

Essentiality, Fate, Ecotoxicity, and Health Effects of Xanthates and Xanthates Based-Compounds—A Review

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Abstract

Xanthates are organic synthesized substances with a potentially wide range of applications. They may serve as essential components of many compounds or materials that also play a vital role in various industrial and socio-economic processes. Addressing the question of the use of xanthates without considering their toxicity, and their decomposition process and products would be ecologically and healthily less sustainable. To date, related information is still dispersed and less known to the public. Therefore, this work provides a comprehensive overview of the existing information on the essentiality, fate, ecotoxicity, and health effects of xanthates and associated compounds. According to available information from scientific, technical, and professional circles, xanthates are diverse, usually with a carbon chain of two to six carbon atoms. They play a crucial role in the sectors of the mining and mineral processing industry, agriculture, wastewater treatment, metal protection, rubber vulcanization, the pharmaceutical industry, and medicine. Xanthates' degradation under different factors and mechanisms, which determine their fate in the environment, leads to the formation of toxic substances, mainly carbon disulfide, carbonyl sulfide, hydrogen sulfide, and hydrogen peroxide. Xanthates and xanthates degradation products are seriously hazardous to humans, animals, soil and aquatic organisms, enzymatic system, etc. Simultaneous exposure to xanthates and metals results in the magnification or reduction of their toxicity level, depending on the exposed organisms. Such toxicological dimensions should attract more scientific and public attention for more safe production, use, storage, and disposal of xanthates. Due to the high affinity of xanthates for metal, xanthates-modified compounds are efficient metal chelating agents. Such a property should be explored to develop potentially low-cost and effective alternatives for metal removal and recovery from contaminated media. The same applies to developing appropriate methods for the evalua-

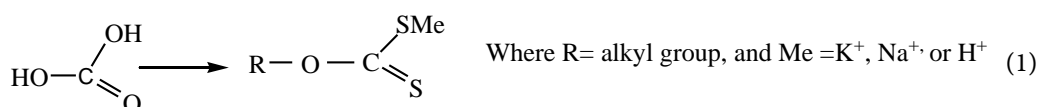
tion and management of the simultaneous presence of xanthates and metals in the environment.

Keywords

Xanthates, Xanthates Compounds, Essentiality, Ecotoxicity, Health Effects

1. Introduction

Xanthates are a group of synthesized toxic organic chemicals widely and hugely involved in various crucial socio-economic processes while being of great ecological and health concern. They are products of carbonic acid in which two oxygen atoms are substituted by sulfur, and one hydrogen atom is replaced by an alkyl group, as shown in the following reaction (Bulatovic, 2007) (Equation (1)).



when metals take place to the active proton of the xanthic acid (ROC(=S)SH), the compounds are referred to as metal xanthates or metal dithiocarbonates.

Xanthates synthesis may involve different processes and substances through a sequence of alkylation and xanthation reactions (Ma, Wang, & Zhong, 2018). However, they are mainly obtained by reacting an alkali hydroxide with carbon disulfide and alcohol (Wills & Napier-Munn, 2006) (Equation (2)) or by the reaction of alkoxide with carbon disulfide.



where R = Alkyl group, and M-Alkali metal.

The obtained final product is a wet mixture that will be dried into various commercial forms (powder, granules, pellets, tablets, or flakes) (Ma, Wang, & Zhong, 2018).

For more than a century, xanthates are used, mainly in mineral beneficiation and processing. However, they serve many other uses, including in the sectors of agriculture (e.g., as pesticides and antifungal agents, medicine, pharmaceutical (e.g., as chemicals synthesis agents), rubber (for rubber vulcanization), metallurgy (e.g., for metal protection and metal plating), etc. The use of xanthate-based products or xanthates-containing compounds expands their application range. Each compound can be used alone or in combination with other substances (Bulatovic, 2007). However, using such hazardous substances can only be environmentally efficient if the manufacturers and users manage to prevent their associated pollution and impacts. The same applies to the substances from which they are made, including those that may occur naturally and whose concentration should remain close to their background values. In most cases, it remains a great challenging deal.

Xanthates may be released into the environment from various sources and

through different ways, including during manufacturing (e.g., residue production), transportation (e.g., accidental spillage), storage, application, and waste disposal (e.g., Seepage from tailings), etc. By dispersing in water and air, xanthates can reach direct and non-immediate environments. Xanthate spreading from flotation tailing dams' failures magnifies their presence in the environmental components. These failures, of which nearly 90% of cases happen in active mines (Rico, Benito, Salgueiro, Díez-Herrero, & Pereira, 2008) account for the most reported mining-related incidents globally (Chen et al., 2011; Edraki et al., 2014; Liu, Liu, Zhang, Borthwick, & Zhang, 2015a; Rico et al., 2008).

Xanthate's release into the environment is more critical as the supply chain may take place in or around environmentally, economically, and socially sensitive areas such as inhabited, agricultural, fishing, and protected areas. Regions with high water stress are also not spared (Musiyarira, Tesh, & Dzinomwa, 2017). In addition, their selection and application are usually based on their effectiveness (high mineral selectivity) and economic advantage (relatively low cost) (Langa, Adeleke, Mendonidis, & Thubakgale, 2014; Pawlos, Konieczny, & Krzeminska, 2016; Urbina, 2003). Conversely, the ecotoxicological and health side is not sufficiently considered.

The environmental concern associated with xanthates is not only due to their toxic nature but also to their instability and decomposition. Xanthates decomposition can lead to the generation of various compounds (Chen, Sun, Li, & Xiong, 2017; Elizondo-Álvarez, Uribe-Salas, & Bello-Teodoro, 2021; Shen, Nagaraj, Farinato, & Somasundaran, 2016) that enlarge their nuisance spectrum. Carbon disulfide (CS₂), Carbonyl sulfide (COS), alcohol (R-OH), carbonate (CO₃²⁻), hydrogen sulfur (HS), etc., are some of their most known decomposition's products. Xanthate's degradation products were the most found in the flotation waste-receiving sites, including tailings ponds (Rostad, Schmitt, Schumacher, & Leiker, 2011).

Depending on the substances and the affected organisms, they may be less, equally, or more toxic than their original compounds. The exposed organisms may undergo their individual or combined action that can result either in lowering, neutralizing, or magnifying the adversity (Bararunyeretse, Ji, & Yao, 2017a; Bararunyeretse, Zhang, & Ji, 2019b; Bulatovic, 2007). Moreover, due to their behavior in the presence of other types of toxicants, such as metals (persistent and non-biodegradable substances) and the associated risks, xanthate's application deserves special attention. This can help to reduce their spreading and effects on the living system, particularly the water and soil organisms (Bararunyeretse, Beckford, & Ji, 2019a; Bararunyeretse et al., 2017a; Bararunyeretse, Zhang et al., 2019b; Li et al., 2020).

From the above described, it is obvious that despite the essentiality of xanthates and xanthates compounds, their application is subject to increasing criticism. It raises a great scientific interest and should be well addressed and un-

derstood with a view to its sustainability. However, fewer studies have focused on this research area. Therefore, it remains crucial to carry out information actions aimed at broad knowledge, by the scientific and public audiences, on the sustainability of the production, use, and handling of these substances. It is in this framework that this review aims to present the state of knowledge and recent development on the use of xanthates and xanthate-based compounds. Particular attention is paid to their ecotoxicological and health effects.

2. Essentiality of Xanthates and Xanthates-Based Compounds

2.1. Xanthates Use in the Mining and Ore Processing Industry

Xanthate's use in the mining and ore processing industry (Aznar-Sánchez, Velasco-Muñoz, García-Gómez, & López-Serrano, 2018; Bulatovic, 2007; Calvo, Mudd, Valero, & Valero, 2016; Elizondo-Álvarez et al., 2021; Han et al., 2020; Nagaraj, 2000; Schmidt, 2018) is crucial. It is still growing along with the increasing demand for raw materials and metals (Calvo et al., 2016; Northey, Mohr, Mudd, Weng, & Giurco, 2014). For example, the global use of cobalt should triple in the 2020-2030 decade (Tijsseling, Dehaine, Rollinson, & Glass, 2019). However, valuable minerals (*e.g.*, gold, nickel, copper, lead, zinc, cobalt, etc.) occur in the earth's crust in a very small proportion, compared to the minerals gangue (Dunne, 2005; Rostad, Schmitt, Schumacher, & Leiker, 2011). Therefore, to efficiently improve their extraction and concentration, a revolutionary process, froth flotation, was introduced at the beginning of the 19th century (Bulatovic, 2007) and became widely adopted (Aznar-Sánchez et al., 2018; Langa, Adeleke, Mendonidis, & Thubakgale, 2014; Liu & Zhang, 2014; Reyes-Bozo et al., 2014; Wright & Czelusta, 2003). At the Minera Esperanza (in Chile), the daily process plant capacity was estimated at 97,000 tons of copper-gold ore (Garner, Naidu, Saavedra, Matamoros, & Lacroix, 2012). Worldwide, billions of tons of ore are annually treated through flotation (Bulatovic, 2007; Salarirad et al., 2021; Yang, Xie, Lu, & Li, 2018). The process relies, greatly and irreplaceably, on the use of flotation reagents, including collectors (Langa et al., 2014). Collectors (ROCS₂M, R, and M referring to, respectively, an alkyl group and an alkali metal such as Na and K) are well-known as water-soluble chemicals. They have a heteropolar molecular structure, comprising a non-polar part (a water-repellent hydrocarbon radical) and a polar group ($S = C - S^-$). The ability of the polar group to interact with water and the polar surface of minerals allows them to selectively bind on minerals in the flotation pulp or slurry. The result is the formation of insoluble metal-xanthate complexes, which are strongly hydrophobic (Wills & Napier-Munn, 2006), and the easy metal recovery from the rest of the gangue (Bulatovic, 2007; Li et al., 2015; Molina, Cayo, Rodrigues, & Bernardes, 2013; Pearse, 2005; Reyes-Bozo et al., 2014). The following figure (Figure 1) illustrates a simple flotation cell for the extraction and concentration of sulfide minerals.

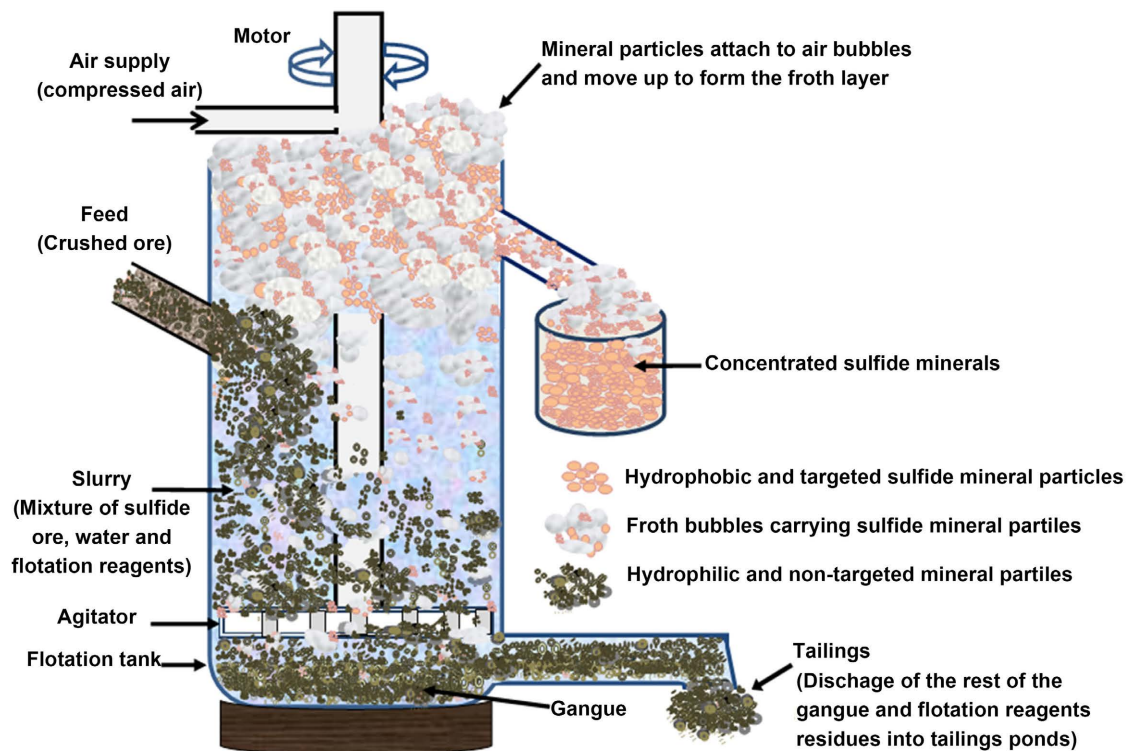


Figure 1. Simple flotation cell for the concentration of sulfide minerals.

Since collectors are chemically and functionally diversified, selecting the most efficient (type and quantity) for a given mineral must be given priority. The optimization generally depends on the selectivity for minerals and their cost effectiveness. Collectors can be specifically formulated to meet individual ore types and site requirements. Xanthates ($\text{ROCS}_2\text{Na}^+/\text{K}^+$), first produced by Zeize in 1882 and first used in froth flotation in 1924 (Bulatovic, 2007), are the most powerful and applied typical collectors (Bulatovic, 2007; Elizondo-Álvarez et al., 2021).

Xanthates are not only highly selective and effective collectors for mineral separation and concentration, but are also relatively cost-effective (Li et al., 2015; Pearse, 2005). They are the most preferred for the flotation of sulfide minerals (metals combined with sulfur), native metallic elements (Bulatovic, 2007; Fu, Feng, Yang, & Yang, 2015; Kempainen, Aaltonen, Sihvonen, Leppinen, & Sirén, 2015; Zhu, Song, Liu, & Li, 2013), and oxidized minerals (e.g., malachite, cerussite, and anglesite). Oxidized minerals are the most demanding in terms of quantity and effectiveness (Wills & Napier-Munn, 2006). Recently, xanthates have proven their effectiveness for the beneficiation of rare earth elements (Anderson, Taylor, & Anderson, 2017; Elizondo-Álvarez et al., 2021; Jordens, Cheng, & Waters, 2013; Marion, Li, & Waters, 2020). Since sulfide minerals are quantitatively the most extensively mined and processed worldwide (Bararunyeretse et al., 2017a, 2017b; Bulatovic, 2007; Salarirad et al., 2021; Yang et al., 2018), xanthates are by far the most quantitatively used collectors, followed by dithiophosphates

(Dunne, 2005; Nagaraj, 2000; Pearse, 2005).

The most commonly used xanthates are Potassium amyl xanthates ($C_6H_{11}OS_2K$) for Cu, Zn, Ni, Cu–Mo, Cu–Au, Cu–Zn, Pb–Zn, Cu–Pb, Cu–Ni, Potassium ethyl xanthates ($C_2H_5OCS_2K$) for Cu, Cu–Pb, Cu–Mo, Pb–Zn, Cu–Zn, and Cu–Pb–Zn, Sodium ethyl xanthates ($C_3H_5NaOS_2$) for Cu, Ni, Pb, Au, Zn, and Cu–Pb, Sodium isoamyl xanthates ($C_6H_{11}NaOS_2$) for Cu, Pb, and Cu–Ni, Sodium isobutyl xanthate ($C_5H_9NaOS_2$) for Cu, Cu–Au, Cu–Zn, Cu–Pb, and Ni, and Sodium isopropyl xanthate ($C_4H_7OS_2Na$) for Cu, Zn, Cu–Pb, Pb–Zn, Cu–Zn, and Cu–Ni. For an optimum application of xanthates, the length of the xanthate's hydrocarbon chain that determines their effectiveness and adhesive power must be balanced with their water solubility level (Bulatovic, 2007; Kim, Kuh, & Moon, 2000; Tu et al., 2011).

The rate of xanthates consumption in sulfide mineral beneficiation, estimated at 20 - 500 g per ton ore (Bulatovic, 2007; Fu et al., 2015; Li et al., 2018; NICNAS, 2000), is continuously increasing over time (Reyes-Bozo et al., 2014). In 2017, Persistence Market Research indicated that the global xanthates consumption in mining was estimated at 52,000 tons in the year 1980 (Somasunclaran et al., 1987), 247,000 tons in the year 2016 and could reach 371,826 tons by the end of 2025. Such a spectacular rise is beyond the expected annual increase of 2% - 3% (Pearse, 2005) and may result from these three main reasons, namely: 1) the gradual depletion of high-grade ore reserves (Calvo et al., 2016; Northey, Mohr, Mudd, Weng, & Giurco, 2014; Reyes-Bozo et al., 2014) and easy-to-process ore (Urbina, 2003) along with 2) the continuous and growing demand for metals, which results in 3) the exploitation of complex and low-grade ore (Elizondo-Álvarez et al., 2021; Ikotun, Adams, & Ikotun, 2017; Rao, Bhaskar Raju, Prabhakar, Subba Rao, & Vijaya Kumar, 2009; Sicupira, Veloso, Reis, & Leão, 2011; Tijsseling et al., 2019; Urbina, 2003) leading to increasing of waste production. Recently, the use of xanthates was explored for the environmental desulfurization of sulphidic mine tailings and coal waste. This could help reduce the risk of Acid Rock Drainage via the removal of sulfide minerals prior to waste disposal (Kunene, 2014).

The above-mentioned raises the question of appropriate management strategies and specific stakeholder responsibilities. The xanthates production and market segment are dominated by a few key players, mainly those from North America (U.S, Canada, Mexico), Europe (U.K, France, Germany, Russia...), and Asia Pacific (China, Japan, South Korea, India...). In China a medium-sized producer can sell 30,000 tons per year (Ma et al., 2018). Thus, with nearly 68% share of the overall xanthates consumption in the Asia Pacific (APAC), which held 51.5% of the world xanthates market share in the year 2016, China could be the leading producer and consumer, followed by Australia.

<https://www.persistencemarketresearch.com/market-research/xanthates-market.asp>.

Conversely, Africa, one of the world's hubs of supplying natural resources (Cu, Au, Ni, Zn, Co, etc.), is much more an importer than a producer of chemi-

cals and could be a field of significant xanthates consumption and hazards.

2.2. Use of Xanthates for Metal Removal and Recovery from Wastewater

2.2.1. Metal Wastewater Treatment Techniques

Wastewater from different sources, including discharges from industries (e.g., mining, refining, tanneries, batteries, paper), municipal and household activities (Agoro et al., 2020), and agriculture (e.g., fertilizers, pesticides) (Opeolu, Bamgbose, Arowolo, & Adetunji, 2010) contain residues of precious metals and metalloids (e.g., Zinc, Lead, Mercury, Gold, Silver, Copper, Arsenic, Cadmium, Cobalt, Chromium, Nickel and Iron). Due to their non-biodegradability, persistence, bioaccumulation, and biotoxicity behavior, these elements are of great environmental and health risk (Homagai, Bashyal, Poudyal, & Ghimire, 2009; Igwe, 2007). Therefore, removing and recovering them from flotation wastewater, in an economical and eco-friendly way (Hegazi, 2013; Zhang, Wu, Huang, Shen, & Sun, 2018) has multiple advantages. The most prominent is that it can generate of extra profit for the industry while facilitating the treatment and reuse of metal-polluted water and preventing pollution.

The conventional methods include chemical oxidation or reduction, chemical precipitation, chemical coagulation, filtration, ion exchange, adsorption using activated carbon, or using natural zeolite, electrochemical treatment, reverse osmosis, membrane technologies, and evaporation recovery (Acharya, Kumar, & Rafi, 2018; Ahluwalia & Goyal, 2007; Fu, Lin, Li, Chen, & Peng, 2018). All these techniques present some disadvantages (e.g., high cost, sludge disposal problem, large chemicals consumption, etc.) that make them economically and environmentally less suitable (Acharya et al., 2018; Gupta, Nayak, & Agarwal, 2015; Hegazi, 2013; Saxena, Bhardwaj, Allen, Kumar, & Sahney, 2017). Alternatively, various sorbents have been tested for their metal sorption capacity and their application as effective, low-cost, and environmentally friendly techniques. These include the use of xanthates and xanthate-based materials (Xu et al., 1988), animals and plants (prokaryotes and eukaryotes) derived biomass (Ahluwalia & Goyal, 2007; Hegazi, 2013; Sekhar, Kamala, Chary, & Anjaneyulu, 2003; Tariq et al., 2018), chemically modified plant wastes (Acharya et al., 2018; Ngah & Hanafiah, 2008), and others types of sorbents such as fly ash, clay, iron-oxide-coated and, sulfonated coal (Bose, Bose, & Kumar, 2003). Their application is critically affected by different factors, comprising the pH condition, the metal and ligand concentration, the particle sizes, the presence of competing ions, and the contact time that lower their effectiveness. Safe disposal of the generated sludge is the most environmentally challenging. To a large extent, using xanthates and xanthates-containing sorbents serves to overcome these limitations (Xu, 1988).

2.2.2. Use of Xanthates and Xanthate Materials for Metal Removal and Recovery

Xanthates and xanthate-modified materials (e.g., starch xanthate, cellulose xan-

thate) are efficient agents for the removal and recovery of metals from contaminated water (Bailey, Olin, Bricka, & Adrian, 1999; Bose et al., 2003; Bricka, 1988; Bricka, Williford, & Jones, 1993; Igwe, 2007). Carbon disulfide (CS₂), which is their functional group and one of their decomposition products (Kim & Lee, 1999; Liang, Guo, Feng, & Tian, 2010; Zhang et al., 2016b), constitutes a major pillar to the process. CS₂ can form complexes with divalent transition metal ions yielding water-insoluble complexes of the xanthate bearing material and metal that can easily settle. As shown in the following lines, the formation of metal-xanthate precipitates by the addition of xanthates to metals solution (Chang, Chang, Lin, & Hsu, 2002) can help solve the metal-containing wastewater problems and meet the sludge disposal goal.

Adding potassium ethyl xanthates (PEX) to copper-containing wastewater drastically reduced copper initial load of 50 - 1000 mg/L to a minimum concentration of 3 mg/L, an acceptable limit for Taiwan EPA's effluents regulations (Arbabi & Golshani, 2016; Chang et al., 2002). Insoluble agro-based starch xanthate (IAX) was the most powerful chelating agent for copper and zinc. This is more advantageous than using other metal sorbents, such as sulfonated coal, biosorbent *G. lucidum*, and iron oxide coated. These sorbents are less effective or unsuitable in the presence of cyanide which inhibits their metals removal capacity (Bose et al., 2003).

From the following examples, we will also understand that the efficiency of xanthates and xanthates compounds is affected by the pH level. Insoluble starch xanthate can significantly remove various metals, with an optimum removal at a pH value above 7 (Bricka et al., 1993). The process can allow quick xanthate-metal sludge settlement and easy dewatering.

Mercury (Hg) was successfully removed from wastewater using starch xanthate (Patterson & Stein, 1997). At a bench scale at a pH value of 1, a mercury concentration of 10 mg/L was more than 97% removed after the wastewater treatment by starch xanthate and sedimentation (Campanella, Cardarelli, Ferri, & Petronio, 1986). Increasing pH could be more advantageous. The process resulted in a Hg concentration dropping from 100 mg/L to 0.001 (Tiravanti, Di Pinto, Macchi, Marani, & Santori, 1987) at the pH value of 5 and with an additional 0.45 µm filtration. Insoluble cellulose xanthate (ICX) is another efficient metal sorbent xanthate-modified material. It exhibited a nickel and copper ions removal rate of up to 83% and 98%, respectively, with a maximal removal capacity of 114.29 mg Ni/g and 126.58 mg Cu/g (Zhang et al., 2016b). Iryani and colleagues (Iryani, Risthy, Resagian, Yuwono, & Hasanudin, 2017) recorded a maximum adsorption capacity of 51.776 mg/g and 54.226 mg/g for Pb²⁺ and Cu²⁺, respectively, by using cellulose xanthate of sugarcane bagasse. From a laboratory test, the solidification of starch xanthates and cellulose xanthates sludges significantly increases the ability of these materials to reduce the leaching of Cd, Ni, and Hg from a synthetic waste solution, with a higher performance superior to that observed using hydroxide sludge (Bricka, 1988). With an initial Cd²⁺ ion concentration of 10 mg/L, a removal rate of 98.72% of Cd²⁺ was achieved by us-

ing 1 g/L of peanut shell cellulose xanthate whose adsorption capacity was 9.87 mg/g after 1.5 h contact time (Pan et al., 2013). Cd²⁺ was also successfully removed from an aqueous solution using the rice straw cellulose xanthate (Pan et al., 2014). For this case study, the high adsorption capacity of the rice straw cellulose xanthate (3.86 mg/g) and the high removal rate of Cd²⁺ (96.41%) were recorded by treating the solution containing 20 mg Cd/L with a rice-straw cellulose xanthate dose of 5.0 g/L for 2 hours.

Lead, cadmium, and nickel were removed from an aqueous solution, with a concentration reduction of 2072 mg/L to 15 mg/L, 1124 to 130 mg/L and 587 to 8 mg/L, for Pb, Cd, and Ni, respectively, by using insoluble cellulose xanthate (Kim & Lee, 1999). Ninety percent (90%) of the metal removal was reached within 30 min in neutral or slightly alkaline conditions (optimum pH) while, in an acidic pH of 2 - 3, the removal rate was limited to 40%. The use of cellulose xanthate as an osmotic membrane was applied as an advanced method for removing metals from water by reverse osmosis or ultra-filtration; the most important parameter to be controlled being the osmotic pressure (Igwe, 2007).

Orange peel xanthate also demonstrated high metal removal capacity, with a maximum metals adsorption capacity of 77.60, 76.57, 218.34, 49.85, and 15.45 mg/g for Cu²⁺, Cd²⁺, Pb²⁺, Zn²⁺, and Ni²⁺ (Liang et al., 2010). The observed performance of orange peel xanthate for Pb²⁺ adsorption was much higher than that recorded by using natural, formaldehyde-treated, and copolymer-grafted orange peel. The maximum adsorption capacity reached using these other materials did not exceed 46.61 mg/g for an initial Pb dose of 150 mg/L under batch and continuous mode (Lugo-Lugo, Hernández-López, Barrera-Díaz, Ureña-Núñez, & Bilyeu, 2009). Moreover, the orange peel xanthate presented a greater adsorption capacity for Pb²⁺ than other agro-based adsorbents, including rice husk, sawdust, seaweed, bagasse, fly ash, palm shell, tea waste, valonia tannin resin, and leaves from various plants species (Saka, Şahin, & Küçük, 2012). However, mercapto-acetic acid-modified orange peel showed higher adsorption capacity for copper (70.67 mg/g) and cadmium (136.05 mg/g) than that observed by using orange peel xanthate (Liang, Guo, Feng, & Tian, 2009). Xanthate-modified apple waste also exhibited high potential ability to remove iron, cadmium, zinc, and lead from an aqueous medium, the ion-exchange process being the dominant sorption mechanism (Homagai et al., 2009).

From these few examples, xanthate-modified materials can be considered as effective and low-cost bio-adsorbents for metals and could be used to reduce environmental pollution from industrial wastewater. Given effect of the pH condition and, since xanthates are unstable in the presence of moisture, the acidification of their containing medium as they degrade (Deo & Natarajan, 1998; Fu et al., 2015) offers more advantages of using insoluble xanthate-modified materials.

2.3. Xanthates Use in the Agriculture Sector

Xanthates have been explored for their potential use in agriculture, particularly

for their antifungal, antibacterial, and pesticide activity. Various xanthates and xanthates-containing compounds, including the mono- and dixanthates of di-propylene glycol and triethylene glycol can be used, individually or synergistically (mixture), as plant growth promoters and regulators. However, to avoid the unwanted side effect, including their toxicity to plants (Harvey et al., 1936), the optimum concentration was estimated at 100 ppm, corresponding to a high rate of chlorophyll accumulation (Danzig & Kinnersley, 1989).

Xanthates can serve as fungicides, with a mycelial growth inhibition rounding at 78% - 100%, and larvicides. They can be used as efficient antifeedant, insect growth regulator, and against plants pathogens such as *Colletotrichum falcatum*, *Fusarium oxysporium*, *Glomerella tucumanensis*, *Curvularia pallescens* that affect the growth and production of sugarcanes (Sengupta, Pandey, Rao, Shahi, & Jaiswal, 1998). Their toxic activity against brine shrimp (*Artemia salina*) has been proved through the use of synthesized alkyl xanthates (Rao, Venkateswarlu, & Raghavan, 2003). On this basis, it was suggested the application of alkyl xanthates in pest management. However, despite the lack of data, their use requires a prior side effect and dose-effect analysis. A 1936 study (Harvey, Zalar, & Landon, 1936) showed that xanthates such as sodium ethyl xanthates harmfully affect the aerial parts of herbaceous plants.

Xanthate-modified agricultural materials, such as starch xanthate and cellulose xanthate, have been reported as industrial synthetic biopolymers and high potential soil conditioners (soil stabilization, reduction of sediment runoff or prevention of soil erosion) (Orts, 2001; Orts et al., 2007; Orts, Sojka, & Glenn, 2000; Orts, Sojka, & Glenn, 2002; Orts, Sojka, Glenn, & Gross, 2013; Wood & Oster, 1985). They may have a higher molecular weight than polyacrylamide based polymers (PAM), well known as effective soil stabilizers (Orts et al., 2002).

Due to their charged disulfide group, xanthates attach to soil aggregates (Orts et al., 2013). They have similar binding ability to clays in soil as polyacrylamide based polymers (Wood & Oster, 1985). One percent (1%) cellulose xanthate solution was successfully applied at 22 kg/ha on sites to cope with the depressed seedling emergence caused by soil capping by weather (Page, 1980). Such material did not show depressive effect on the growth of the crops under experiment (carrots, onions, leeks, lettuce, and sugar beet) and did not present any interaction with herbicides. Although polyacrylamide based polymers are the most effective soil stabilizers (Orts et al., 2013), their non-biodegradability would limit or avoid their use along with the organic farming operations (Orts et al., 2007). Therefore, biodegradable compounds such as xanthate-modified materials were recommended as promising alternative. Nevertheless, the subject related research efforts seem to take a step back in the recent literature.

2.4. Use of Xanthates for Metal Protection

Xanthates are efficient corrosion inhibitors for metal protection (Becerra, Salvarizza, & Arvia, 1987). This capability is mainly due to their high affinity for

metal and subsequent sorption on the metal surface that can lead to the formation of ametal-xanthate layer. The process may be associated with a hydrophilic/hydrophobic transition on the metal surface (Chanturiya, Vigdergauz, Sarkisova, & Dorofeev, 2004). For example, Copper anodization in ethyl xanthate aqueous solution significantly enhanced the metal resistance to the corrosive attack of chloride ions. The higher performance was achieved through the combination of xanthates and benzotriazole (Souto & González, 2002). A similar phenomenon was observed for copper protection by potassium ethyl xanthate (Baeza, Guzman, & Lara, 2013; Becerra et al., 1987; Scendo, 2005; Souto, Fox, Perez, Laz, & Gonzalez, 1995).

2.5. Use of Xanthates in the Rubber Sector

Xanthates and xanthates-containing compounds (e.g., zinc alkyl xanthates, starch xanthates) are very reactive and very labile accelerators of the vulcanization (Buchanan, Weislogel, Russell, & Rist, 1968; Komatsu, 2009; Luo et al., 2013; Palaty, Devi, & Joseph, 2011; Sasidharan, Palaty, Gopalakrishnan, George, & Joseph, 2010; Wang et al., 2009). This fundamental process in the rubber industry consists of a complex chemical process enabling crosslinking of the long chains of rubber molecules and making them change the predominant plastic/viscous properties to elastic properties (Joseph, George, Madhusoodanan, & Alex, 2015) through reaction with the vulcanization agents (Luo et al., 2013). In the absence of accelerants, the vulcanization with sulfur alone is generally inefficient (*e.g.*, need of long period reaction, a large quantity of sulfur, and a high temperature of 140°C - 150°C) and generally with low-quality end products (Joseph et al., 2015; Komatsu, 2009; Zhang et al., 2016a). Alkyl xanthates reactions are ultrafast and active at low temperatures, even at room temperature as low as 25°C (Nitin, Scott, & Brendan, 2007), with better quality end products (Sasidharan et al., 2010). A successful xanthates reaction was performed to develop an environmentally friendly coupling agent for the surface modification of the precipitated silica-filled natural rubber compounds (Pattanawanidchai, Loykulnant, Sae-Oui, Maneevas, & Sirisinha, 2014). This process resulted in the formation of zinc salt of dixanthate-modified silica (ZMS) with smaller agglomerate size and superior dispersion when incorporated into a natural rubber matrix. Increasing the degree of xanthation led to increased filler dispersion. Moreover, a significant increase in cure efficiency and subsequent enhancement in the mechanical properties of the rubber vulcanizates were observed along with the system reinforcement with ZMS.

2.6. Use of Xanthates in the Pharmaceutical Industry and Medicine

Recent studies reported xanthates properties that could be explored for therapeutic intervention (Friebolin, Schilling, Zöller, & Amtmann, 2005; Sangeetha & Sekar, 2017; Shen et al., 2016). The most reported xanthate-containing com-

pound was the tricyclodecan-9-yl-xanthogenate (D609) which has a protective effect against amyloid beta-peptide (1-42)-induced oxidative stress (Sultana, Newman, Mohmmad-Abdul, Keller, & Allan Butterfield, 2004; Sultana et al., 2006). On this basis, the authors suggest that xanthate's properties could be useful for the treatment of Alzheimer's disease and other oxidative stress-related disorders. Moreover, xanthates could be therapeutically explored for their anti-tumor properties (Amtmann, 1996; Amtmann & Sauer, 1987; Amtmann et al., 1987; Friebolin et al., 2005; Larsson & Öberg, 2011). Xanthates have also shown antiviral activity, *i.e.*, inhibition of various DNA and RNA virus species (Sauer et al., 1984) in acidic pH conditions (Amtmann et al., 1987) and potential therapeutic intervention for HIV infections (Görgülü, Arslan, & Çıl, 2006; Mellert, Amtmann, Erfle, & Sauer, 1988).

3. Xanthates Ecotoxicity and Health Concern

In this article, the word "Ecotoxicity" refers to the properties and potential impacts of pollutants on organisms, populations, and communities of a given ecosystem. Xanthates and xanthate compounds are toxic chemicals potentially hazardous to terrestrial and aquatic living systems, which defines their ecotoxicity nature. Similarly, they are harmful to human health. The following lines summarize the available information on their toxic effects on humans and mammals, as well as on some soil and aquatic organisms.

3.1. Xanthates Toxicity to Humans and Mamals

The adversity of xanthates to humans and animals is a significant local and global issue (Shen et al., 2016). However, the subject has not yet attracted much scientific attention. The most available information is from technical and professional circles. These include the Materials Safety Data Sheets (MSDS) provided by xanthates manufacturers and suppliers. Among them, one can cite those set up by Redox Pty Ltd (Australia) for Sodium isobutyl xanthate (Revision 4), Mining chemicals (A division of CPCHEM, USA) for Sodium Isopropyl Xanthates, VAN WATERS & ROGERS INC.(USA) for Sodium ethyl xanthate, Brenntag Canada Inc. (Canada) for Potassium amyl xanthates (Revised in 2009), Xiamen Joyforce Chemical Industrial Co., Ltd (China) for Sodium/potassium isobutyl xanthate, Alfa Aesar and Central Drug House (P) Ltd (India) for Potassium ethyl xanthate (Revised in 2006), etc. Despite the importance of these MSDS, none can pretend to be sufficiently inclusive. Some of them are even very limited concerning certain fundamental aspects (including their ecotoxicity) in place of which is noted: "not known" or "no data available." Thus, they must be regularly updated while users must diversify the sources of information for proper handling and better impact prevention and management.

Some countries and institutions have also set up guidelines on mining chemicals. Among the most relevant and online available regulatory frameworks, one can cite the REACH (Registration, Evaluation, Authorization, and restriction of

Chemicals) established by the European Chemicals Agency (ECHA), the Convention for the Protection of the Marine Environment, set up by the OSPAR Commission (for the North East Atlantic), the National Industrial Chemicals Notification and Assessment Scheme (NICNAS) in Australia, the Canadian Environmental Protection Act (CEPA, 1999), the Regulations on Mineral Resources and Toxic Substances, under the control of the United States Environmental Protection Agency (US EPA), the guidelines established by the Queensland Department of Natural Resources and the Greenland Mineral Resource Authority.

From this information, it is largely stated that various xanthates have similar adverse effects (Bach, Nørregaard, Hansen, & Gustavson, 2016; Sasseville, Muhn, & Al-Sowaidi, 2003). Risks from xanthates are mainly associated with their 1) acute toxicity nature; 2) instability and decomposition that lead to the formation of various toxic and flammable products such as carbon disulphide (CS₂), alcohols, etc., (spontaneous combustion that generates harmful products (e.g., carbon dioxide, carbon monoxide, and sulphur dioxide); 3) low order explosion from the ignition of decomposition products; and 4) stench. According to the criteria of the United Nations Globally Harmonized System of Classification and Labeling of Chemicals (GHS), xanthates are classified in different categories, including category 1 (Self-heating substances and mixtures), category 2 (skin corrosion/irritation) category 2A (serious eye damage/irritation), and category 4 (oral acute toxicity and dermal acute toxicity). Liquid xanthates are particularly classified in category 1 (metal corrosion).

Solid xanthates are classified as class 4.2 (spontaneous combustible) under UN 3342 PGII, while their liquid mixture is classified as class 8 (corrosive) and sub-risk 6.1 (toxic) under UN 2922. Under the UN Globally Harmonized System of Classification and Labeling of Chemicals, xanthates are classified in Category 1, Category 2A, and categories 4, respectively because of being Self-heating (individually and as mixtures), serious eye damage or irritation, dermal and oral acute toxicity. The diversity of exposure routes, including skin contact and skin absorption, eye contact, inhalation, ingestion, etc., increases the vulnerability of exposed individuals. Conversely, the magnitude of the threat depends on the route of entry, the duration of exposure, and the dose.

From various MSDS, brief contact with xanthates may cause skin irritation (reddening, rash, scaling, swelling, blistering, etc.) and eye irritation. Conversely, excessive exposure may cause severe skin corrosion, and skin and eye burns. Inhalation of xanthates may lead to the drying of mucous membranes of the nose and throat, severe irritation of the nose, and throat, coughing, bronchopneumonia, pulmonary edema, and pulmonary malfunction. Ingestion may irritate the mouth and throat, lead to a burning sensation, and abdominal pain, and may be fatal. Repeated or prolonged exposure may lead to chronic damage to the liver, kidneys, and spleen, peripheral nervous system effects, and central nervous systems depression (NICNAS, 2000), cardiovascular effects, respiratory failure (due

to overexposure) that may result in coma and possible death. Some of these effects may occur late and damages are not necessarily accompanied by sensation or onset of pain. Accordingly, zero level of exposure for humans was recommended (Li et al., 2015). Damage to the enzymatic system of humans and animals (e.g., rats, and mice) was reported. They are selective mechanism-based inactivators (Stoyanova, Lessigiarska, Mikov, Pajeva, & Yanev, 2017) of Cytochromes such as cytochrome P450 2B6 P450 2B1 (Stoyanova et al., 2017; Yanev, Kent, Roberts, Ballou, & Hollenberg, 2000) and Cytochrome P450 2E1 (Stoyanova et al., 2017). Xanthates are likely to interact differently with the active sites of similar cytochromes, including those of cytochrome P450 isomorphs, CYP4A11, and CYP2E1, which are involved in fatty acid metabolism. Since fatty acids have a similar structure as long alkyl chain xanthates, their metabolism is negatively affected by exposure to xanthates. The observed differences in the induced enzyme's activities modifications justify the use of xanthates as probing tools to examine enzymatic active sites. It is particularly beneficial for the selection of suitable and selective compounds able to affect fatty acid homeostasis (Stoyanova et al., 2017).

Few studies set up lethality testing that can help determine the lethal dose (LD) or lethal concentration (LC). Rats, rabbits, and mice are the most exposed mammals for experimental purpose. **Table 1** provides some related toxicological

Table 1. Toxicological data on xanthates toxicity to mammals (rats, rabbits, and mice).

Chemicals	animals	Toxicity level	References
Sodium ethyl xanthate	Rats	500 mg/kg bw LD0	Kirk-Othmer, 1984; NICNAS, 2000
Sodium isopropyl xanthate	Rats	250 mg/kg bw LD0 1250 mg/kg bw LD50	ECHA https://echa.europa.eu/registration-dossier/-/registered-dossier/13542/7/3/2#
	Mice	730mg/kg bwLD50 (Oral)	Kirk-Othmer, 1984; NICNAS, 2000
Potassium ethyl xanthates	Rat	LD50 = 1700 mg/kg	Alfa Aesar-Thermo Fisher Scientific Chemicals, Inc., 2020. Potassium ethyl xanthates, MSDS https://www.alfa.com/it/msds/?language=EN&subformat=AGHS&sku=A11450
	mouse	583 mg/kg bw, LD50	Kirk-Othmer, 1984; NICNAS, 2000
Sodium isobutyl xanthate	Rats	500 mg/kg bw - LD50	Redox, Ltd, 2019. Safety Data Sheet. Sodium Isobutyl Xanthate (SIBX). Revision 5, Date 22 Jul 19 https://redox.com/products/sodium-iso-butyl-xanthate/
	Rats	1 000 mg/kg - LD50 (Oral)	Brenntag Canada Inc., 2009. Potassium-amyl xanthate, solid, MSDS- http://www.brenntag.ca
Potassium amyl xanthate	Rabbits	1 000 mg/kg - LD50 (Oral)	
	Mouse	99 mg/kg LD50 (Intravenous)	https://pubchem.ncbi.nlm.nih.gov/compound/Potassium-amylxanthate#section=Hazards-Identification&fullscreen=true
Potassium n-butyl xanthates	Mouse	411- 465 mg/kg bw LD50 (Oral)	Kirk-Othmer, 1984; NICNAS, 2000

bw = Body weight. LD stands for lethal dose; LD50 refers to lethal dose that cause death of 50% of the exposed population; the value is expressed in milligrams of the tested toxic substance per kilogram of animal body weight (mg/kg).

data. It can be observed that xanthates toxicity level, expressed as LD50, ranged from 400 - 730 mg/kg for mice. Since Xanthates are hydrolysable by gastric acid, intoxication would come from their hydrolysis products, including alcohol and carbon disulfide (Xu et al., 1988). Accordingly, MSDS comprises some precautions for the safe handling of xanthates. They are mostly related to exposure controls, appropriate engineering controls, personal protective equipment (including skin protection, eye/face protection, body protection, and respiratory protection), and environmental exposure Control.

3.2. Toxicity of Xanthates to Aquatic Living System

3.2.1. Water Pollution by Xanthates

Water is home to large biodiversity, supports aquatic and terrestrial ecosystems, regulates the climate, and is essential for agriculture, food, energy, transport, etc., that sustain life on earth. Unfortunately, water bodies such as lakes, rivers, streams, and springs are among the main destinations of various hazardous substances (Brantes & Olivares, 2008; Northey, Mudd, Werner, Haque, & Yellishetty, 2019; Reyes-Bozo et al., 2014) including xanthates. Regarding the flotation, only half of the total xanthates quantity supplied to the circuit (20 - 500 mg/soil) (Bulatovic, 2007; Li et al., 2015; Liu, Sun, Ouyang, Zhang, & Hu, 2015b; Reyes-Bozo et al., 2014) is effectively consumed (Li et al., 2015). The excess and unreacted portion, estimated at hundred thousand tons annually, is dumped into tailing dam or drained by flotation plant effluent to surrounding water bodies and land (Bach et al., 2016; Chockalingam, Subramanian, & Natarajan, 2003; Molina et al., 2013; Panayotova & Panayotov, 2021; Pearse, 2005; Yan et al., 2016). The phenomenon is magnified by xanthates leakage from tailing and tailing dam failure which constitute the most mining-reported major incidents (Edraki et al., 2014; Liu et al., 2015a; Rico et al., 2008), 90% of cases happening in active mine (Rico et al., 2008). In this context, wastewater recycling and reuse in the flotation circuit can ideally help solving the problem of water scarcity (e.g., in water-stressed areas) and the environmental pollution. However, residual flotation reagents and their byproducts usually negatively affect the flotation process by altering the chemistry of the flotation system (Fu et al., 2018; Kempinen, Aaltonen, Sihvonen, Leppinen, & Siren, 2015). Moreover, while removing these residual reagents should help improve water quality (Fu et al., 2018), treating the flotation wastewater remains a significant challenge (Panayotova & Panayotov, 2021). The biodegradation techniques which should be more ecologically sustainable, are time-consuming (several days or weeks) (Chen et al., 2017) and not directly applicable on the site, particularly when rapid intervention is needed (Yan et al., 2016). Therefore, groundwater (the main source of freshwater worldwide) and surface water pollution by xanthates is critically increasing (Chen et al., 2011).

3.2.2. Xanthates Toxicity to Aquatic Life

Xanthates are strong poisons for water life, as shown in the following examples.

They exhibited detrimental and long-lasting effects on various water organisms, including freshwater planktonic crustaceans (Webb et al., 1976; Xu et al., 1988), invertebrates (Xu et al., 1988), and algae (Bach et al., 2016; Li et al., 2021; Xu et al., 1988). Xanthates have a teratogen effect on frog embryos (Li, 1990) and fish embryos (Chen et al., 2011; Fu et al., 2015) and may similarly affect other organisms. Xanthates are adversely active at an insignificant concentration (Deo & Natarajan, 1998), less than 1 mg/L (Rostad et al., 2011). The sensitivity of water organisms to xanthates varies depending on various factors, including the xanthate chemical structure and the type of exposed organism. A dose-effect relationship is commonly observed. For example, xanthates exhibited 96 h LC50 of 0.01 to 0.1 mg/L and 0.1 to 1.0 mg/L, respectively, for *Daphnia magna* and *Natrapis athernoides* (Hawley, 1972). **Table 2** illustrates the toxicity level of xanthates in some aquatic organisms.

Lemna minor (fresh water plants, common duckweed) population was 100% eliminated after 72 hours of exposure to above five (5) mg/L of Sodium isopropyl xanthate concentration. A shorter carbon chain xanthate, Na-ethylxanthate (C₂ alkylated xanthates), showed tenfold acute 24 h toxicity in the *Daphnia magna* population compared to relatively long chain xanthates, C₃-C₅ alkylated xanthates which have a comparable toxicity level (Xu et al., 1988).

On this basis and for water living system protection, more than 2 mg/L of xanthates in water was considered very hazardous. Later analyses led to establishing 0.05 ng/mL as the permissible xanthates concentration in water bodies (Li et al., 2015). However, interactive effect studies may lead to reconsidering the standard. For example, the presence of xanthates in water may increase heavy metal uptake by fish. It was the case for the xanthates-cadmium complexes that increased the ¹⁰⁹Cd bioavailability and uptake by *Phoxinus phoxinus* and *Oncorhynchus mykiss* (Block & Glynn, 1992). Increased availability of the cadmium-xanthates complex may also happen in the case of the complex Nickel-butyl xanthate that was more toxic on *Chlorella pyrenoidosa* (freshwater algae) than the single elements (Li et al., 2021). Xanthates form hydrophobic complexes with heavy metals and may potentially facilitate the metal uptake by fish. The increased availability is due to the hydrophobic properties of the complexes (Block & Glynn, 1992).

3.3. Toxicity of Xanthates to Soil Microorganisms

Soil is a major recipient of waste and hazardous pollutants, including xanthates, which exert a great negative effect on its living organisms and, thus, undermine its role in sustaining life on earth. Soil is home to more than a quarter of living organisms (Gadd, 2010) which perform multiple actions that largely determine soil quality and functions (Deshmukh, 2012; Nannipieri et al., 2003). The most documented are soil microorganisms which constitute its most active component (Rong, Huang, Jiang, Cai, & Liang, 2007; Schulz et al., 2013) and are the most responsible for biogeochemical and biotransformation

Table 2. Toxicological data on the toxicity of xanthates to aquatic organisms.

Chemicals	Organisms	Toxicity level	References
Sodium ethyl xanthate	Planktonic crustacean (<i>Daphnia magna</i>)	0.33 - 0.35 mg/l EC50	(Bach, Nørregaard, Hansen, & Gustavson, 2016; Xu et al., 1988)
	Fish (<i>Oncorhynchus mykiss</i>)	13 mg/l LC50	
	Algae (<i>Lemna minor</i>)	<10 mg/l EC50	(Bach, Nørregaard, Hansen, & Gustavson, 2016; Xu et al., 1988)
	<i>Oncorhynchus mykiss</i> (rainbow trout)	30 - 50 mg/l - 96 h LC50	(Webb et al., 1976)
Sodium isopropyl xanthate	Planktonic crustacean (<i>Daphnia magna</i>)	3.7 mg/l EC50	(Bach, Nørregaard, Hansen, & Gustavson, 2016; Xu et al., 1988)
		0.1 - 1.0 mg/l - 96 h LC50	
	Notropis anterinoides	0.01 - 0.1 mg/l - 96 h LC50	(Alto, Broderius, & Smith, 1978; Hawley, 1972)
	<i>Pimephales promeras</i>	0.32 - 5.6 1mg/l - 96 h LC50	
	Catfish	>10 1mg/l - 96 h LC50	
	Snails	10 - 100 mg/l - 96 h LC50	(Alto et al., 1978)
	Tadpoles	10 - 100 mg/l - 96 h LC50	
	<i>Salmo gairdnei</i>	10 - 180 mg/l - 96 h LC50	(Alto et al., 1978; Webb et al., 1976)
	Algae (<i>Pseudokirchneriella subcapitata</i>)	0.5 mg/l EC50	(Vigneault et al., 2012; Bach, Nørregaard, Hansen, & Gustavson, 2016)
	Invertebrate (<i>Ceriodaphnia dubia</i>)	3 mg/l EC50	(Vigneault et al., 2012; Bach, Nørregaard, Hansen, & Gustavson, 2016)
Sodium isobutyl xanthate	Planktonic crustacean (<i>Daphnia magna</i>)	3.6 mg/l EC50	
	Algae (<i>Lemna minor</i>)	<10 mg/l EC50	(Bach, Nørregaard, Hansen, & Gustavson, 2016; Xu et al., 1988)
Sodium isopentyl xanthate	Algae (<i>Lemna minor</i>)	<10 mg/l EC50	
Potassium amyl xanthate	Algae (<i>Pseudokirchneriella subcapitata</i>)	0.5 mg/l EC50	(Vigneault et al., 2012; Bach, Nørregaard, Hansen, & Gustavson, 2016)
	<i>Oncorhynchus mykiss</i> (rainbow trout)	30 - 50 mg/l - 96 h LC50	(Webb et al., 1976)
	Planktonic crustacean (<i>Daphnia magna</i>)	3.67 mg/l EC50	(Bach, Nørregaard, Hansen, & Gustavson, 2016)
	Invertebrate (<i>Ceriodaphnia dubia</i>)	3 mg/l EC50	(Bach, Nørregaard, Hansen, & Gustavson, 2016; Vigneault et al., 2012)
	Fish (<i>Danio rerio</i>)	>10 - 100 mg/l LC50	(Bach, Nørregaard, Hansen, & Gustavson, 2016)
	<i>Oncorhynchus mykiss</i> (rainbow trout)	30 - 50 mg/l - 96 h LC50	(Webb et al., 1976)
Butyl xanthate	<i>Chlorella pyrenoidosa</i> (Algae)	19, 25 mg/L - 96 h EC20	(Li et al., 2021)
	Invertebrate (<i>Daphnia magna</i>)	3.0 mg/l EC50	(Xu et al., 1988)
K-pentyl xanthate	<i>Oncorhynchus mykiss</i> (rainbow trout)	52 mg/l - 96 h LC50	Central Drug House (P) Ltd-MSDS Potassium ethyl xanthates
	<i>Brachydanio rerio</i> (zebrafish)	5.26 mg/l - 8 days NOEC	
	<i>Gammarus fasciatus</i> (freshwater shrimp)	52 mg/l - 96 h LC50	(Bach, Nørregaard, Hansen, & Gustavson, 2016)

ECx, LCx, and NOEC refer to, respectively, the effective concentration or concentration at which x% toxic effect on exposed population is observed compared to the control, the lethal concentration (concentration that causes death of x% of the exposed population, and the no observed effect concentration or the highest tested concentration for which there are no statistical significant difference of effect compared to the control.

processes taking place in soil (Chakraborty, Saha, & Roy, 2016; Gadd, 2010; Li et al., 2009; Xian, Wang, & Chen, 2015; Zhang, Wu, Chen, Jiang, & Li, 2009) and determine soil quality and functions (Aislabie & Deslippe, 2013; Chakraborty, Saha, & Roy, 2016; Gadd, 2010; Ortiz & Sansinenea, 2022; Pankhurst & Lynch, 1995; Rao, Scelza, & Gianfreda, 2014; Schulz et al., 2013; Timmis & Ramos, 2021). All of these processes depend on the catalytic action of various soil enzymes (Caldwell, 2005; Green, Stott, & Diack, 2006; Hermans, Buckley, Case, Curran-Cournane, & Lear, 2020; Rao et al., 2014; Schnürer & Rosswall, 1982; Zhan, Wu, Zhou, Liang, & Jiang, 2010). Therefore, due to the high sensitivity of soil microbes and enzymes to variations in the soil environment (Bararunyeretse et al., 2017b; Chen et al., 2014; Guo et al., 2016b; Li et al., 2020; Rao et al., 2014), all those functions may not be achieved in the presence of xanthates or xanthates mixture with other substances. The subject has recently attracted more scientific attention.

Microcalorimetry-based analyses revealed that Individual xanthates doses of 5 - 300 $\mu\text{g}\cdot\text{g}^{-1}$ soil inhibited the total soil microbial activity, with a relatively low effective concentration and a significant dose-effect relationship (Bararunyeretse, Beckford et al., 2019a; Bararunyeretse et al., 2017a, 2017b) that varies between substances, as shown in **Table 3**.

From these data (**Table 3**), and based on the example of Nickel and copper, metals can be considered relatively less toxic than their mineral collectors. Sensitive microorganisms would not survive above a threshold dose of 150 $\text{mg}\cdot\text{kg}^{-1}$ soil, or at least their metabolic activity would be inhibited (Li et al., 2018).

Table 3. Data on inhibition level of soil microbial activity by some individual xanthates and metals.

Chemical	Inhibitory concentration (IC)					Reference
	IC ₁₀ $\mu\text{g}\cdot\text{g}^{-1}$	IC _{12.5} $\mu\text{g}\cdot\text{g}^{-1}$	IC ₂₀ $\mu\text{g}\cdot\text{g}^{-1}$	IC ₂₅ $\mu\text{g}\cdot\text{g}^{-1}$	IC ₅₀ $\mu\text{g}\cdot\text{g}^{-1}$	
Butyl xanthates	n.a	n.a	47.3			
Sodium diethyldithiocarbamate	n.a	n.a	38.36	n.a	n.a	(Guo et al., 2016b)
Butyl dithiophosphate	33.34	n.a	n.a	n.a	n.a	
Sodium isopropyl xanthates	13.15	n.a	42.24	n.a	225.76	
Sodium ethyl xanthates	3.901	n.a	10.484	n.a	74.08	
Potassium ethyl xanthates	3.552	n.a	7.37	n.a	39.653	(Bararunyeretse et al., 2017a)
Nickel	143.8		219.708		438.69	
Potassium amyl xanthates	n.a	28.05	n.a	54.15	158.3	(Bararunyeretse, Beckford et al., 2019a)
Sodium isoamyl xanthates	n.a	35.83	n.a	41.34	83.95	(Bararunyeretse, Beckford et al., 2019a)
Copper	n.a	106.25	n.a	220.00	447.5	(Bararunyeretse, Beckford et al., 2019a)

n.a = not available. IC = Inhibitory concentration; IC_x is the chemical concentration that causes x% decrease in microbial growth rate.

Similar results were observed through microbial growth analysis (microbial cell counts and spectrophotometric analysis (Bararunyeretse et al., 2017b). The difference in sensitivity and adaptation of soil bacteria to xanthates was evaluated through a molecular biology-based analysis (Bararunyeretse, Zhang et al., 2019b). It was concluded that some bacterial species, including those belonging to the genera *Enterobacter*, *Lysobacter*, *Microvirga*, *Acinetobacter*, *Cupriavidus*, and *Bacillus* are less sensitive and can proliferate in the presence of a Xanthates dose of 50 to 100 $\mu\text{g}\cdot\text{g}^{-1}$ soil while many others have difficulty surviving in the same conditions (Table 4(a)). Analysis of the effects of xanthates on moderately thermophilic bioleaching microorganisms (Okibe & Johnson, 2002) reported similar effects. Potassium amyl xanthates minimum inhibitory concentration was as follows: 0.5 $\mu\text{g}\cdot\text{ml}^{-1}$ for *Leptospirillum* sp. (strain MT6), 25 $\mu\text{g}\cdot\text{ml}^{-1}$ for *Ferroplasma acidiphilum* (strain MT17), 200 $\mu\text{g}\cdot\text{ml}^{-1}$ for *Acidithiobacillus caldus* (strain KU) and *Sulfobacillus acidophilus* (strain NC), and 500 $\mu\text{g}\cdot\text{ml}^{-1}$ for *Acidimicrobium ferrooxidans* (strain ICP).

3.4. Xanthates Toxic Effects on Enzymes

Studies reported strong xanthates toxic effect on enzymes, including those playing a significant physiological role in humans, animals, plants and microorganisms. Within a 10-day period, different doses (5 - 100 $\mu\text{g}\cdot\text{g}^{-1}$ soil) of sodium isobutyl xanthate and sodium isopropyl xanthate inhibited the activity of soil catalase (an antioxidant enzyme) and Fluorescein diacetate hydrolase (FDA), with a dose-effect relationship (Bararunyeretse et al., 2017b). Similar results were found with butyl xanthate (Guo et al., 2016b; Li et al., 2018), butyl dithiophosphate, and sodium diethyl dithiocarbamate (Guo et al., 2016b). Exposure to sodium isobutyl xanthates revealed high sensitivity of soil sucrase to xanthates (Li et al., 2020). This digestive enzyme catalyzing the sucrose hydrolysis is present in yeast, animal's intestinal mucosa, and in plants. The urease activity and nitrification are also inhibited by the soil exposure to xanthates such as potassium xanthates (Ashworth, Akerboom, & Crepin, 1980). This enzyme is present

Table 4. (a) Relative abundance (percentage of 16S rRNA gene sequences) of the major genera in the presence of individual and mixture of nickel and its mineral collectors. Sequences that do not reach 0.1% abundance in at least one sample are merged and named as “others”. Sequences that could not be classified into any known genus are labeled “norank” or “unclassified” (Bararunyeretse, Zhang et al., 2019b); (b) Pollutant concentration for each treatment as used in (a) (From Bararunyeretse et al., 2019b).

(a)

Bacterial Genus	Relative Abundance of Each Bacterial Genus Per Sample									
	CS	Ni	PEXa	PEXb	SIPXa	SIPXb	M1a	M1b	M2a	M2b
Cupriavidus	0.83	0.08	14.68	7.55	17.53	12.84	19.19	5.06	36.51	20.33
Bacillus	19.10	10.54	3.31	4.74	1.79	0.41	19.93	19.40	31.90	12.81
Pseudomonas	0.11	0.05	2.00	3.51	0.74	1.08	21.87	37.37	7.55	12.86
unclassified_f_Enterobacteriaceae	1.76	0.00	11.06	27.23	5.82	13.28	0.50	1.17	0.07	0.06
Lysobacter	6.37	0.70	5.84	2.95	13.82	13.81	1.00	0.70	1.12	1.35

Continued

norank_c__Acidobacteria	5.03	8.01	4.82	1.50	2.82	4.17	2.01	3.34	0.70	4.95
Microvirga	5.45	0.83	6.62	3.23	8.55	5.65	0.32	1.01	0.27	0.87
Domibacillus	0.15	0.33	0.06	0.03	0.00	0.00	13.42	2.19	5.69	0.34
Enterobacter	0.60	0.01	5.45	7.74	4.36	6.89	1.09	0.67	0.16	0.16
Acinetobacter	1.30	0.00	2.70	4.59	1.67	5.14	0.20	1.11	0.36	0.03
unclassified_f__Micrococcaceae	0.36	11.78	0.29	0.12	0.35	0.24	0.18	0.27	0.09	0.54
Sphingomonas	3.64	1.07	0.54	0.56	2.31	1.46	0.23	0.44	0.21	0.83
Pseudarthrobacter	0.79	4.71	0.62	0.27	0.75	0.60	0.37	0.73	0.23	1.17
norank_o__JG30-KF-CM45	1.14	1.68	1.48	1.12	0.85	1.10	0.39	0.91	0.29	1.13
Isopetricola	1.29	7.15	0.24	0.21	0.66	0.17	0.17	0.06	0.10	0.14
norank_c__KD4-96	1.19	1.85	1.30	0.66	1.04	1.20	0.46	0.95	0.22	1.11
norank_c__Actinobacteria	0.85	1.45	1.12	0.55	1.13	1.10	0.71	0.98	0.22	1.25
Gaiella	1.42	1.31	0.98	0.99	0.97	0.82	0.39	0.77	0.40	1.27
Ensifer	0.55	0.19	2.81	2.12	1.60	1.72	0.07	0.26	0.05	0.17
norank_o__Gaiellales	1.23	1.03	0.98	0.94	0.94	0.71	0.39	0.67	0.35	1.25
Streptomyces	0.82	2.02	1.07	0.31	1.55	0.43	0.18	0.29	0.19	0.50
Nitrospira	1.21	1.20	0.91	0.68	0.60	0.67	0.25	0.60	0.25	0.81
norank_f__Nitrosomonadaceae	0.87	1.11	0.73	0.67	0.70	0.48	0.34	0.67	0.25	1.03
Paenibacillus	1.14	2.14	1.04	0.37	0.43	0.06	0.69	0.17	0.32	0.17
Nocardioides	0.74	1.37	0.60	0.63	0.40	0.49	0.20	0.37	0.23	0.70
Blastococcus	1.16	0.74	0.60	0.52	0.50	0.49	0.20	0.37	0.24	0.69
Azotobacter	1.34	0.00	0.58	2.20	0.59	0.62	0.08	0.20	0.05	0.03
Bhargavaea	0.00	-	-	-	-	-	0.24	0.38	0.15	4.34
Microbacterium	0.31	1.81	0.19	0.10	0.10	0.15	0.20	0.04	1.58	0.17
Agromyces	1.60	1.63	0.34	0.24	0.33	0.21	0.06	0.10	0.05	0.20
unclassified_f__Rhizobiaceae	0.28	0.03	1.33	0.97	0.90	0.90	0.00	0.10	0.00	0.01
Pseudoxanthomonas	0.64	0.04	0.12	0.13	1.23	0.48	0.12	0.13	0.19	0.67
Fictibacillus	0.24	0.03	0.12	0.02	0.05	0.00	1.71	0.03	0.22	0.23
Achromobacter	0.07	0.03	0.50	1.08	0.10	0.14	0.09	0.12	0.04	0.12
Others	6.38	35.06	24.97	21.45	24.82	22.49	12.77	18.36	9.77	27.71

(b)

Samples Code	Control Sample	Single Chemical Treatments					Mixed-Chemical Treatments (Ni + Xanthates)			
		Ni	PEXa	PEXb	SIPXa	SIPXb	Ni + PEX		Ni + SIPX	
Dose ($\mu\text{g-g}^{-1}$ soil)	CS	300	50	100	50	100	M1a	M1b	M2a	M2b
	0	300	50	100	50	100	300 + 50	300 + 100	300 + 50	300 + 100

CS = Control sample; Ni = Nickel; PEX = potassium ethyl xanthate; SIPX = sodium isopropyl xanthate; M = Mixture (M1a = Ni + PEXa, M1b = Ni + PEXb, M2a = Ni + SIPXa, and M2b = Ni + SIPXb).

in many bacterial species [including humans pathogen bacteria for which it play the role of virulence factor (Konieczna et al., 2012)], in yeast, plants, and algae, animal tissues and intestinal microorganisms. It is involved in the hydrolysis of urea into ammonia and carbon dioxide (Dahlén, Hassan, Blomqvist, & Carlén, 2018). It critically harms human cells (Agarwal, Singh, Singh, & Singh, 2019). Xanthates such as $C_3H_7OCS_2Na$, $C_4H_9OCS_2Na$, and $C_5H_{11}OCS_2Na$ exhibited a negative effect on cresolase and catecholase of mushroom tyrosinase (Alijanian-zadeh, Saboury, Mansuri-Torshizi, Haghbeen, & Moosavi-Movahedi, 2007). The inhibition of the activity of tyrosinase, a copper-containing enzyme, is critical. The molecule is highly conserved in various species, including plants, vertebrates, bacteria, and fungi, to catalyze an enzymatic darkening process (biosynthesis of melanin) (Jungbluth & Busam, 2019). It is also involved in immunological, biotechnological and environmental processes (Agarwal et al., 2019; Jungbluth & Busam, 2019).

3.5. Toxicity of the Mixtures of Metal and Xanthates

In the real environment, the living system is not exposed to individual substances but to their consortia. In the context of mining and mineral processing, the soil microorganisms and enzymes are undoubtedly exposed to consortia of toxic elements including minerals (e.g., metals), xanthates, and xanthates decomposition products. Exposure to combined substances may lead to different types of reactions, mainly additive, synergistic, antagonistic, or neutral action (Hertzberg & MacDonell, 2002; Rodea-Palomares, Gonzalez-Pleiter, Martin-Betancor, Rosal, & Fernandez-Pinas, 2015; Yang et al., 2015).

It was reported that the mixture of metals (nickel and copper) and xanthates was less toxic than single xanthates but more toxic than single metal (Bararunyeretse, Beckford et al., 2019a; Bararunyeretse et al., 2017a). Similarly, the simultaneous presence of heavy metals and xanthates in water may increase metal uptake by fishes. Xanthates-cadmium mixtures increased the ^{109}Cd bioavailability and uptake by *Phoxinus phoxinus* and *Oncorhynchus mykiss* (Block & Glynn, 1992). A nickel-butyl xanthate complex exhibited a higher toxic effect on *Chlorella pyrenoidosa* (freshwater algae) than the single elements (Li et al., 2021). A similar situation could be observed with other metal xanthates combinations and other organisms. However, the related study is still scarce, while the mixture toxicity is still less understood.

From a molecular biology based analysis and relative abundance of bacterial genera in the presence of Nickel and its mineral collectors, individually or as mixture (Table 4(a)) (Bararunyeretse, Zhang et al., 2019b), some bacterial species such as those belonging to the genera of *Cupriavidus*, *Bacillus*, *Pseudomonas*, *Domibacillus* (highly affected by individual xanthates), were less affected or were likely to be favored by the metal-xanthates mixture. Others such as those belonging to the genera of *Lyzobacter*, *Microvirga*, *Enterobacter*, *Acinetobacter*, and *unclassified_f_Enterobacteriaceae* that are seemingly proliferated in the

presence of single xanthates exhibited high sensitivity to nickel and nickel mixture with xanthates.

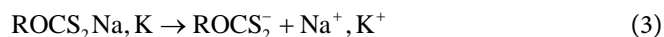
Sample's codes, corresponding to each soil pollutant treatment, are as follows (Table 4(b)).

4. Xanthates Decomposition and Its Ecotoxicological Implication

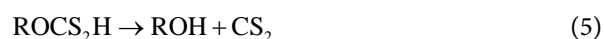
4.1. Xanthates Decomposition and Fate in the Environment

Unlike metals and metalloids which are naturally occurring in the environment and known for their non-biodegradability, persistence and bioaccumulation characteristics (Tam & Wong, 2000), xanthates are manmade organic chemicals and are subject to various natural degradation processes. They may undergo thermal degradation, chemo degradation (pH conditions), aerobic oxidation, photodegradation, biodegradation, etc. The following examples (Equations (3)-(9)) are the most reported conditions and modes of their decomposition.

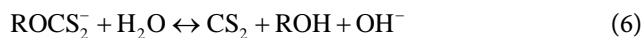
In the presence of moisture or an aqueous solution, xanthates can decompose through hydrolytic, dissociation, and oxidation reactions. Their dissociation releases alkali metal cations (Na^+ , K^+) and xanthates anions (ROCS_2^-) (Equation (3)).



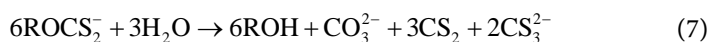
Subsequently, xanthates anions hydrolysis will lead to the formation of unstable xanthic acid (ROCS_2H) that further decomposes, readily and irreversibly, into carbon sulfide (CS_2) and alcohol (Bulatovic, 2007; Molina et al., 2013; Shen et al., 2016; Sun & Forsling, 1997) as it is commonly observed in acidic conditions (Equation (4)-(5)).



It is widely reported that xanthates degradation is function of pH, the maximum reaction being observed at low pH (about pH 2.2). Conversely, the CS_2 formation decreases with the pH reduction (Shen et al., 2016), while xanthates are more stable in neutral pH, although they may also decompose to CS_2 (Equation (6)):

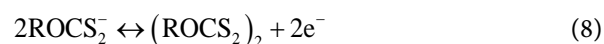


In a weakly alkaline medium, xanthates hydrolysis leads to the formation of trithiocarbonate (CS_3^{2-}) that can further decompose into carbon disulfide (CS_2) and sulfur (S^-) (Bulatovic, 2007; Molina et al., 2013) (Equation (7)).



Under strong alkaline conditions, xanthates degradation generates various compounds, including alcohol, carbon disulfide, oxocarbon anion (CO_3^{2-}), sulfur (S^-), hydrogen sulphide (H_2S), etc.

Xanthates can also undergo atmospheric oxidation and degrade as follows (Molina et al., 2013) (Equation (8)-(9)):



Xanthates may also be involved in other various intermediate reactions, such as those concerning trithiocarbonate, xanthic acid, alcohol, and carbon disulfide, that may lead to the formation of hydrogen sulfide (H₂S), carbon dioxide, and other intermediate compounds (Bulatovic, 2007; Molina et al., 2013; Sun & Forsling, 1997).

From the above reactions, it is obvious that more carbon disulfide (CS₂) is generated under acidic conditions than under alkaline conditions. The latter allow the formation of many other compounds, including per-xanthate, dioxanthogen, monothio- and dithio-carbonates, and trithiocarbonate. Moreover, CS₂ is the main decomposition product through a hydrolytic process (Equation (7)), which is the main expected principal degradation pathway in the flotation process.

Xanthate's fate in the environment is not only depending on pH, humidity, and atmospheric conditions (Bulatovic, 2007; Molina et al., 2013; Shen, 2016; Shen et al., 2016) but also on other factors such temperature (Sun & Forsling, 1997), the retention time (Shen et al., 2016), and xanthates concentrations (Deo & Natarajan, 1998). Therefore, for more stability and a low generation of toxic decomposition products, particularly H₂S and CS₂, xanthates could be kept at cool (or cold) and dry places and under relatively neutral or weakly alkaline pH (Fu et al., 2018). These conditions are not necessarily the same as those encountered in the real environment. In this regard, xanthates could not persist in an acidic environment of mining and flotation tailings dams. Accordingly, and to avoid or limit the release of environmental contaminants, tailings dams should be sealed with a protective geomembrane to prevent failures and water influx or efflux. On the other hand, xanthates can last relatively longer in water bodies, which offer a relative neutral or weakly alkaline environment. In this situation, they undergo slow hydrolysis, although they cannot accumulate because of their ionic nature.

It is well known that microbial and enzymatic mediated processes (e.g., bio-transformation, biodegradation, and co-metabolic conversion) constitute the main degradation mechanism of organic compounds in the environment (Aysha, Hamsavathani, & Valli, 2015; Chen et al., 2011; Dabrowska, Kot-Wasik, & Namiesnik, 2004; Deo & Natarajan, 1998). These processes are generally dose and time-dependent and follow first-order kinetic reactions (Chen et al., 2011). Various efficient bacterial species in the xanthates degradation have been reported. *Bacillus polymyxa* (Chockalingam et al., 2003; Deo & Natarajan, 1998), *Paenibacillus polymyxa* and *Pseudomonas putida* (Lam, 1999; Natarajan & Sa-

bari Prakasan, 2013), *Hypomicrobium*, and *Sporosarcina* can synergistically completely degrade butyl xanthate (Lin, Qin, Dong, & Li, 2022). *Shewanella oneidensis* have demonstrated high effectiveness in xanthates degradation (Chen et al., 2019). A 16S rRNA sequence-based analysis showed that bacteria belonging to the genera *Cupriavidus*, *Enterobacter*, *Lysobacter*, *Microvirga*, *Acinetobacter*, and *Bacillus* proliferated in the presence of xanthates, sodium isopropyl xanthate and potassium ethyl xanthates (Bararunyeretse, Zhang et al., 2019b). Some bacterial strains such as *Bacillus* sp., *Pseudomonas* sp, etc., are capable to use xanthates as their source of nutrients (C, N, S, etc). The fact that some bacteria, such as *Bacillus polymyxa* can use them as their only source of carbon (Deo & Natarajan, 1998), justifies that microbes are more efficient in xanthates degradation and removal from the environment.

Considering that microorganisms are generally more efficient by acting in synergy (consortia) than individually (Aysha et al., 2015; Ghazali, Rahman, Saleh, & Basri, 2004; Lin et al., 2022; Okibe & Johnson, 2002), several microbial species would coalesce for the degradation of xanthates in soil and aquatic environment.

4.2. Impact of Xanthate Decomposition Products on the Environment and Health

It is generally expected that the degradation of xenobiotic and toxic substances serves reducing or eliminating their adversity to the environment. However, it is not always the case, as it can lead to unwanted situations. Toxic chemical decomposition may result in the following three main situations: 1) environmental detoxification (production of products that are less or not harmful than the parent compounds); 2) the formation of new elements that are equally or more dangerous than those of origin; or 3) the biosynthesis of persistent elements (Alexander, 1981; Fetzner, 2002). In case of xanthates, such degradation does not appear to alleviate their heavy burden on health and the environment. It leads to the release of toxic decomposition products, such as carbon disulfide (CS₂), hydrogen sulfide (H₂S), and carbonyl sulfate (COS) into the environment (Bulatovic, 2007; Molina et al., 2013; Sun & Forsling, 1997) whose ecotoxicological dimension is described in the following lines.

4.2.1. Carbon Disulfide (CS₂)

It is already shown that carbon disulfide (CS₂) is the main xanthates decomposition product.

However, CS₂ is mainly released into the environment from natural sources (Abadin & Liccione, 1996; EFSA, 2017), and anthropogenic sources (Abadin & Liccione, 1996; EFSA, 2017; Rich & Patel, 2015; Tan et al., 2000; U.S. EPA, 2011). CS₂ is involved in the manufacture of various products such as viscose rayon fibers (Crookes, Diment, & Dobson, 1993; Tan et al., 2000), sodium sulfide, dyes, cellophane film, carbon tetrachloride, xanthogenates, and electronic vacuum tubes. It is used in the purification of single-walled carbon nanotubes and serves

as a good solvent for rubbers, phosphorus, selenium, iodine, sulfur, bromine, lipids, sulfur monochloride, resins, and fats (Abadin & Liccione, 1996).

Unfortunately, CS₂ is known as a harmful chemical to humans, terrestrial and aquatic life (Abadin & Liccione, 1996; Abdollahi & Hosseini, 2014; U.S. EPA, 2011; WHO-CICADs, 2002; Zeng, Dlugogorski, Oluwoye, & Altarawneh, 2019).

From the literature (Abadin & Liccione, 1996; NRC, 2009; Voss, Rodgers, & Woodall, 2009; WHO, 2010) and diverse material safety data sheets, CS₂ can enter the body in different ways, mainly by inhalation, skin contact, and eye contact. It is associated with both acute and chronic forms of poisoning, with a varied range of dose-response levels and symptoms, depending on the targeted categories of organisms or organs (Abadin & Liccione, 1996; Abdollahi & Hosseini, 2014; Rim, 2017; Sharma, Choudhary, Patel, & Kumar, 2022). Human exposure revealed the neurotoxicity, cardiotoxicity, and reproductive toxicity (Guo, Ma, Chen, & Cheng, 2016a; Meyer, 1981) of CS₂. The induced mitochondrial dysfunction may play a vital role in the CS₂ harmful effects on male sexual hormones (Guo et al., 2016b) and semen quality (Guo et al., 2016a; Ma et al., 2010; Meyer, 1981). From a cross-sectional study, exposed workers manifested a higher rate of sexual dysfunction, lower number of sexual encounters and shorter sexual encounters, loss of semen quality, longer liquefaction time, lower acrosomal membrane integrity rate, vitality and density, and more deformity of semen compared to the non-exposed workers (Ma et al., 2010). The central nervous system is deleteriously affected (Krstev, Peruničić, Farkić, & Banićević, 2003), with acute toxicity manifesting in various symptoms (headaches, dizziness, vertigo, autonomic nervous system reactions, nausea, vomiting, central paralysis, and narcosis) (NRC, 2009). Accordingly, xanthates manufacturers, users and stock managers could be among the victims and should avoid any exposure to this main xanthates decomposition product.

Hazards studies in animal (e.g., mice, rabbit, rat, dog, cat, and Guinea pigs), revealed that exposure to CS₂ may seriously affect the nervous system, respiratory system, cardiovascular system, reproductive health, ocular system, and can damage the liver, heart, kidneys, etc. (Abadin & Liccione, 1996; Sharma et al., 2022; Song, Yu, Zhao, Zhang, & Xie, 2006; Voss et al., 2009). The most reported symptoms include hyper excitability, stupor, nausea, vomiting, diarrhea, abdominal pain, skin and eye irritation, skin drying, cracking, redness and blisters, weakness, ataxia, personality and behavior changes (e.g., depression, anxiety, irritability), mental disorder, sexual dysfunction (Voss et al., 2009) respiratory arrest and death (NRC, 2009). For this reason, animals should be kept away from their production sites and discharge areas that can serve as food and water supply sites.

Due to its toxicity, CS₂ has long been used as an effective fumigant for grains (EFSA, 2017; FAO-WHO, 2015), food storage and packaging rooms, and transportation materials. It also serves to preserve fresh fruit, nursery stock and as pesticides against invertebrates (e.g., insects, nematodes, rodents) and soil con-

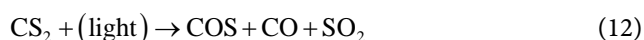
taminants (e.g., microorganisms) (Crookes et al., 1993), a toxicity nature that makes it less biodegradable.

In terms of reactivity and fate in the environment, CS₂ is susceptible to different reactions processes (Abdollahi & Hosseini, 2014; DeMartino, Zigler, Fukuto, & Ford, 2017) that may determine its life-time and adversity. Of the CS₂ most environmentally and healthily worrying reactions, one can cite the following three mechanisms (Equation (10)-(13) that lead to the formation of toxic elements, mainly carbonyl sulfide (COS) and hydrogen sulfide (H₂S), and to the formation of a greenhouse gas, carbon dioxide (CO₂) (Rich & Patel, 2015).

The first reaction mechanism is CS₂ hydrolysis into carbonyl sulfide, hydrogen sulfide, and carbon dioxide (Equation (10)-(11)), the half-life of the reaction being estimated at 1.1 years at pH 9 in an aqueous solution (DeMartino et al., 2017).



The second mechanism is the CS₂ photolysis that leads to the formations of carbonyl sulfide (COS), carbon monoxide (CO) and sulfur dioxide (SO₂) (Equation (12)



The third reaction is the combustion and subsequent formation of sulfur dioxide and carbon dioxide (Equation (13)) (Zeng et al., 2019), a reaction that is associated with its high flammability.



4.2.2. Carbonyl Sulfide (COS)

Carbonyl sulfide (COS) is one of the indirect products of xanthates degradation. It was above mentioned that COS is directly associated with reactions involving CS₂, the main product of the decomposition of xanthates (e.g., Equation (10) & (12)). However, there are various anthropogenic and natural processes from which carbonyl sulfide is released into the environment (soil, water, air) (Bartholomaeus & Haritos, 2005; Chou et al., 2016; Meredith et al., 2019; Rodriguez & Alexeeff, 2014; U.S. EPA, 2015; Wright, 2003). Since COS can relatively persist in the atmosphere (2 - 10 years) and can be transported to groundwater by infiltration, as it does not bind to soil (Andreae & Ferek, 1992; Chou et al., 2016), manufacturers and users should limit its emission into the air and soil to the strict minimum.

Investigation on Carbonyl sulfide adversity to animals has shown that a wide range of pests is sensitive (Chou et al., 2016; Haritos & Dojchinov, 2005; Weller & Morton, 2001; Tan et al., 1998; Zettler, Leesch, Gill, & Mackey, 1997). COS is fast-acting and harmful to all life stages, at a relatively low dose, short contact time, and reasonable temperature (Weller & Morton, 2001). On this basis, COS is widely used as a fumigant for pest control of stored products and durable

commodities (Chou et al., 2016; Desmarchelier, 1994; Haritos, 2001; Rodriguez & Alexeeff, 2014; Wright, 2003; Tan et al., 1998) and to increase plant resistance to insects (Chou et al., 2016). For many applications, COS can substitute methyl bromide, as well as it can replace phosphine, particularly in cases of significant insect resistance (Wright, 2003).

About animal and human health, COS can enter the body either by inhalation, dermal contact, or oral exposure. Studies in animals, such as rats and rabbits, revealed both acute and chronic effects, particularly on the nervous system (Banks, Desmarchelier, & Ren, 1996; Herr et al., 2007). Higher or repeated exposure may affect the regions of the brain involved in the control of movement and processing of sound information (Chou et al., 2016). It can lead to convulsion, sudden collapse, and even death. Other effects include irritation of the skin, eyes, nose, throat, and lungs, pulmonary edema, arrhythmia, weakness, and muscle cramps (New Jersey Department of Health, 2009).

Carbonyl sulfide adversity could be magnified by the outcomes of its reactions. The most critical processes are hydrolysis (DeMartino et al., 2017; Palmaa et al., 2019; Rich & Patel, 2015; Zhao et al., 2013) (Equation (14)) and the biodegradation (Haritos, 2001; Meredith et al., 2019) that results in the formation of hydrogen sulfide and carbon dioxide.



This process can contribute to global climate change (Rich & Patel, 2015) by increasing the atmospheric load of CO_2 (Sze & Ko, 1980), a well-known greenhouse gas. Conversely, as it is detailed hereafter, hydrogen sulfide is an extremely hazardous gaseous compound.

4.2.3. Hydrogen Sulfide (H_2S)

Although hydrogen sulfide is primarily released into the environment from natural sources and industrial sources (ATSDR, 2006), it was above shown that it can result from the reactions involving xanthates decomposition products such as carbonyl sulfide (COS).

Concerning its health effects, H_2S can enter the body through the skin contact and inhalation followed by a wide distribution throughout the body. The most targeted organs are the neurological, ocular, respiratory, and cardiovascular systems (ATSDR, 2006; Chou et al., 2016; Fiedler et al., 2008; PHE, 2016; Rubright, Pearce, & Peterson, 2017; Yalamanchili & Smith, 2008). From these authors, the most reported H_2S health hazards include, among others, the irritation of skin, eye, throat, and lungs, frostbite, respiratory paralysis, pulmonary edema, poor memory, tiredness, headaches, balance problems, cardiac arrhythmias, nausea, dizziness, poor memory, confusion, loss of consciousness, even death (Chou et al., 2016).

Hydrogen sulfide decomposition results in the production of hydrogen peroxide, which provoke serious cell damage, and depletion of oxygen (Equation (15)), a toxicity mechanism that leads to H_2S -associated oxidative stress (Beck et

al., 1981).



5. Conclusion

This work provides an overview of the research advancement and existing information on the essentiality, fate, ecotoxicity, and health effects of xanthates and xanthates based-compounds. It is proved that xanthates play an essential role in the sectors of the mining and mineral processing industry, metal removal and recovery from wastewater, agriculture, metal protection, rubber vulcanization, pharmaceutical industry, and medicine. Due to the affinity of xanthates for metal, the use of xanthates modified compounds may constitute a great potential and low-cost alternative in the treatment of metal-contaminated wastewater as well as for metal recovery from the contaminated media. Developing appropriate related methods could be economically and ecologically advantageous. Xanthates degradation, under different mechanisms and factors, results in the generation of various toxic substances, mainly carbon disulfide (CS₂) Carbonyl Sulfide (CS), hydrogen sulfide (H₂S), and Hydrogen peroxide (H₂O₂) which are likely to magnify their adversity to humans, animals, soil and aquatic living system. For the sustainability of the production, use, storage, and disposal of xanthates, more scientific and public involvement is still needed. Particular interest should be paid to laboratory and *in situ* evaluation of the fate and environmental and health effects of these toxic substances, individually or as simultaneously presence.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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