Polysaccharides-based pyrite depressants for green flotation separation: An overview

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A B S T R A C T

Froth flotation is an essential processing technique for upgrading low-grade ores. Flotation separation would not be efficient without chemical surfactants (collectors, depressants, frothers, etc.). Depressants play a critical role in the selective separation of minerals in that they deactivate unfavorable mineral surfaces and hinder them from floating into the flotation concentration zone. Pyrite is the most common and challenging sulfide gangue, and its conventional depressants could be highly harmful to nature and humans. Therefore, using available, affordable, eco-friendly polymers to assist or replace hazardous reagents is mandatory for a green transition. Polysaccharide-based (starch, dextrin, carboxymethyl cellulose, guar gum, etc.) polymers are one of the most used biodegradable depressant groups for pyrite depression. Despite the satisfactory flotation results obtained using these eco-friendly depressants, several gaps still need to be addressed, specifically in investigating surface interactions, adsorption mechanisms, and parameters affecting their depression performance. As a unique approach, this review comprehensively discussed previously conducted studies on pyrite depression with polysaccharide-based reagents. Additionally, practical suggestions have been provided for future assessments and developments of polysaccharide-based depressants, which pave the way to green flotation. This robust review also explored the depression efficiency and various adsorption aspects of naturally derived depressants on the pyrite surface to create a possible universal trend for each biodegradable depressant derivative.

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1. Introduction

The tremendous increases in base metals' demands have made processing low-grade ores meaningful. Sulfides, as the main potential resources of low-grade base metals, have been processed more than ever due to the modernized world's ever-increasing need for these valuable metals. However, the presence of iron sulfides (such as pyrite) has caused severe challenges in various beneficiation processes (such as pyrometallurgy [1], hydrometallurgy [2,3], magnetic separation [4], and flotation [5,6]). Pyrite (FeS_2) is one of the most abundant gangue phases for the valuable base metal ores (valuable sulfides like chalcopyrite ($CuFeS_2$), sphalerite (ZnS), galena (PbS)) [7,8]. As a result of its high sulfur content, pyrite

can cause SO_2 emission when pyrometallurgical processes are conducted on other valuable sulfide ores, which leads to severe technical and environmental problems such as acid rain [9,10]. In addition, during hydrometallurgical processes of non-ferrous metals, pyrite causes iron to enter the solution, necessitating more steps and materials to remove it from the solution, which causes a reduction in the final product quality [3]. On the other hand, sulfur is one of the most important impurities that, if present in iron concentrate, can have detrimental effects on the produced steel [11]. Thus, pyrite removal has always to be considered at an early stage of the beneficiation processes [12].

Froth flotation is the most practical pretreatment for fine-disseminated low-grade sulfide ores [13]. Various surfactants improve froth flotation by increasing surface hydrophobicity [14,15]. The best-known anionic collector for making precious sulfides hydrophobic is xanthate ions ($ROCSS^-$) [16]. Table 1 shows

the electrochemical processes that lead to the xanthate adsorption onto sulfides. As an unfavorable mineral, pyrite can readily report to the concentrate owing to di-xanthogen formation [17,18]. Froth flotation is the most common way to prevent pyrite from interacting with xanthate [19,20]. pH variation directly affects pyrite-xanthate adsorption and the production or decomposition of xanthate compounds or di-xanthogen (Fig. 1) [21]. The flotation of pyrite is pH-dependent, and pH 5 is a boundary value where pyrite has a naturally hydrophobic surface with both negative and positive hydroxy iron groups ($Fe(OH)_3$, $Fe(OH)_2$, $Fe(OH)^{2+}$) [22]. Thus, pH regulators, such as lime (CaO), sulfur-oxy species, sodium hydroxide (NaOH), and sodium carbonate (Na_2CO_3), have been widely used to regulate the pH of the flotation environment thereby selectively depressing pyrite in various flotation systems [17,23–25]. This increase in pH after adding these reagents implies an increase in the dosage of hydroxyl ions that adsorb on pyrite's surface, thereby facilitating depression. The creation of iron hydroxyl would hinder xanthate adsorption on the pyrite surface (i.e., depressing pyrite particles) [26].

Biodegradable depressants have various sources, which makes these reagents available for use in froth flotation separation and demonstrates excellent practical features. These flotation reagents can minimize the environmental impacts of mineral processing activities [28–31]. Several investigations indicated that inorganic and toxic reagents could be promisingly assisted or even replaced by these reagents in various flotation conditions [7,20,32]. These green depressants could be polysaccharide-based, wood extracts (lignosulfonate-based biopolymers), organic acids, tannin-based (tannic acid and quebracho), humates, etc. Regarding the structure's complexity and the fractured heterogeneous surfaces of minerals, biodegradable reagents interact complexly with mineral surfaces. However, these interactions can be classified into four general categories, as shown in Fig. 2 [19,33]. In the case of pyrite, numerous eco-friendly depressants have been successfully examined to replace or assist inorganic depression reagents for selective flotation separation. Their hydrophilic functionalities improve the surface's hydrophilic properties, reduce bubble-particle attachment, and facilitate pyrite depression.

In froth flotation separation, the first use of polysaccharides dates back to 1928 and has continued up to now [34]. Although several polysaccharides have been recently synthesized and extensively used for pyrite depression in different mineral processing plants, no comprehensive review article has universally explored their adsorption mechanisms, interactions, and effectiveness on metallurgical responses. Since it is essential to understand the behavior of pyrite as a troublesome gangue mineral in the presence of these depressants, the present review aims to robustly explore the performance of various polysaccharides-based depressants used in the flotation separation of pyrite in different conditions. Several factors that must be considered for their applications have been reviewed, their performance was analyzed, and gaps within each area were highlighted.

Table 1
Various electrochemical reactions in xanthate adsorption onto sulfide mineral surfaces.

No.	Reaction	Description
1	$X^- \rightarrow X_{ads} + e^-$	Xanthate ion chemisorption through charge transfer
2	$2X^- \rightleftharpoons X_2 + 2e^-$	Di-xanthogen formation through xanthate oxidation
3	$MS + 2X^- \rightarrow MX_2 + S + 2e^-$	Metallic xanthate formation

Note: X^-: xanthate ions; X_{ads}: adsorbed xanthate; X_2: di-xanthogen; MS: sulfide mineral; MX_2: metal xanthate; S: elemental sulfur or polysulfide.
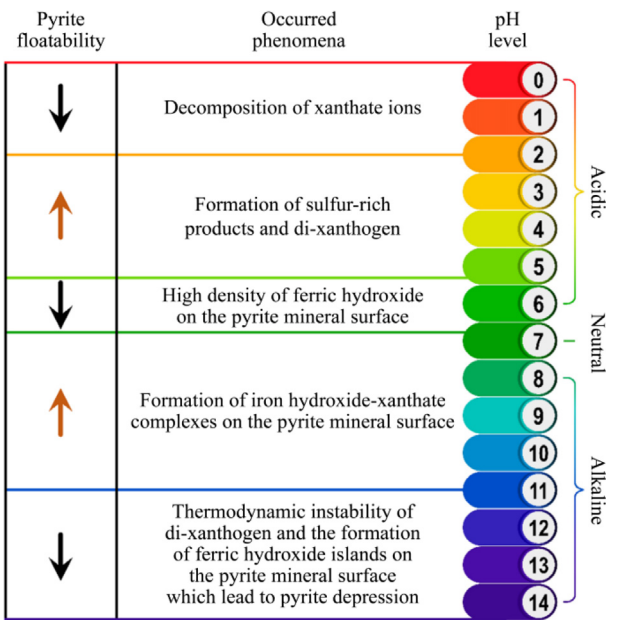
Fig. 1. The effect of pH on the pyrite-xanthate interaction (Ethyl xanthate: 2×10^{-5} mol) [27].

2. Polysaccharides-based depressants

The connection of monosaccharide units (sugar monomers) leads to the formation of various complex macromolecular polymers called polysaccharides [35]. These natural products, categorized in the condensed polymers group and generally possess high molecular weights, have been widely employed in various industries. Thus, they are readily available in large quantities and have shown promising results [36]. It has to be noted that the depression processes using polysaccharides, like other polymers, highly depend on both polymers' chemical characteristics and the flotation system conditions. The most critical parameters that may affect the adsorption of polysaccharides onto minerals' surfaces have been illustrated in Fig. 3 [37].

Generally, the process of pyrite depression by polysaccharides occurs due to the hydrophilic surface coating phenomenon. This procedure is different from the depression process by inorganic materials where depressants like lime and cyanide alter pyrite's surface, preventing the collector adsorption (xanthate) [38]. An oily compound, di-xanthogen, forms on the surface of pyrite through electrochemical reactions and spreads on hydrophobic sites of the pyrite surface [39]. On the other hand, the molecules of polysaccharide-based depressants attach to iron hydroxides formed on the pyrite surface. These phenomena could be because polysaccharide (depressant) and xanthate (collector) are present simultaneously in a pyrite-containing flotation system; co-adsorption of these two reagents occurs. This is because the pyrite surface is heterogeneous, enveloping the adsorbed di-xanthogen (Fig. 4) [40]. Di-xanthogen, which has been formed because of the xanthate adsorption on the pyrite surface, is surrounded by macromolecules of polysaccharide-based depressants. Hydroxyl functional groups of adsorbed polysaccharide molecules can lead to the formation of a hydrophilic layer on the pyrite surface. These interactions decrease the stability of bubble-mineral attachment enhancing pyrite inhibition [41]. This inhibition mechanism fails at high collector dosages. Thus, the sequence of flotation reagent addition (polysaccharide and xanthate) significantly affects their adsorption on the mineral surface [38]. Polysaccharide-based depressants' structure and carbon chain length are other essential
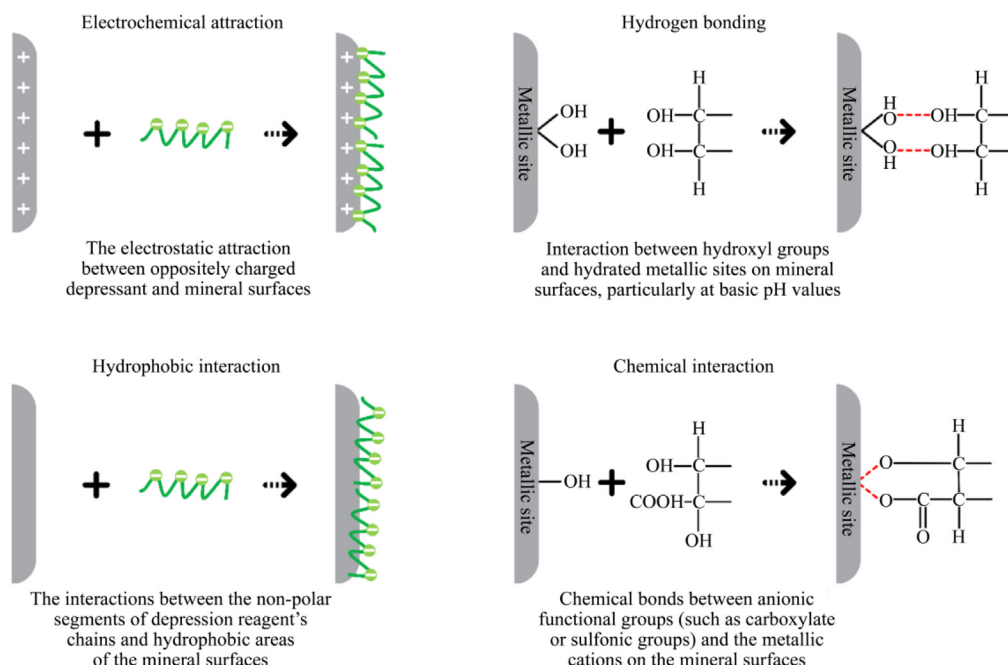
Fig. 2. Possible mechanisms for adsorption of natural depressant on mineral surfaces [19].
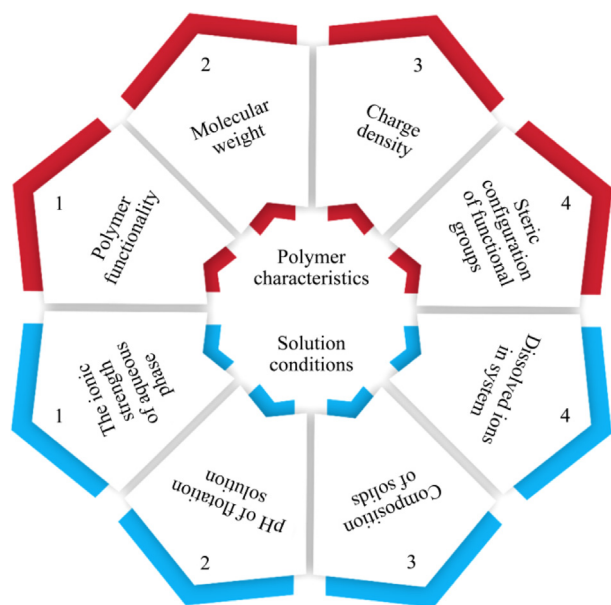

Fig. 3. The most important parameters affecting polysaccharides' adsorption onto minerals' surfaces [37].
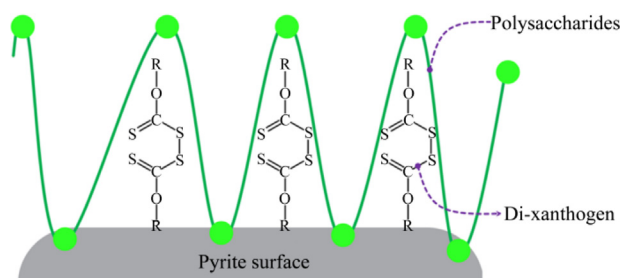

Fig. 4. Enveloping the di-xanthogen adsorbed on the surface of pyrite by polysaccharide-based depressant [40].

factors in their depression performance. They are divided into different types based on their compositions (Fig. 5).

It has been documented that the isoelectric points (IEPs) of pyrite can vary from pH 2 (unoxidized pyrite) to pH 7 (completely oxidized pyrite). This wide variation could be due to the partial oxidation of the pyrite surfaces [42]. Additionally, in some cases, pyrite can show two different IEPs. The main reason for this phenomenon is the presence of ferric hydroxide on the pyrite surface [43]. Table 2 lists pyrite's IEP in the absence and presence of various polysaccharide-based depression reagents. Zeta potential analysis also demonstrated that the presence of Ca^{2+} ions decreases the pyrite surface's negative charge due to the positively charged Ca$(OH)^+$ adsorption. This reduces the repulsive electrostatic force between pyrite particles and negatively charged polysaccharides [44].

By comparing the results, it is evident that, under different conditions, various depressant reagents have different effects on the isoelectric point of pyrite. Using non-modified starch can lead to an increase or decrease in the isoelectric point of pyrite. However, tricarboxylate sodium starch (TCSS), a negatively charged depressant, always lowers the pyrite's IEP. This also applies to dextrin, which always reduces the IEP value of pyrite. Locust bean gum and konjac glucomannan are two depressants that increase the IEP value of the pyrite surface, although it is a small amount.

2.1. Starches

As an odorless, tasteless white substance and a hydrophilic macromolecule polysaccharide, starch ($[C_6H_{10}O_5]_n$) can be produced from various natural sources such as corn, rice, maize, wheat, potatoes, etc. [52]. Native starches have limited functionalities, hindering their industrial applications [53]. Thus, various techniques, including gelatinization, solubility, retrogradation properties, pasting, and swelling, are employed to produce modified starch [54]. In this way, some properties of starch can be effectively altered to obtain polymers with required features for different applications [53,55]. Starch is an essential food source for many human beings' daily caloric intake. This has caused starch to have a special place in the food industry [56,57]. Since it is an
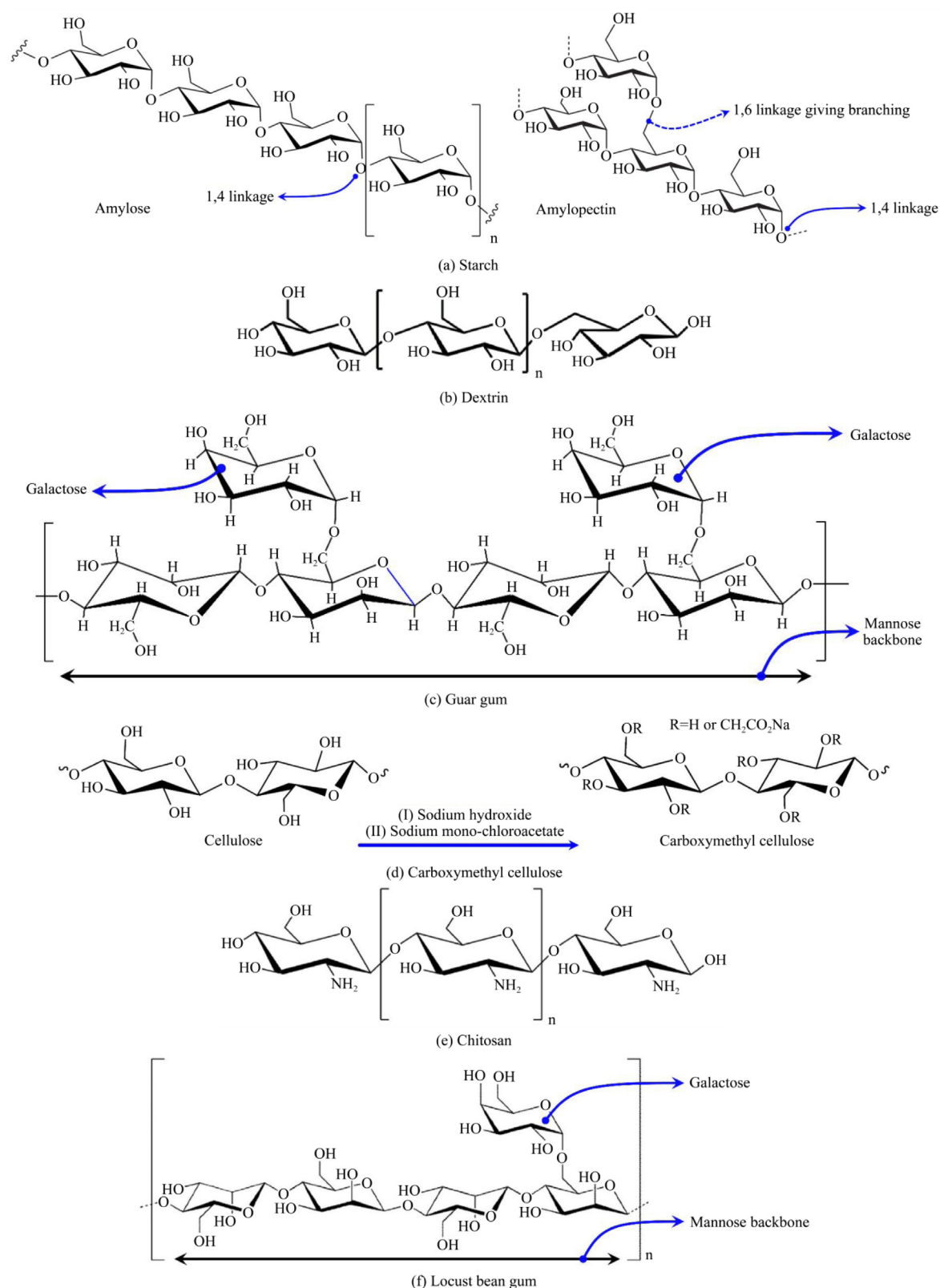
Fig. 5. Chemical structures of polysaccharide-based polymers used for pyrite depression.

inexpensive, biodegradable, and non-hazardous polymer, the interest of non-food industries in using starches is increasing daily. The annual global consumption of starch in industries reaches millions of tons for various purposes, such as bonding reagents in the paper industry, coagulants in wastewater treatment, and flocculant

or depression reagents in froth flotation. Although different types of starches (from different sources) possess distinct characteristics, such as chain configuration, impurity contents, and chain lengths [35], their common feature is that all types have been formed mainly by two different glucose polymers, namely amylose (linear)
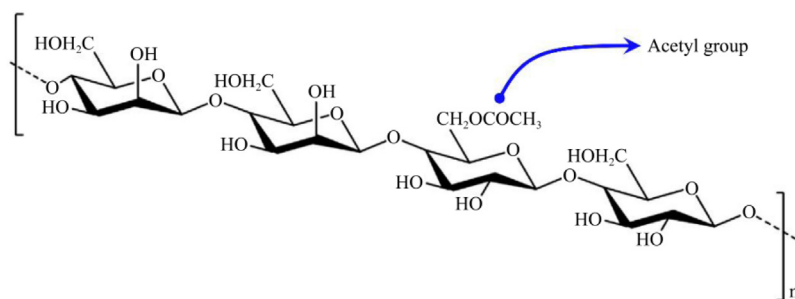
(g) Konjac glucomannan

Fig. 5 (*continued*)

Table 2
The isoelectric points of pyrite with and without the addition of polysaccharides.

Absence of depressant	Presence of depressant	Depressant	Dosage (mg/L)	Ref.
3.6	Slightly increased	Starch	20	[45]
3.6	3.9	Starch	100	[45]
6.8	5.4	Tricarboxylate sodium starch (TCSS) + CaO	60	[46]
Always negative at 6 < pH < 12	Decreased (More negative)	Tricarboxylate sodium starch (TCSS) + CaO	30	[47]
3.5 and 7.5	Always negative	Dextrin	50	[48]
3.5 and 7.5	Always negative	Dextrin	100	[48]
6.6	Slightly decreased	Dextrin	10	[49]
6.6	6.2	Dextrin	50	[49]
6.4	Slightly decreased	Dextrin	10	[41]
6.4	About 5.5	Dextrin	25	[41]
6.4	About 4	Dextrin	100	[41]
3.3	3.5	Locust bean gum	50	[50]
Always negative at 2 < pH < 12	Increased but Still Negative	Konjac glucomannan	10	[51]

and amylopectin (branched) which make starch play the role of a depressant reagent [58,59]. The hydrophilicity of starch molecules is attributed to the presence of numerous hydroxyl functional groups in the monomer unit, D-glucose [60]. As with many other minerals such as calcite [61], chlorite [62], hematite [63], forsterite [64], dolomite [65], and graphite [66], a high affinity has been reported between starch and pyrite (Table 3). This is because starch macromolecules can interact with active Fe atoms on the surface of pyrite particles. However, starch molecules have limited and unstable interaction with fewer active Fe atoms on the chal-

copyrite surface [45]. Similar phenomena to this interaction between pyrite and other polysaccharides, such as dextrin and guar gum, have also been reported [67].

Bulut et al. [68] indicated that starch could effectively depress pyrite even with low concentration (1.7 mg/L). The starch performance at high pH (pH 10) was better than that at natural pH (pH 6.5) (this could be due to the enhancing pyrite depression in high pHs as well). They noted that unmodified starch could adsorb onto the surface of pyrite through highly pH-dependent interactions with iron-hydroxylated species [68]. It was reported that starch

Table 3
Application of various starch types for pyrite depressant (SE: separation efficiency).

Valuable minerals	Depressant	Depressant dosage (g/t)	pH	Collector	Metallurgical responses	SE	Ref.
Chalcopyrite	Starch	50	6.9	Aerophine 3418 A	Cu recovery: 23.8% Cu grade: 11.91%	67.51	[68]
Chalcopyrite	Starch	50	12.1	Aerophine 3418 A	Cu recovery: 52.2% Cu grade: 19.92%	75.92	[68]
Chalcopyrite	Starch	200	8	Sodium butyl xanthate	Pyrite recovery: 24.22% Chalcopyrite recovery: 93.77%		[45]
Chalcopyrite	TCSS	75	6	Sodium butyl xanthate	Cu recovery: 77% Cu grade: 24.5%		[46]
Chalcopyrite	Native Starch	700	9	Isopropyl ethyl thiocarbamate	Pyrite recovery: 4%		[69]
Chalcopyrite	Oxidized Starch	500	9	Isopropyl ethyl thiocarbamate	Pyrite recovery: 2%		[69]
Chalcopyrite	Starch	200	11	Sodium isobutyl xanthate	Pyrite recovery: 57% Chalcopyrite recovery: 70%		[13]
Chalcopyrite	Starch	500	11	Sodium isobutyl xanthate	Pyrite recovery: 20% Chalcopyrite recovery: 25%		[13]
Chalcopyrite	TCSS	300	6	Sodium isobutyl xanthate	Cu grade: 25.35% Pyrite recovery: 14% Chalcopyrite recovery: 65%	42.15	[13]
Chalcopyrite	TCSS	25	6	Sodium butyl xanthate	Cu grade: 21.85% S grade: 33.78% Cu recovery: 77.43% S recovery: 20.94%	76.67	[70]

could have a favorable depressive impact on pyrite versus chalcopyrite, even at low concentrations. Still, by increasing its dosage, its depressive performance can be improved without altering other sulfide floatability (in the single mineral flotation) (Fig. 6). However, for the polymetallic sulfides, since the molecular structure of native starch is highly complex, its selectivity could be limited in high dosages [45].

As a novel modified starch, tricarboxylate sodium starch (TCSS) can be produced through a starch modification process using H_2O_2, NaOH solution, and $FeSO_4 \cdot 7H_2O$ as an oxidant. Fig. 7 depicts a schematic illustration of the synthesis process of TCSS. The oxidation process results in reducing the molecular weight of starch because of the molecular depolymerization phenomenon and forming grafted polar groups. From a chemical point of view, TCSS contains three —COOH and several —OH functional groups in its structure,
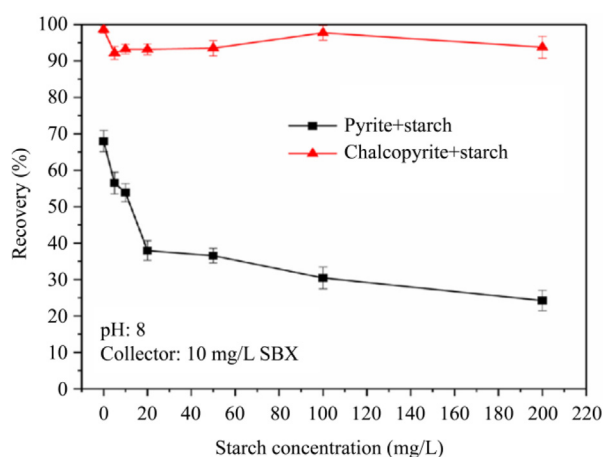

Fig. 6. The effect of starch concentration on the recovery of chalcopyrite and pyrite (SBX: sodium butyl xanthate) [45].
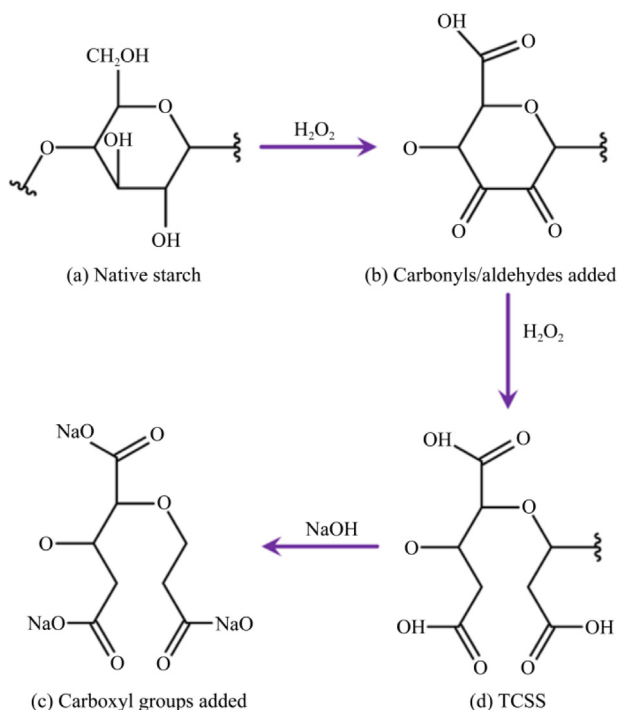

Fig. 7. Schematic illustration for synthesis process of TCSS [46].

which makes it an excellent green depressant for pyrite [13]. Khoso et al. [46] reported satisfactory pyrite depression by TCSS. However, they indicated that even using TCSS, the floatability of both pyrite and chalcopyrite could be reduced in single mineral flotation experiments at a pH range of 4–6. However, the depression impact of TCSS on the pyrite surface was considerably stronger than for the mixture of these two minerals. The highest selectivity was attained in a neutral flotation solution (pH~6) with sodium butyl xanthate as a collector. Adsorption analyses revealed that the TCSS chemically interacted with pyrite particles, while its interaction with the chalcopyrite surface was physical [46].

A comparison between TCSS and native starch indicated that TCSS had an improved selective depression effect on pyrite particles. Its depression impact is much more efficient than non-modified starch. When using native starch, pyrite depression only occurred under very alkaline circumstances (pH>11). However, modified starch (TCSS) provided a satisfactory inhibitory effect on the pyrite particles even at low pH levels (pH 2–7). In other words, TCSS could enhance flotation metallurgical responses (Cu recovery and grade) [13]. The same principle could be observed in the batch scale [70]. Combining organic depressants with conventional inorganic depressants can reduce the massive consumption of inorganic chemicals, decrease operational costs and environmental impacts, and improve selectivity in some cases. The synergistic effect of lime (CaO) and TCSS caused a strong depression of pyrite through its flotation separation from chalcopyrite in a wide pH range of 7–12. The metallurgical responses showed that the combination of lime and TCSS was much more efficient than their individual ones. This improvement was attributed to Ca^{2+} species dissolved from lime and present in a flotation environment. Through preferential adsorption of calcium cations on the surface of pyrite particles, the negative charge of pyrite (at pH 9–10) decreased, which could increase TCSS adsorption onto its surface (Fig. 8). This is due to the fact that TCSS is a polymeric depressant with anionic surface. The negativity of its surface leads to its great affinity towards positive surfaces through electrostatic attraction [47]. A comparative study of pyrite depression by native wheat starch (NWS) and modified wheat starch of Cu-activated pyrite followed a similar pattern. It showed that H_2O_2 can even mildly oxidize pyrite, enhance NWS adsorption onto the pyrite surface, and led to pyrite depression enhancement [69].

2.2. Dextrin

Dextrin $(C_6H_{10}O_5)_n$ is a colloidal polysaccharide-based substance produced by the starch hydrolysis process in a slightly acidic environment. It also can be produced in a dry mode, in which dry starch is heated. In the hydrolysis process, the main process of dextrin production, polymer molecules of glucose that have low molecular weight are linked together through glycosidic bonds, resulting in a highly branched polysaccharide [71]. Dextrin provides strong hydrophilicity and has anionic characteristics in alkaline environments due to a considerable amount of carboxyl functional groups, which are ionized and converted to carboxylic acid functional groups [72,73]. Dextrin has been widely employed in froth flotation of oxide and sulfide minerals, specifically fine minerals [48,74]. Dextrin molecule's structure (Fig. 5b) is similar to the branched section of starch (amylopectin). However, its molecular weight (from 800 to 70000) is much lower than that of starch [35,75]. Dextrin is an effective depressant to reduce the floatability of pyrite. Table 4 lists the application of dextrin as a green pyrite depressant in various flotation systems.

Dextrin, instead of a toxic reagent such as sodium cyanide (NaCN), not only can reduce the cost and harmful effects on humans and the environment but also can improve the depression process of pyrite [41]. It was observed that the pyrite recovery in
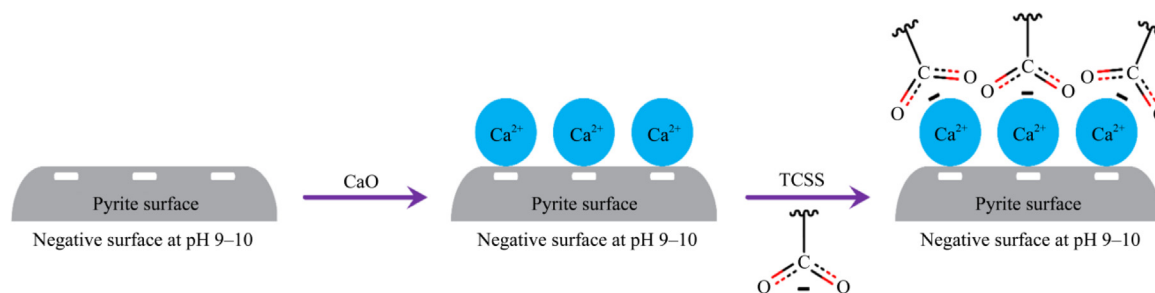
Fig. 8. The simplified adsorption process of CaO and TCSS on the surface of pyrite [47].

Table 4
Application of dextrin as a pyrite depressant.

Valuable minerals	Depressant dosage (mg/L)	pH	Collector	Metallurgical responses	Ref.
Sphalerite	50	4	PEX	Zn recovery: 75% Zn grade: 28%	[76]
Galena	4	10	DDTC	Max. recovery difference: 65%	[77]
Sphalerite	12	7	NaAX	Max. recovery difference: 67.7%	[49]
Sphalerite	12	9	NaAX	Max. recovery difference: 68.1%	[49]
	100	8	SPX	Pyrite recovery: ~15%	[48]
	100	8	PEX	Pyrite recovery: ~12%	[48]
	150	7	PAX + KIPX	Pyrite recovery: 88.75%	[78]

Notes: PEX: potassium ethyl xanthate; DDTC: diethyldithiocarbamate; NaAX: sodium amyl xanthate; SPX: sodium propyl xanthate; PAX: potassium amyl xanthate; KIPX: potassium isopropyl xanthate.

the absence of a depressant is over 80% when pH is below 10; however, 10 mg/L dextrin can depress pyrite particles and reduce its recovery to below 40% at pHs higher than 6. Increasing the amount of this polysaccharide-based reagent can show a negligible effect on pyrite depression (Fig. 9). It was reported that at pH below 4, dextrin cannot adsorb onto the pyrite surface [41]. As illustrated in Fig. 10, dextrin molecules can adsorb on the ferric oxyhydroxide sites, while xanthate ions only adsorb on anodic sites of the non-oxidized surface of pyrite [41,76,79]. The importance of the iron hydroxide species' formation for pyrite depression has also been reported in various investigations [48,80]. López-Valdivieso et al. [48] realized that the highest amount of hydroxide species was present on the surface of oxidized pyrite at pH 7.5, while the greatest dextrin depression occurred at pH 8 [48]. Sun et al. [49] indicated that dextrin did not affect the adsorption of sodium amyl xanthate (NaAX) on the sphalerite surface, while depressing Cu-activated pyrite (pH 7–9) [49]. They realized that dextrin adsorption onto pyrite occurred because the hydroxyl functional groups present in the dextrin structure could react with metallic hydroxyl species on the pyrite surface. This formed a passivation layer on
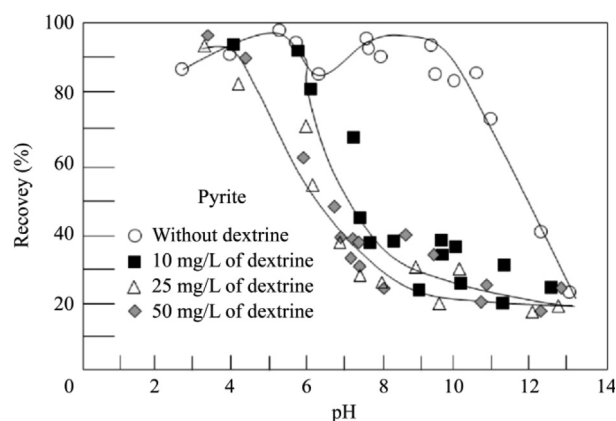

Fig. 9. Pyrite recovery as a function of pH in the absence and presence of various dosages of dextrin as a depressant and 1×10^{-4} mol/L sodium isobutyl xanthate (SIBX) as a collector [41].

pyrite particles, leading to pyrite depression [49]. Surface sites in which metal species are not accessible cannot absorb the dextrin molecule. However, after surface oxidation or the presence of metal ion impurities, dextrin appears on those surface sites (the type of metal ions is not essential for dextrin adsorption) [80,81].

Wang et al. [77] studied the combined depression impact of dextrin and calcium hypochlorite [Ca(ClO)$_2$] in the galena-pyrite flotation system. At pH 10, micro flotation test results revealed that combining these two depressants could efficiently depress pyrite particles and selectively separate them from galena. This combined depressant attained an enhanced recovery difference between the minerals (more than 60%). X-ray photoelectron spectroscopy (XPS) measurement demonstrated that the pretreatment using Ca(ClO)$_2$ could oxidize pyrite and galena surfaces. However, the oxidation effect was stronger on pyrite particles than on galena. After adding Ca(ClO)$_2$, hydroxyl compounds formed species on the pyrite surface through oxidation were more detected than on the galena surface. The higher surface oxidation species enhanced dextrin adsorption on the pyrite surface. It was also reported that dextrin's active groups interacted with metallic hydroxyl compounds formed on the pyrite surface through chemical coordination [77]. In other words, such as in starch (Fig. 8), the presence of bivalent cations in the solution, for example, Ca^{2+}, improves the adsorption and, therefore, the depression effect of dextrin [47,73,82]. These cations can play the "bridges" role between carboxymethyl cellulose (CMC) molecules and the surface of minerals [35]. Ca-containing ions are found in various species, such as Ca^{2+}, Ca(OH)$^+$, and Ca(OH)$_2$. After their adsorption or precipitation on the mineral surfaces, they considerably improve the bonding strength between the hydroxyl functionalities (present in polysaccharides structure) and mineral sites [44,73].

2.3. Guar gum

Guar gum (GG) is a naturally occurring water-soluble polysaccharide obtained from seeds of a plant of the Leguminosae family, and its average molecular weight is between 100000 and 2000000. It provides high viscosities to aqueous solutions even at low concentrations (≤1% w/v) [83,84]. GG contains a complex polysaccha-
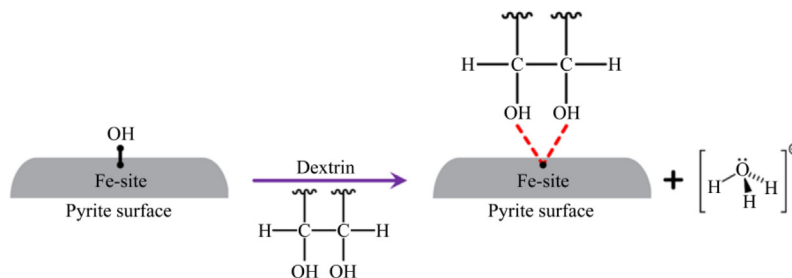
Fig. 10. The adsorption of dextrin onto pyrite surface [76].

ride called galactomannan, which is a polymer of D-galactose and D-mannose (Fig. 5c) [85]. It has nine —OH groups in each unit of its structure. These —OH groups are accessible for the GG molecule to attach via hydrogen bonding to mineral surfaces and water molecules [44]. These features have made GG powder extensively applicable in various industries, including cosmetics, pharmaceuticals, textiles, and food [84]. In flotation separation technology, GG has been used for the depression of calcite [86], talc [87], hematite [88], and quartz [89]. Also, it was reported that GG could be a promising depressant for pyrite.

Bicak et al. [44] showed that GG, even in a low concentration (0.1 mg/L), could significantly decrease pyrite recovery. It was noted that the difference in GG molecular weight had no tangible effect on the pyrite floatability; however, pH played a key role in this respect. The pyrite depression by GG was effective in an alkaline environment because of the hydrophilic iron oxyhydroxide coating formation [44]. In other words, GG could be more easily adsorb onto pyrite surface in the pH range of 7.5–11, and the most efficient pyrite depression was observed at approximately pH 10. It was also reported that under the same condition, GG could be more easily absorbed on the pure pyrite surface than dextrin [67]. Like other polysaccharides, the hydroxyl functional groups in the GG structure chemically interacted with the iron hydroxy, and forming complexes on the pyrite surface at a pH of 5.5 to 8.5 [67].

GG also showed a reasonable pyrite depression efficiency during chalcopyrite flotation using seawater at pH 8 in copper ore beneficiation plants (Fig. 11). The pyrite depression by GG coincided with the forming of massive aggregates, which were generated due to the flocculation phenomenon. These aggregates were so massive that the air bubbles could not transfer them to the froth zone of the flotation cell. However, an overdose of GG decreased

agglomerates' stabilization, reducing the inhibition of GG on pyrite particles [90]. However, unlike starch, CMC, and dextrin, Ca species cannot significantly affect the adsorption of GG onto the pyrite surface at pH 9, where the predominant species in solution are Ca^{2+} and $Ca(OH)^+$. This is probably due to the higher innate affinity of GG toward pyrite surface, compared to other polysaccharides, for which the presence of Ca species facilitates the adsorption through enhancing the bonding between —OH functionalities on mineral surfaces and polysaccharides' structure or decreasing the electrostatic repulsion between them [44]. The properties of GG also can be improved by modification techniques. To produce low molecular weight, GG can be de-polymerized and modified. Partial hydrolysis, by thermal processes, ultrasonication, acidic solutions, or enzymes, is the most common method for GG modification. Additionally, some weaknesses of GG, such as its limited hydration capability and low thermal stability, can generally be modified with grafting in the presence of polyacrylamide [91]. However, there is no research related to the role of the modification process in the effectiveness of GG as a pyrite green depressant, and this fundamental gap needs to be filled.

2.4. Carboxymethyl cellulose (CMC)

Carboxymethyl cellulose (CMC) is an organic substance derived from cellulose, the most abundant polymer on the earth and a linear polysaccharide of anhydrous glucose. CMC is a water-soluble anionic reagent with a molar mass varying from 50000 to 800000, in whose structure repeating units are linked by β-1,4-glycosidic bonds. The presence of carboxymethyl functional groups (i.e., —CH_2COOH) in the CMC skeleton is its main difference from cellulose molecules. These anionic functional groups have been substituted by hydrogen atoms in hydroxyl groups on cellulose molecules (Fig. 5d) [92,93].

Due to its important properties, such as availability, affordability, and non-toxicity, CMC has been extensively used in various applications, including adhesives, food, tissue engineering, pharmaceuticals, construction, mineral processing, etc. [94–96]. In froth flotation, CMC has been employed as a green depressant for various oxide and sulfide minerals [97–99]. Compared to the molecular structure of GG, CMC possesses negative carboxylic functional groups, which could improve its selectivity in the flotation of sulfide minerals. The main reason for such an improvement is that hydroxyl groups preferentially attach to metal hydroxyl complexes, whereas carboxyl groups (present in GG skeleton) are likely to react with various metallic species on mineral surfaces [44,99].

As mentioned, the GG adsorption mechanism onto mineral surfaces is affected by its molecular weight, whereas CMC adsorption is affected by its charge, as represented by the degree of substitution and not molecular weight [100]. Bicak et al. [44] investigated the influence of two forms of CMC depressants, namely LDS (low degree substitution, 0.47) CMC and HDS (high degree substitution, 0.86) CMC for pyrite depression at pH 9. They indicated that the depression efficiency of LDS CMC was higher than that of HDS CMC. This
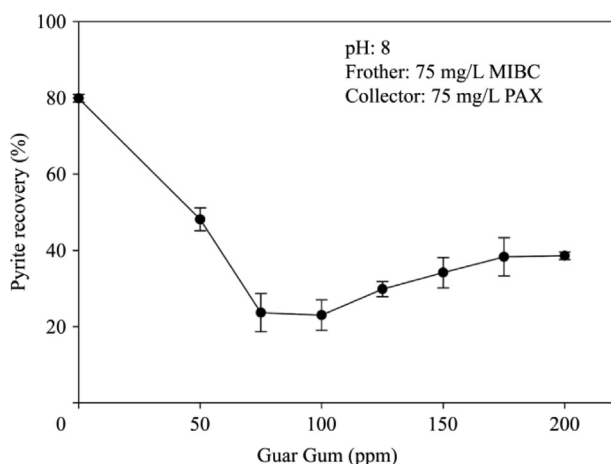

Fig. 11. The effect of GG dosage on the pyrite floatability (MIBC: methyl isobutyl carbinol) [90].

was attributed to lower electrostatic repulsion between LDS CMC and pyrite particles, which is less negatively charged than HDS CMC, leading to more CMC adsorption onto the pyrite surface. For effective depression of pyrite, CMC needs a relatively high concentration (500 mg/L LDS CMC). Moreover, since pH influences carboxyl functional groups, pyrite surface hydroxylation, and its surface charge, CMC adsorption onto pyrite surface is pH-dependent. Adsorption isotherms exhibited that the amount of adsorbed CMC on the pyrite surface slightly decreased when pH exceeded 9. This phenomenon occurred due to the intensified electrostatic repulsion between the negatively charged pyrite surface and CMC [44].

Like dextrin and starch, Ca cations can improve the CMC adsorption onto pyrite and enhance its depression impact, specifically in the case of HDS CMC at pH 9 [35,44]. In general, $Ca(OH)^+$ species attracted on the pyrite surface can highly facilitate CMC adsorption through an electrostatic attraction process. Another phenomenon assists electrostatic attraction force in CMC adsorption on pyrite surface. When calcium hydroxide precipitated on pyrite, the metallic hydroxide sites on the mineral surface would increase. Therefore, the probability of H-bonding attachment between —OH functional groups (in the structure of both pyrite surface and CMC) enhanced, facilitating pyrite depression. Moreover, carboxylic acid functional groups may also interact with Ca $(OH)^+$ and Ca^{2+} via chemical mechanisms [44]. Meanwhile, CMC chain coiling can occur in a highly ionic environment, which also improves the CMC adsorption onto pyrite. This is because, under these circumstances, the electrical charge of CMC is screened, resulting in more efficient pyrite depression [35,44]. Also, coiled CMC molecules can be an effective depressant, which passivates the mineral surface and prevents collector adsorption [35].

Unlike dextrin and starch, CMC's inhibition of pyrite floatability is because of competition between CMC and xanthate for adsorption on the pyrite surface (Fig. 12) [40]. This makes the CMC absorption process on pyrite highly dependent on the order of adding flotation reagents and their concentration. Feng et al. [101] indicated that the sequence for adding potassium amyl xanthate (PAX) and CMC significantly affects depression efficiency in a pyrite-chlorite flotation system. They revealed that CMC could not only be used as a chlorite depressant but could also affect pyrite floatability when added before PAX. On the other hand, the diminished depression impact of CMC on the pyrite surface in the presence of a pre-adsorbed layer of PAX is attributed to the competitive adsorption of CMC and PAX [101]. Ahmadi et al. [78] investigated the depression strength of various CMC dosages (50, 100, and 150 ppm) in a pyrite-containing flotation system in the presence of PAX plus potassium isopropyl xanthate (KIPX) as mixed collectors. They noted that high concentrations of CMC are required to effectively cover the pyrite surface to prevent xanthate

adsorption, and depress pyrite [78]. However, it was suggested that the pyrite depression by CMC increases only up to an optimum concentration value. It was documented that in the case of native and oxidized starches, larger molecular size (compared to CMC) allows them to adsorb a much greater number of hydroxyls on the pyrite particle sites. Free branches of polymer, which can extend from the mineral surface into the aqueous environment, are a probable explanation for why pyrite recovery remains dependent on starch concentration but is independent in the case of CMC at concentrations higher than 300 g/t [69].

2.5. Chitosan

Chitosan is also one of the most available polysaccharide-based substances and is an extensively used cationic biopolymer. Chitosan is generally produced in the process of chitin deacetylation. The presence of amino groups in its chemical structure enables it to become cationized in acidic environments. Therefore, chitosan can adsorb readily onto anionic sites through electrostatic attraction force. The amino and hydroxyl groups can also provide suitable active sites for forming metallic species [102]. Most chitin and chitosan are obtained from marine crustaceans' shells, particularly prawns and lobsters. Chitosan can also be produced from other sources, including honeybees, mushrooms, and silkworms [103]. Chitosan structure (Fig. 5e) is generally characterized by two important factors: molar mass and deacetylation degree. The number of various functional groups in the chitosan structure depends on these factors, and synthesizing mechanisms make chitosans vary in structural features [102,104]. Chitosan has also been used as an adsorbent reagent in wastewater treatment to remove heavy metal ions. This is because of the presence of hydroxyl and amine functionalities in the structure of chitosan, providing it with a strong chelating ability [104,105]. Since the complexity of mineral ores and environmental protection requirements have recently risen, eco-friendly and effective chemicals such as chitosan have gained widespread attention in froth flotation (Table 5) [105–107].

Huang et al. [105] investigated the depression ability of chitosan. They indicated that chitosan had a depressive impact on both galena and pyrite at a concentration of 0.67 mg/L, but its depression effect on pyrite was much stronger than on galena. A decrease in galena and pyrite recoveries was observed when the pH of the pulp was increased. In the mixed binary of galena and pyrite tests, it was found that chitosan could selectively inhibit pyrite floatability, whereas galena remained floated at pH 4. It was noted that chitosan preferentially interacted with pyrite particles, and surface analyses by time-of-flight secondary ion mass spectrometry (ToF-SIMS) confirmed this mechanism. However, according to ToF-SIMS results, a greater amount of chitosan was
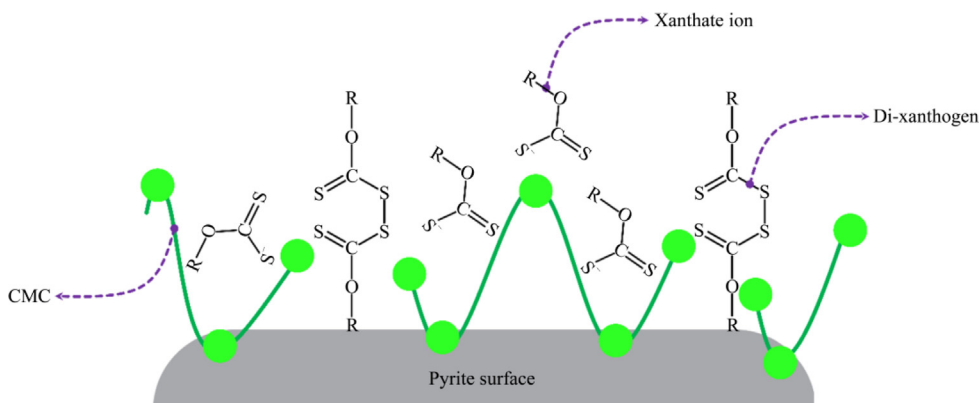

Fig. 12. The influence of CMC pre-adsorption on xanthate adsorption on pyrite surface [40].

Table 5
Application of chitosan as pyrite depressant.

Valuable minerals	Depressant dosage (g/t)	pH	Collector	Metallurgical responses (%)	Ref.
Galena	0.67	4	Potassium ethyl xanthate	Pyrite recovery: 23% Galena recovery: 68%	[105]
Galena	50	7	Sodium isopropyl xanthate	Maximum separation efficiency	[108]
Chalcopyrite Sphalerite Galena Chalcopyrite	85	7.8	Sodium isobutyl xanthate	Pyrite-galena system: ~61% Pyrite-chalcopyrite system: ~15% Pb grade: 9.84%	[107]
				Fe grade: 3.06% Cu grade: 1.70% Pb recovery: 83.41% Fe recovery: 15.33% Cu recovery: 63.37%	

absorbed on the surfaces of galena and pyrite in a neutral environment (pH 6) compared to acidic conditions (pH 4). XPS analysis showed that hydroxyl and amine functionalities in the chemical structure of chitosan interacted with the pyrite surface and caused chemisorption [105]. The selective interaction of chitosan with pyrite rather than galena surface was attributed to greater affinity of iron cations (Fe^{2+} and Fe^{3+}) existent on pyrite surface than lead cation (Pb^{2+}) on the galena surface towards chitosan [105].

Monyake et al. [108] studied the depression ability of chitosan-grafted-polyacrylamide (Chi-g-PAM) in separating a complex sulfide ore from Mississippi Valley comprising chalcopyrite, galena, sphalerite, and pyrite (Fig. 13). Flotation outcomes revealed that Chi-g-PAM was preferentially adsorbed onto pyrite particles among all other ore minerals. These experiments confirmed that this organic polymer could selectively depress pyrite in a complex sulfide ore under specific circumstances. XPS results revealed that the chemisorption mechanism was responsible for the interaction between Chi-g-PAM and pyrite. A comparison between the performance of Chi-g-PAM and sodium cyanide clearly showed that Chi-g-PAM (which is not toxic, unlike sodium cyanide) could improve the separation efficiency (the recovery difference was 35%) [108].
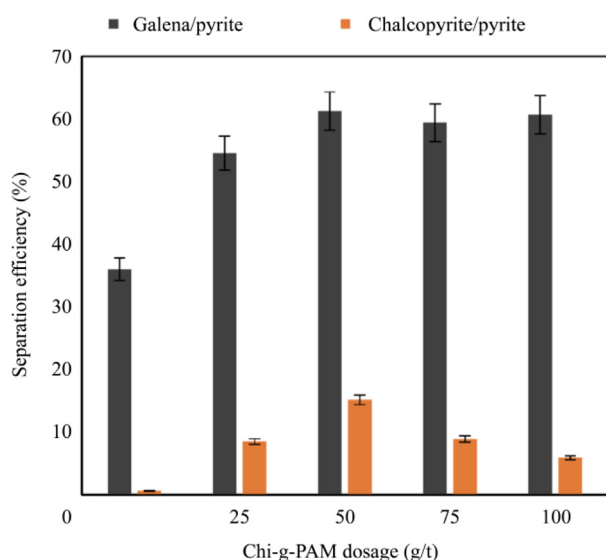
2.6. Locust bean gum (LBG)

Locust bean gum (LBG) is a polysaccharide-based polymer with a high molecular weight that shares identical monomeric struc-

Fig. 13. The effect of Chi-g-PAM concentration on the separation efficiencies in a complex ore containing base metal sulfides [108].

tures with GG as another galactomannan polysaccharide. However, the mannose/galactose ratio in LBG is greater than that in GG by a factor of approximately 4. This white to creamy white powder is obtained after milling the seed endosperm of the fruit pod of the carob tree. Hence, LBG is also known as carob gum. It can be sufficiently hydrated in hot water (80–85 °C) to increase the solution viscosity. Therefore, it is extensively used as an additive (e.g., emulsifier, modulator, thickener, stabilizer, etc.) in various pharmaceutical, textile, and food industries [51,109,110]. LBG (Fig. 5f), as a member of galactomannans, is a linear polysaccharide consisting of -(l–4)-mannose backbone with single D-galactopyranosyl units attached via -(l–6) linkages as a side branch. These side branches are not distributed uniformly in the main backbone chain [110,111]. Some unsubstituted -D-mannopyranosyl chain segments are also present, alternating with -d-mannopyranosyl units substituted with -D-galactopyranosyl side branches [112,113].

LBG has been employed as a green depression reagent to effectively separate various base metal sulfides, including galena, sphalerite, and chalcopyrite [32,114]. However, its depression impact on pyrite particles has rarely been investigated. Shen et al. [50] used pure pyrite and chalcopyrite samples to investigate the LBG's depression effectiveness in the flotation separation when using sodium butyl xanthate (SBX) as a collector. Micro-flotation experiments indicated that the pyrite recovery significantly diminished when adding LBG as a depressant (pH 8), while the chalcopyrite recovery was comparatively unchanged. Contact angle, zeta potential, and surface adsorption analyses indicated that LBG had a stronger affinity to the surface of pyrite rather than chalcopyrite. Fourier transform infrared spectroscopy (FTIR) and XPS analyses confirmed that LBG was physically adsorbed onto the pyrite particles. In this adsorption mechanism of LBG on the pyrite surface, H-bonding and acid/base interactions could play an important role. Simultaneously, the hydrophobic sites on the pyrite surface may attract LBG's hydrophobic section, improving the adsorption process [50].

2.7. Konjac glucomannan (KGM)

Konjac glucomannan (KGM) (Fig. 5g) is a natural white powder that is categorized into neutral polysaccharide groups. It is mainly obtained from the underground part (tuber) of amorphophallus konjac. The core chain of KGM comprises D-glucose and D-mannose residues linked by-1, 4 glucosidic linkages in the ratio of 1:1.6, with the portion of branches connected by C-3 bond of D-glucosyl and D-mannosyl residues. There is approximately 1 acetyl in 19 residues through ester linkage [115,116]. Because of its functional and eco-friendly properties, such as water solubility, cohesiveness, and biocompatibility, KGM has been employed for

Table 6
Application of KGM as a pyrite depressant.

Associated mineral	Depressant Dosage (mg/L)	pH	Collector	Metallurgical responses	SE	Ref.
Talc	0	7	Potassium butyl xanthate		18.97	[118]
Talc	35	7	Potassium butyl xanthate	Talc recovery: ~90% Pyrite recovery: 20%	55.1	[118]
Chalcopyrite	10	9	Potassium butyl xanthate	Pyrite recovery: <5% Chalcopyrite grade: 83.69% Cu recovery: 85.64%	50.53	[51]

various applications. In flotation separation, the effectiveness of KGM as a depressant for decreasing the talc floatability in a talc-chalcopyrite mixture has been previously proved [117]. Deng et al. [118] studied the influence of KGM on the flotation efficiency between talc and pyrite. The obtained results showed that the pyrite recovery was also reduced with the addition of KGM. The contact angle analyses confirmed that adding potassium butyl xanthate (PBX) as a collector before KGM could increase the contact angles of pyrite. However, the addition sequence of KGM/PBX slightly affected talc contact angles. The adsorption measurements indicated that KGM could adsorb on talc and pyrite surfaces, while PBX only adsorbed on the surface of pyrite. The addition sequence of KGM/PBX affected their adsorption on the pyrite surface but not the talc surface [118].

Liu et al. [51] systematically examined the depression behavior of KGM in the pyrite-chalcopyrite flotation system. They also compared the performance of KGM to other green depressants, such as GG, dextrin, and starch. The results from single mineral flotation experiments showed that KGM had a greater depression impact on the pyrite surface than other natural depressants at pH 5–11. However, KGM slightly affected chalcopyrite floatability over the entire examined pH range. The better adsorption of KGM on the pyrite surface than on the surface of chalcopyrite was also verified by various analyses, such as adsorption measurements, FT-IR analysis, and zeta potential measurements. Moreover, XPS analyses showed that KGM adsorbed pyrite through physical attraction, and H-bonding and Bronsted acid-base interaction were considered the major attraction forces [51]. The application of KGM as a pyrite depressant has been summarized in Table 6.

3. Summary and conclusions

Pyrite removal is an important step in the upgrading of base metal sulfides. Pyrite has a strong affinity for xanthates, which are commonly used sulfide minerals collectors and can float along with valuable minerals, necessitating its deactivation. Studies have shown that biodegradable polysaccharides as available substances can selectively depress pyrite while leaving valuable minerals unaffected. These naturally derived organic chemicals, obtained from plants, have a wide range of molecular weights, meet environmental requirements, and contribute to green and sustainable production. These depression reagents interact with the pyrite surface through various adsorption mechanisms, including hydrogen bonding, chemical interaction, electrochemical attraction, and hydrophobic interaction, with some cases exhibiting multi-mechanism absorption.

Certain polysaccharides, such as starch, dextrin, and chitosan, have demonstrated better inhibitory effects and selective depression in specific binary systems involving pyrite and other minerals. Adding electrolytes, particularly calcium species, can enhance the affinity between depressants and the pyrite surface. Cationic calcium species (Ca^{2+} and $Ca(OH)^+$) significantly strengthen the depression effect of these depressants on the pyrite surface by reducing electrostatic repulsion and enhancing bonding with hydroxyl functionalities.

4. Future research

While biodegradable depressants have shown efficient depression on the pyrite surface, comprehensive studies on their applications, apart from starch, are limited. Conducting surface analyses using techniques such as XPS, Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), and FTIR is necessary to understand better the adsorption mechanism of novel depressants and collectors on pyrite surfaces. Despite promising results in some cases, there is still a significant gap in the fundamental studies to confirm the effectiveness of polysaccharides-based depressants in various flotation systems and conditions and understand the absorption mechanism.

Reducing the reagent concentration used in froth flotation and employing polysaccharides-based polymers to assist or replace conventional hazardous pyrite depressants are essential to moving toward green flotation. Understanding the effects of various parameters, such as particle size, pulp chemistry, flotation kinetics, and synergistic reagent interactions, is necessary when using biodegradable depressants. Most investigations have been conducted on laboratory-scale pure and artificial mixtures, leaving room for exploration with natural ores and also larger experimental scales (batch-pilot). Furthermore, understanding interactions within polysaccharides-based depressants and other flotation reagents during pyrite flotation depression are other areas that require further investigation to advance green flotation.

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