic iron-oxy/hydroxy compounds. Also, after treatment with LA, the hydrophobic sulfur species decreased from 13.46% to 9.59%. These phenomena enhanced the hydrophilicity of the pyrite surface [89].

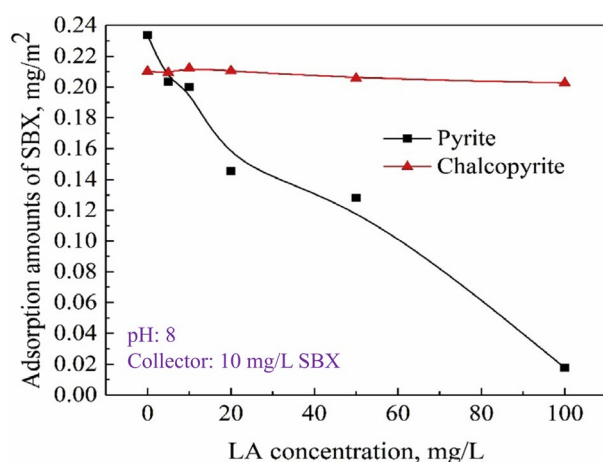
Polyglutamic acid

Polyglutamic acid (PGA), which is also named poly-γ-glutamic acid (γ-PGA), is a polymeric chemical derived from glutamic acid (GA). PGA molecule structure contains d- and l-GA units, which have been bound through amide connections between α-amino and γ-carboxylic acid functionalities [104–106]. PGA is an anionic renewable biopolymer with high solubility in water [106,107] and can be produced through the fermentation process by microorganisms. This method can be commercially used because of its: lower

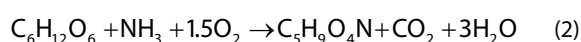
Table 3. The isoelectric point of pyrite with and without the addition of biodegradable acids.

Absence of depressant	Presence of depressant	Depressant (dosage, mg/L)	Description	Ref.
3.6	5 and 5.9	LA (20)	LA can strongly interact with the pyrite surface (both physically and chemically) even at a low dosage, making hydrophilic surface.	[89]
5.5	Always negative at 5 < pH < 12	PGA (35)	A significant reduction in the zeta potential of pyrite was attributed to the adsorption of PGA anions onto the pyrite surface.	[90]
Always negative at 6 < pH < 12	Slightly decreased	PGA (15)+CaO (200)	CaO, which originates cations such as Ca ²⁺ significantly increases the electrical charge of the pyrite surface. However, PGA functionalities with a negative charge (RCOO ⁻ and R(COO) ₂ ²⁻) decrease it.	[91]
3.6	Always negative at 3 < pH < 10	PA (100)	PA adsorption onto the pyrite surface occurred through simultaneous chemical and physical mechanisms.	[92]
3.6	4.7	SA (20)	After treatment with SA, the isoelectric point of pyrite increases and continues with rising SA dosage. Both chemical and physical adsorption mechanisms were simultaneously observed.	[93]
3.6	6.5	SA (100)		
Always negative at 6.5 < pH < 13	Decreased	NaHu (50)	Adding NaHu reduced the zeta potential of pyrite to more negative levels. This is because humate anions could be adsorbed onto the surface of pyrite particles.	[94]
Always negative at 4 < pH < 11.5	Significantly decreased	PCA (60)	PCA strongly adsorbed onto the pyrite surface, resulting in a significant reduction of zeta potential.	[98]
3.6	Always negative at 4 < pH < 11.5	TA (100)	Measurements reveal that the adsorption process of TA onto the pyrite surface occurred through simultaneous chemical and physical mechanisms.	[97]

LA: lactic acid; PGA: polyglutamic acid; PA: pyrogallallic acid; SA: salicylic acid; NaHu: sodium humate; PCA: polypropylene carboxylic acid; TA: tannic acid.

**Figure 5.** The adsorption amount of SBX onto the surfaces of chalcopyrite and pyrite as a function of LA dosage (pH: 8, SBX: 10 mg/L) [89].

negative impact on the environment, higher purity of PGA, and milder production conditions than other techniques [104]. However, the extensive use of this technology is restricted by its high production cost [104,107]. For PGA synthesis, glucose molecules (C₆H₁₂O₆) need to be converted into L-GA at the first step (Equation (2)). Subsequently, L-GA is racemized into D-GA via L-alanine and D-alanine. Lastly, D-GA and L-GA are incorporated into the growing biopolymer of PGA [104].



Since PGA is a biodegradable biomolecule [107], its degradation starts with its initial disintegration into D- and L-GA. More oxidation of GAs leads to the formation of ammonia water (NH₄OH) and carboxylic acids (such as pyruvic, maleic, and oxalic acids). In the final step, produced carboxylic acids are gradually converted into H₂O and CO₂. PGA is biodegradable and nontoxic; thus, its optimal usage in mineral processing systems can considerably decrease the environmental threats of using inorganic materials [106,107].

As a green depressant, PGA can be used to selectively separate pyrite from chalcopyrite through the flotation technique (SBX was the collector). The depressive performance of PGA on the pyrite surface was significantly stronger than that on chalcopyrite at a pH range of 8–10 (acts as a selective depressant). The highest efficiency was observed in artificially mixed samples at pH 9 (recovery was ~20% for pyrite and ~85% for chalcopyrite). Adsorption assessments indicated a higher amount of PGA on the pyrite surface than on the chalcopyrite surface, which was also confirmed by zeta potential results. XPS and IR analyses indicated that PGA chemically interacted with the pyrite surface. Through the pretreatment, a strong layer of PGA formed on the pyrite surface; thus, its surface was passivated and could not adsorb SBX. On the other hand, the interaction between PGA and chalcopyrite was weak, and xanthate ions from SBX could effectively be oxidized to di-xanthogen on the surface of chalcopyrite, improving its floatability in PGA presence [90].

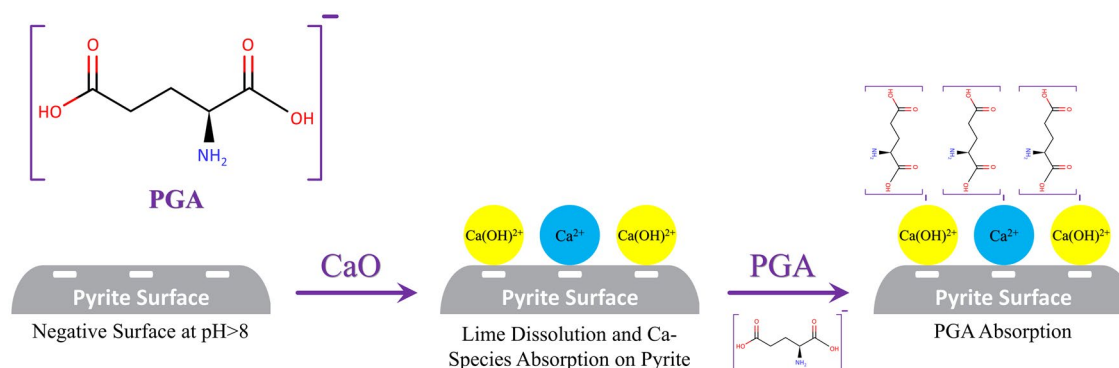


Figure 6. The molecular structure of PGA and the two-step mechanism in the process of pyrite depression using lime and PGA [91].

Khoso et al. [91] investigated the combined effect of PGA and lime in a pyrite-chalcopryrite flotation system (SBX as a collector). It was reported that the pretreatment of pyrite using lime and PGA could form hydrophilic compounds on its surface. This phenomenon blocked the electrochemical reaction between the pyrite surface and xanthate ions, which prevented di-xanthogen formation. This mixed depressant showed a slight inhibitory impact on chalcopryrite particles. Therefore, a significant recovery difference (approximately 60%) was achieved between chalcopryrite and pyrite using PGA+CaO in a broad pH range (7–12). XPS and FT-IR analysis illustrated a chemisorption mechanism responsible for the PGA adsorption on the surface of pyrite particles when using the mixture of PGA+CaO, leading to the formation of calcium- γ -PGA species (Figure 6) [91].

Pyrogalllic acid

Pyrogalllic acid (PA), with the chemical formula $C_6H_3(OH)_3$, is an organic water-soluble white powder; however, due to its sensitivity toward oxygen, its color typically changes to brownish. This bio-degradable compound is one of three isomers of trihydroxybenzenes (1,2,3-benzenetriol). PA has been widely utilized as a preservative in the food industry. Also, it is an essential ingredient in the chemicals industry for producing new photosensitive substances [108–110]. Since it shows a solid affinity for metallic sites on the surface of minerals, PA has recently gained attention in the flotation of some ores, such as Ca-containing minerals [111–113]. However, its application as a green inhibitor for pyrite depression has rarely been investigated.

Chen et al. suggested that carboxyl functionalities in PA's chemical structure were not strong enough to apply sufficient reductive potential for a desorbing collector from a mineral surface [10]. However, the micro-flotation experiments conducted by Han et al.

[92] exhibited that PA reduced the pyrite floatability under low-alkalinity conditions, and its impact on the pyrite surface was stronger than that of chalcopryrite, leading to selective separation. Surface analysis measurements indicated that sodium butyl xanthate (NaBX), used as a collector, was negligibly attached to the surface of pyrite particles at an optimum PA concentration at pH 8. IR and zeta potential analyses demonstrated that the chemisorption mechanism was responsible for PA adsorption on the pyrite surface. Also, according to results obtained from XPS analysis, PA molecules are probably adsorbed on the pyrite surface through chemisorption interaction with Fe atoms. This could strengthen the pyrite hydrophilicity and result in its depression. These promising results show that PA can be considered a clean selective depressant for the standard chalcopryrite-pyrite flotation system in low-alkaline environments [92].

Salicylic acid

Salicylic acid (SA) (also known as 2-hydroxybenzoic acid) is a colorless, bitter-tasting organic chemical that is obtained from natural sources, particularly plants. It has been widely employed for treating skin problems due to its bactericidal, antibiotic, and antiseptic features [114,115]. SA is also used for producing cosmetics, such as dermatitis treatment, and clinical medicines, such as aspirin [116,117]. Carboxyl and phenolic hydroxyl groups present in SA's structure are the functionalities that can interact with unsaturated atoms on the fractured mineral surface by oxygen atoms in the polar functional groups [10,118]. It has been reported that chelating agents with small molecules can be strong pyrite depressants in pyrite-chalcopryrite flotation systems [89]. An SA molecule can quickly bond to a pyrite surface *via* its functional groups and hinder its collector adsorption. Pyrite particles that adsorb SA become hydrophilic, facilitating the effective separation

process of pyrite from chalcopyrite [93]. Han et al. [89] indicated that the collector adsorption (SBX) onto the surface of pyrite mineral is negligible when using high dosage of SA. Zeta potential and IR analytical measurements showed the simultaneous SA chemical-physical adsorption onto the surface of pyrite particles. XPS and ToF-SIMS analyses showed that active iron atoms on the pyrite surface could be appropriate sites for interaction with SA, and form hydrophilic species. This phenomenon led to increasing hydrophilicity of pyrite particles. SA showed high selectivity, and chalcopyrite, even in high SA dosages, exhibited excellent floatability [93].

Thioglycolic acid

Thioglycolic acid (TGA) is the organic compound containing both thiol and carboxylic acid functional groups. It is a colorless liquid with a strong unpleasant odor. TGA has rarely been reported as an organic reagent in the flotation separation of sulfide minerals. Chen et al. [10] investigated its inhibitory strength on the pyrite particles in a comparative study. The obtained results revealed that organic depressants that have only one functional group, such as hydroxyl ($-OH$), amino ($-NH_2$), or carboxyl ($-COOH$), in their structure, cannot effectively depress pyrite. This is why oxalic acid, melocol, and glycerin are not powerful pyrite depressants. However, TGA, which possesses both carboxyl and thiol ($-SH$) functional groups, can enhance the depression of pyrite particles [10]. Thiol is an intensive reductive functional group. This feature lowers the flotation environment potential as well as the pyrite rest potential, leading to its depression [119].

Humic acids

Sodium humate (NaHu) is the salt of humic acid. Its commercial production can be performed through alkaline extraction of natural substances, such as lignite, weathered coal, peat, etc. Because of its affordability, availability, and eco-friendliness, NaHu can be used for a wide range of applications, such as removing heavy metals from wastewater (as a scavenger), oil drilling (as mud adjuster), and food industry (as additives) [51,94]. The obtained results from laboratory- and industrial-scale experiments indicated that NaHu is an efficient depression reagent for pyrite. It had a strong activity affected by the pulp pH through the flotation separation of pyrite from chalcopyrite. Even though the floatability of chalcopyrite was negligibly reduced in the presence of NaHu, pyrite particles were effectively depressed by NaHu in the alkaline

environment. In the presence of ethyl and butyl xanthates as collectors and pH adjusted at 10–10.5, a high-grade chalcopyrite concentrate (24% Cu) was obtained with the addition of NaHu as a depressant (40–60 g/t). Using NaHu reduced CaO consumption, and the recovery of valuable metals (Au, Ag, and Mo) were improved in the froth zone of the flotation cell. IR spectra measurements revealed that NaHu could strongly interact with the pyrite surface through a chemical adsorption mechanism [94].

Various micro-flotation tests revealed that the depression efficiency of NaHu on pyrite particles could be considerably enhanced by Ca-species originating from CaO dissolution. A mixture of CaO and NaHu could selectively inhibit the pyrite floatability with negligible effect on the sphalerite at high alkaline pH levels (11.5–12.0). Under optimum conditions (pH 11.5, 30 g/t NaHu, and 850 g/t CaO), a sphalerite concentrate with around 90% recovery and 46% grade was obtained. Adsorption analyses showed that Ca-containing cations, such as $Ca(OH)^+$ and Ca^{2+} , could considerably improve NaHu adsorption onto the pyrite surface. It was proven that functionalities present in the NaHu structure chemically interacted with adsorbed Ca on the pyrite surface. However, the adsorption of NaHu molecules onto sphalerite was weaker [95]. The same trend has been observed when ammonium humate (NH_4Hu) as a salt of humic acid has also shown a high selectivity toward pyrite through its separation from chalcopyrite from a plant tailing by using iso-butyl ethionine (Z200) and sodium n-butyl xanthate (SNBX) as collectors. The FTIR and XPS analysis revealed that NH_4Hu chemically interacted with the pyrite surface, making pyrite particles hydrophilic. Thus, the comprehensive recycling of valuable minerals from the copper tailing was fulfilled successfully [96].

Polypropylene carboxylic acid

Polypropylene carboxylic acid (PCA) is a recently introduced flotation surfactant utilized as a green depression reagent for separating pyrite from chalcopyrite. Micro-flotation test results indicated that, in the presence of a collector (SBX) without any depressant, the recovery of both minerals exceeded 93% in the pH range of 4–10 (no separation). With the addition of 60 mg/L PCA, a considerable decrease in pyrite recovery (from ~94% to ~23%) was observed. However, the chalcopyrite floatability was slightly affected (from 96.88% to 90.46%). After optimization of the affecting parameters (15 mg/L SBX, 60 mg/L PCA, pH 8.16), the process could be turned into a selective separation (90.88% for chalcopyrite and 1.29% for pyrite). FTIR,

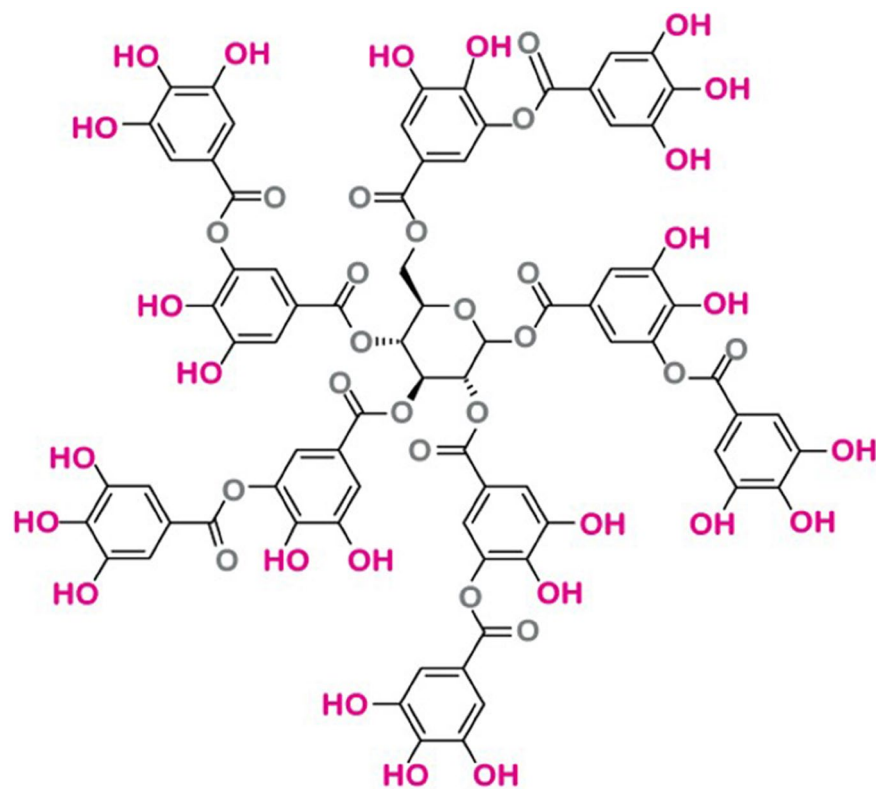


Figure 7. Chemical structure of tannic acid containing phenols, hydroxyl groups, and benzene rings [121].

XPS, and Zeta potential measurements also confirmed the selective depressive mechanism of PCA on the two minerals. The obtained outcomes showed that PCA molecules preferentially chemisorbed on the pyrite surface's iron sites, inhibiting collector adsorption. However, the interaction of PCA molecules with chalcopyrite was negligible, and the collector could attach to the chalcopyrite surface even after pretreatment with PCA [98].

Tannic acid

Tannic acid (TA), with the chemical formula $C_{76}H_{52}O_{46}$, is a biodegradable tannin-based chemical extracted from different parts of vegetation [120]. The existence of phenols and hydroxyl ($-OH$) groups attached to a carbon atom in a benzene ring in the TA's structure (Figure 7) has made it a weakly acidic liquid [121]. TA has been used as a flocculation reagent in purifying wastewater to remove fine particles. Additionally, it is a potential green depressant for metal-bearing minerals [122–124,125]. Investigations on pyrite depression by TA are quite limited. Han et al. [89] investigated pyrite depression by TA in a pyrite-chalcopyrite system at low-alkaline. After using SBX as a collector, the pyrite surface analysis (Figure 8) clearly showed that, at high TA concentration, the collector adsorption was

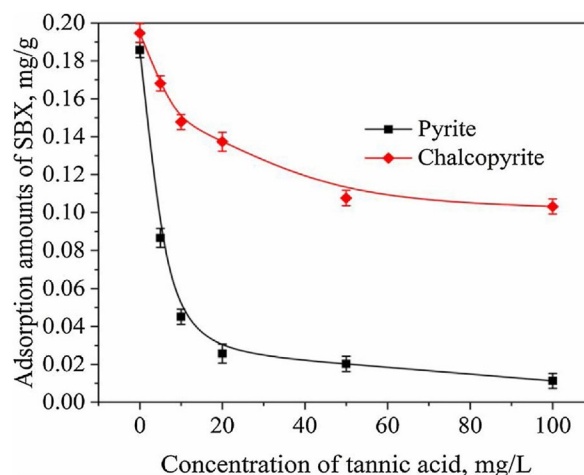


Figure 8. TA dosage's effect on SBX adsorption onto the surface of chalcopyrite and pyrite (pH: 8, SBX: 10 mg/L) [97].

negligible on the pyrite surface. IR and zeta potential analyses suggested both physical and chemical mechanisms simultaneously led to TA adsorption onto the pyrite surface. XPS and ToF-SIMS also indicated that TA interacted with active iron atoms on the pyrite surface. This led to forming many hydrophilic groups on pyrite and its surface deactivation. Flotation experiments confirmed these results and demonstrated that TA had a noticeable inhibitory impact on pyrite floatability.

Chalcopyrite, however, invariably revealed efficient floatability regardless of the presence of TA under the same circumstance [97].

Summary

Pyrite, as the most abundant sulfide mineral, has low economic value, and its unfavorable association with various minerals causes serious challenges in mineral processing processes and environmental pollution. Froth flotation can be employed for pyrite rejection early in the beneficiation procedures. However, the selectivity problem is a main challenge in pyrite-containing flotation systems. Due to the natural hydrophobicity of pyrite particles through flotation separation and its high affinity to xanthates (the most common collectors for flotation of sulfide minerals), satisfying the desired selectivity could be exceptionally difficult without pyrite depression. Using inorganic and toxic depressants (e.g., cyanides, lime, and sulfur-oxy compounds) has been the conventional solution for overcoming this problem. They have been widely employed in flotation despite various practical problems related to: handling, high costs, toxicity, causing poisoning, and several environmental hazards. Therefore, alternative, eco-friendly, and inexpensive organic substances have been recently investigated.

Biodegradable acids are green and eco-friendly pyrite depressants that satisfy environmental requirements for moving toward cleaner and sustainable production. Various hydrophilic functionalities (such as hydroxyl, carboxyl, etc.) have made these chemicals promising for assisting or replacing traditional inorganic pyrite depressants. Also, their depression efficiency can be enhanced by having thiol (–SH) functional groups. Although the effective depression performance of these biocompatible chemicals on pyrite surfaces has been proven, detailed and comprehensive studies on their applications are pretty limited. Moreover, some parameters have not been considered through the conducted investigations, such as the effect of mineral particle size and reaction kinetics. It has been reported that the functional group of these green depressants (LA, TA, PA, and SA) can interact with the iron sites of the pyrite surface through simultaneous chemical and physical adsorption. However, the interaction mechanism of other depressants is still unknown, necessitating more surface measurements, such as zeta potential, XPS, TOF-SIMS, and FTIR, better to understand the interaction between them and various sulfide minerals.

Since pyrite is a semiconductor mineral, its depression using novel reagents can be extremely influenced by parameters, such as the electrochemical potential of

the flotation environment, the presence of activating metallic cations (copper and lead), the oxygen content of slurry, etc. However, no research has been conducted in these areas. Additionally, the investigation on the depression behavior and performance of biodegradable acid depressants is limited to a few artificially mixed flotation systems and on the laboratory scale. They are mostly examined for separating pyrite from chalcopyrite at a limited size range (+38–74 µm). Therefore, their ability to remove pyrite from: polymetallic sulfides, complex systems, and other valuable minerals, as well as coal cleaning, both on a laboratory and industrial scale at a wide range (from ultrafine to coarse particles), needs to be investigated. There are some other biodegradable acids, such as gallic acid, citric acid, succinic acid, oxalic acid, and malic acid, of which their effects on pyrite depression can be examined. It should also be noted that these biodegradable acids are more expensive than polysaccharide-based depressants. However, a comparative study and optimization are necessary to comment on their economic superiority. Thus, several rooms are open for working on various aspects of pyrite depression using these green alternative depressants to address existent gaps by conducting further investigations.

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