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Dedications

With deepest reverence and heartfelt devotion, I dedicate this doctoral dissertation to the cherished of my beloved parents, whose unwavering dedication to excellence and discipline shaped the very essence of my journey, guiding me to this pinnacle of achievement.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SCHEMAS

LIST OF ABBREVIATIONS

XRD	X-Ray diffraction
FTIR	Fourier Transform Infrared Spectroscopy
SEM	Scanning electron microscopy
EDS	energy dispersive spectrometer
JCPDS	Joint Committee on Powder Diffraction Standards (now the International Centre for Diffraction Data, ICDD)
C	Carbon
Cu	Copper
Cu(I)	Cuprous ion
Cu(II)	Cupric ion
$Cu(NO_3)_2$	Copper (II) Nitrate
CuSO	Copper (II) Sulfate
Cu^{2+}	Cupric Ion
Dm	Maximum Flotable Particle Size
Eh	Electrochemical Potential
EX^-	Ethyl Xanthate Anion
Fc	Centrifugal / Gravitational Force
Fe	Iron
FeS_2	Pyrite
Ff	Flotation Force
K	Potassium
KAX	Potassium Amyl Xanthate
KBX	Potassium Butyl Xanthate
KEX	Potassium Ethyl Xanthate
KIAX	Potassium Isoamyl Xanthate
KIBX	Potassium Isobutyl Xanthate
KIPX	Potassium Isopropyl Xanthate
KPX	Potassium Propyl Xanthate
Na	Sodium
NaOH	Sodium Hydroxide
NO_3^-	Nitrate Ion
O	Oxygen
Pb	Lead

$Pb(OH)_2$	Lead (II) Hydroxide
$PbCO_3$	Lead (II) Carbonate
PbS	Galena (Lead (II) Sulfide)
$PbSO_4$	Lead (II) Sulfate
Pb^{2+}	Plumbous Ion (Lead Ion)
Pm	Particle Perimeter
S	Sulfur
S^{2-}	Sulfide Ion
SO_4^{2-}	Sulfate Ion
EDTA	Ethylenediaminetetraacetic acid
Vm	Maximum Volume of the Particle
Y^{4-}	Fully Deprotonated Ethylenediaminetetraacetic acid
Zn	Zinc
ZnS	Sphalerite
γc	Acceleration
γlg	Liquid-Gas Surface Tension
θ	Contact Angle
ρs	Particle Density
CIP	Cold Isostatic Press
DFT	Density Functional Theory
FCC	Face-Centered Cubic

ABSTRACT

The froth flotation of galena (PbS), a cornerstone process for lead production, is fundamentally challenged by the mineral's propensity for surface oxidation. The formation of hydrophilic passivation layers severely impedes the adsorption of thiol collectors, such as xanthates, thereby depressing flotation performance. While copper activation is a standard industrial practice to overcome this issue, this thesis investigates a sequential strategy based on the central hypothesis that pre-treatment with a chelating agent, Ethylenediaminetetraacetic acid (EDTA), can chemically clean the mineral surface. This cleaning is posited to facilitate a more complete and robust copper activation, leading to significantly enhanced xanthate adsorption. The study further aims to systematically compare the efficacy of copper sulfate ($CuSO_4$) and copper nitrate ($Cu(NO_3)_2$) as activators.

A multi-technique surface analysis approach was employed, utilizing Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS), Fourier-Transform Infrared Spectroscopy (FTIR), and X-ray Diffraction (XRD) to characterize the morphological, elemental, and molecular changes on the galena surface following a series of systematic treatments.

The results unequivocally establish a clear hierarchy of efficacy. The sequential treatment involving EDTA pre-cleaning followed by copper sulfate activation and xanthate addition yielded the most robust collector adsorption. This was evidenced by extensive particle agglomeration (SEM), the highest surface concentrations of sulfur and copper (EDS), and the most intense vibrational peaks for copper-xanthate complexes (FTIR). Furthermore, the investigation confirmed that copper sulfate is an inherently superior activator to copper nitrate under the studied conditions, highlighting the critical influence of the counter-ion on the activation mechanism.

In conclusion, this thesis validates the synergistic effect of a sequential cleaning-activation strategy, demonstrating that removing inhibitory oxidation products with EDTA is a critical step for maximizing activator performance. The findings provide a fundamentally improved conditioning protocol for enhancing galena flotation and contribute to a deeper understanding of the complex interfacial chemistry governing mineral processing systems.

Keywords : Adsorption ; Activator; Sulfide ; Xanthate ; flotation

Résumé

La flottation par mousse de la galène (PbS), procédé fondamental de la production de plomb, est fondamentalement compromise par la propension de ce minéral à l'oxydation superficielle. La formation de couches de passivation hydrophiles entrave fortement l'adsorption des collecteurs de thiols, tels que les xanthates, réduisant ainsi les performances de la flottation. Si l'activation par le cuivre est une pratique industrielle courante pour pallier ce problème, cette thèse explore une stratégie séquentielle fondée sur l'hypothèse centrale qu'un prétraitement avec un agent chélateur, l'acide éthylènediaminetétraacétique (EDTA), permet de nettoyer chimiquement la surface du minéral. Ce nettoyage est censé faciliter une activation par le cuivre plus complète et plus robuste, conduisant à une adsorption des xanthates nettement améliorée. L'étude vise également à comparer systématiquement l'efficacité du sulfate de cuivre ($CuSO_4$) et du nitrate de cuivre ($Cu(NO_3)_2$) en tant qu'activateurs. Une approche d'analyse de surface multitechnique a été employée, utilisant la microscopie électronique à balayage couplée à la spectroscopie de rayons X à dispersion d'énergie (MEB-EDS), la spectroscopie infrarouge à transformée de Fourier (FTIR) et la diffraction des rayons X (DRX) afin de caractériser les modifications morphologiques, élémentaires et moléculaires de la surface de la galène suite à une série de traitements systématiques.

Les résultats établissent sans équivoque une hiérarchie d'efficacité claire. Le traitement séquentiel comprenant un pré-nettoyage à l'EDTA, suivi d'une activation au sulfate de cuivre et de l'ajout de xanthate, a permis d'obtenir l'adsorption du collecteur la plus robuste. Ceci a été mis en évidence par une agglomération importante des particules (MEB), les concentrations superficielles les plus élevées de soufre et de cuivre (EDS) et les pics de vibration les plus intenses pour les complexes cuivre-xanthate (FTIR). De plus, l'étude a confirmé que le sulfate de cuivre est un activateur intrinsèquement supérieur au nitrate de cuivre dans les conditions étudiées, soulignant l'influence cruciale du contre-ion sur le mécanisme d'activation. En conclusion, cette thèse valide l'effet synergique d'une stratégie de nettoyage-activation séquentielle, démontrant que l'élimination des produits d'oxydation inhibiteurs par l'EDTA est une étape cruciale pour optimiser les performances de l'activateur. Les résultats obtenus proposent un protocole de conditionnement fondamentalement amélioré pour optimiser la flottation de la galène et contribuent à une meilleure compréhension de la chimie interfaciale complexe qui régit les systèmes de traitement des minéraux.

ملخص

تُعدّ عملية التعويم الرغوي لغالينا (كبريتيد الرصاص)، وهي عملية أساسية في إنتاج الرصاص، تحديًا جوهريًا يتمثل في ميل المعدن للأكسدة السطحية. يُعيق تكوّن طبقات التخميل المحبة للماء بشدة امتصاص مُجمّعات الثيول، مثل الزانثات، مما يُقلّل من كفاءة التعويم. في حين أن تنشيط النحاس يُعدّ ممارسة صناعية شائعة للتغلب على هذه المشكلة، تبحث هذه الأطروحة في استراتيجية متسلسلة تستند إلى الفرضية المركزية القائلة بأن المعالجة المسبقة بعامل مُخلّب، وهو حمض الإيثيلين ثنائي الأمين رباعي الأسيتيك(EDTA) ، يُمكنها تنظيف سطح المعدن كيميائيًا. يُفترض أن يُسهّل هذا التنظيف تنشيطًا أكثر اكتمالًا وفعالية للنحاس، مما يؤدي إلى تحسين امتصاص الزانثات بشكل ملحوظ. تهدف الدراسة أيضًا إلى ($CuSO_4$)ونترات النحاس ($Cu(NO_3)_2$) المقارنة المنهجية لفعالية كبريتات النحاس كمنشطاستُخدم نهج تحليل سطحي متعدد التقنيات، شمل المجهر الإلكتروني الماسح مع مطيافية تشتت طاقة الأشعة السينية(SEM-EDS) ، ومطيافية الأشعة تحت الحمراء بتحويل فورييه(FTIR) ، وحيود الأشعة السينية(XRD) ، لتوصيف التغيرات المورفولوجية والعنصرية والجزيئية على سطح الغالينا بعد سلسلة من المعالجات المنهجية.

أثبتت النتائج بوضوح وجود تسلسل هرمي للفعالية. وقد حققت المعالجة المتسلسلة التي تضمنت التنظيف المسبق باستخدام ،الحمض متبوعًا بتنشيط كبريتات النحاس وإضافة الزانثات، أعلى امتصاص للمادة الجامعة. وتجلى ذلك من خلال التكتل الواسع للجسيمات(SEM) ، وأعلى تركيزات سطحية للكبريت والنحاس(EDS) ، وأعلى قمم اهتزازية لمركبات النحاس-زانثات .(FTIR) علاوة على ذلك، أكدت الدراسة أن كبريتات النحاس مُنشِّطٌ فائقٌ بطبيعته مقارنةً بنترات النحاس في ظل الظروف المدروسة، مما يُبرز التأثير الحاسم للأيون المُعاكس على آلية التنشيط.

وختامًا، تُؤكد هذه الأطروحة التأثير التآزري لاستراتيجية التنظيف والتنشيط المتسلسلة، مُوضحةً أن إزالة نواتج الأكسدة باستخدام خطوةٌ أساسيةٌ لتعظيم أداء المُنشِّط. تُقدِّم هذه النتائج بروتوكولًا مُحسَّنًا جذريًا لتكييف عملية التنشيط والتنظيف قبل تعويم الغالينا، وتُسهم في فهمٍ أعمق للكيمياء السطحية المُعقدة التي تُحكم أنظمة معالجة المعادن.

GENERAL INTRODUCTION

In the context of the global mining industry, the beneficiation of base metals constitutes an essential economic and technological pillar. Lead (Pb), in particular, remains an indispensable metal for numerous industrial applications, including the manufacturing of batteries, alloys, and radiation shielding. Galena (PbS) is the primary mineral source for this metal, and its efficient processing is a prerequisite for a stable and profitable supply chain. The hydrometallurgical process of froth flotation has long been established as the technology of choice for concentrating galena, owing to its selectivity and economic efficiency. This process relies on a fundamental physicochemical principle: the controlled modification of the target mineral's surface hydrophobicity to allow its selective adhesion to air bubbles and separation from the gangue. To propose reliable adsorption mechanisms, it is essential to understand the microscopic chemical composition of mineral particle surfaces before and after treatment with flotation reagents (1–3)

The implementation of galena flotation is, however, challenged by a major issue inherent to the mineral's nature: its strong chemical reactivity in aerated aqueous environments. Exposure of galena to dissolved oxygen and water leads to its surface oxidation, a complex phenomenon highly dependent on grinding conditions and mineral origin .Fundamental studies have shown that a preliminary alteration of the surface by oxidation is a prerequisite for xanthate anion adsorption; indeed, in the absence of oxygen, xanthate anions do not adsorb onto pure lead sulfide surfaces (1,4,5). However, excessive oxidation leads to the formation of passivating hydrophilic species such as lead sulfate ($PbSO_4$), lead carbonate ($PbCO_3$), and lead hydroxide ($Pb(OH)_2$) (1,6,7) .This oxidation layer acts as a barrier that severely inhibits the adsorption of collectors. The resulting adsorbed layer is often a heterogeneous phase that may contain not only various forms of lead xanthate (monolayer, or precipitated) but also dixanthogen, especially after wet grinding (7) .

To overcome this passivation, industrial practice widely employs a chemical activation step. The use of copper salts, particularly copper sulfate ($CuSO_4$), is a well-established strategy. The activation mechanism involves an electrochemical interaction in which cupric ions (Cu^{2+}) in solution modify the galena surface. Research has shown that while treatment with copper ions depresses the collectorless flotation of galena, it exerts an activating effect on flotation in the presence of potassium ethyl xanthate (KEX) (8) These modified surface sites exhibit a much higher affinity for xanthate molecules, leading to the formation of highly stable and strongly hydrophobic copper-xanthate (specifically, Cu(I) xanthate) and lead xanthate complexes, which restores and enhances the mineral's floatability (6,9–11). It is also important to note that

dissolved lead ions, originating from the mineral itself, can induce a "self-activation" by increasing the available cationic surface sites for subsequent xanthate anion adsorption .

Despite the recognized effectiveness of this approach, gaps remain in the detailed understanding of activation mechanisms. On one hand, the influence of the anion associated with the copper salt on activation efficiency remains poorly documented (9). On the other hand, a pre-existing oxidation layer can limit the access of activator ions to the underlying sulfide surface, reducing the overall efficiency of the treatment. An alternative strategy involves chemically "cleaning" the mineral surface. Ethylenediaminetetraacetic acid (EDTA), a powerful chelating agent, is known for its ability to selectively dissolve oxidation products. Studies have confirmed that EDTA can extract metal hydroxides from mineral surfaces and solubilize oxidation products, like oxides and hydroxides, without attacking the underlying metal sulfide (3,7,12) .This cleaning capability is corroborated by work showing that washing with an EDTA solution removes the detectable portion of oxidation products from galena (2).

This thesis is positioned at the intersection of these challenges and proposes to investigate an innovative sequential approach. The central hypothesis is that a pre-treatment of galena with EDTA, acting as a surface cleaning agent, can remove inhibitory oxidation layers, thereby exposing a purer and more reactive mineral surface (13). This "prepared" surface should then allow for a more uniform and complete activation by copper ions, leading to significantly enhanced xanthate adsorption and the formation of a more robust and hydrophobic collector layer than that obtained by activation alone. This approach is supported by research on pyrite which has shown that EDTA favors xanthate adsorption by removing formed oxides and hydroxides, allowing for similar results with lower collector concentrations (11,13) .

To test this hypothesis, this study pursues several objectives:

To systematically evaluate and compare the efficacy of copper sulfate ($CuSO_4$) and copper nitrate ($Cu(NO_3)_2$) as activators for Galena.

To characterize the morphological, elemental, and molecular changes on the galena surface after each treatment step (cleaning, activation, and collector adsorption).

To demonstrate and quantify the synergistic effect of EDTA pre-treatment on the efficiency of copper salt activation and subsequent xanthate adsorption.

To achieve these objectives, a multi-analytical approach was adopted, combining state-of-the-art surface characterization techniques, including Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDS), Fourier-Transform Infrared Spectroscopy (FTIR), and X-ray Diffraction (XRD). This methodology is consistent with established

approaches for studying adsorption on galena, where spectroscopic techniques such as Attenuated Total Reflection Infrared (ATR-IR) spectroscopy have been used to determine the resulting changes on the galena surface (3). The use of such surface analytical techniques is crucial for understanding the complex chemistry of flotation.The results of this research aim to provide a deeper fundamental understanding of the interfacial mechanisms and to propose an optimized conditioning strategy capable of improving the efficiency and sustainability of the lead flotation process.

PhD Thesis Objectives and Manuscript Outlin

The primary objective of this thesis is to establish the theoretical and industrial context for the research, addressing the central challenge of galena surface oxidation in froth flotation.

ChapterI: This introductory chapter will critically review the formation of hydrophilic passivation layers and their inhibitory effect on the adsorption of xanthate collectors. It will then evaluate the two principal, yet traditionally separate, strategies employed to mitigate this issue: chemical activation with copper salts and surface cleaning with chelating agents like EDTA. By synthesizing the existing literature, this chapter will identify a crucial research gap—the absence of a systematic investigation into a combined, sequential cleaning-and-activation strategy. This culminates in the formulation of the thesis's central hypothesis: that a sequential EDTA pre-treatment followed by copper activation can synergistically enhance xanthate adsorption far more effectively than conventional methods alone.

ChapterII: The second chapter presents the initial phase of the experimental investigation, with the objective of systematically comparing the efficacy of copper sulfate ($CuSO_4$) and copper nitrate ($Cu(NO_3)_2$) as activators for galena. The aim is to isolate and understand the influence of the activator's counter-ion on the surface modification process and subsequent adsorption of potassium ethyl xanthate (KEX). Through a multi-technique approach using XRD, FTIR, and SEM-EDS, this section will meticulously characterize and contrast the chemical and morphological changes induced by each activator. The analysis will establish a clear hierarchy of performance, providing foundational insights into the mechanisms of activation and serving as a critical baseline for the more advanced conditioning protocols investigated later.

ChapterIII: The third chapter forms the empirical core of the thesis, designed to rigorously test and validate the central hypothesis that pre-treatment with EDTA can synergistically enhance copper-activated xanthate adsorption. This investigation details a sequential strategy where the galena surface is first "cleaned" with EDTA to remove inhibitory oxidation products

before being activated with either copper sulfate or copper nitrate, followed by collector addition. The primary objective is to demonstrate and quantify the enhancement in collector uptake resulting from this protocol. Through comprehensive surface analysis, this chapter will provide unequivocal evidence of the synergistic effect by comparing the resulting surface morphology, elemental composition, and molecular signatures against those achieved through activation alone.

Finally, the concluding chapter will synthesize the collective findings to provide a cohesive and definitive summary of the research. It will reaffirm that a sequential cleaning-and-activation strategy, particularly using EDTA pre-treatment followed by copper sulfate activation, is demonstrably superior for promoting robust xanthate adsorption on galena. The chapter will consolidate the evidence supporting the proposed mechanism, articulating the novel contributions of this work to both fundamental mineral surface chemistry and applied mineral processing.It culminates in the proposal of a validated, optimized conditioning protocol and outlines promising avenues for future research, including pilot-scale validation and the application of this synergistic strategy to other complex sulfide systems.

CHAPTER I:
THEORETICAL FRAMEWORK AND LITERATURE REVIEW

I.1. Introduction

The efficient recovery of lead from its primary ore, galena (PbS), through froth flotation is a cornerstone of mineral processing (14). The fundamental principle of flotation relies on rendering the target mineral surface hydrophobic to facilitate its attachment to air bubbles and subsequent separation. This is typically achieved through the addition of thiol collectors, such as xanthates. However, the galena flotation system is fundamentally challenged by the mineral's inherent tendency to oxidize upon exposure to air and water.

Surface oxidation is a complex and dual-natured phenomenon in this context. On one hand, a degree of oxidation is a necessary prerequisite for collector adsorption. Studies have demonstrated that xanthate anions do not adsorb onto freshly cleaved or unoxidized galena surfaces in deoxygenated solutions; an initial alteration of the surface to an oxidation product is required for the collector to attach (15). On the other hand, uncontrolled and excessive oxidation leads to the formation of hydrophilic passivation layers, composed of species such as lead sulfates, carbonates, and hydroxides, which severely impede collector adsorption and depress flotation. The resulting adsorbed layer on an oxidized surface is often a heterogeneous mixture of products. Depending on process conditions, this can include various forms of lead xanthate (e.g., monolayer, and precipitated forms) and dixanthogen, the neutral dimer of xanthate (16,17).

To overcome the detrimental effects of passivation, the mineral processing industry widely employs chemical activators, typically copper salts such as copper(II) sulfate ($CuSO_4$) and copper(II) nitrate ($Cu(NO_3)_2$), to create new, highly reactive sites for collector attachment. The mechanism of copper activation is an electrochemical process wherein aqueous Cu^{2+} ions interact with the sulfide mineral surface and are reduced to Cu^{+}, which is the true activating species(18). These newly formed Cu(I) sites exhibit a high affinity for xanthate, leading to the formation of a stable and robust copper(I)-xanthate complex on the surface, which effectively restores hydrophobicity(11,19).

The chemical environment of the flotation pulp is further complicated by the presence of various other dissolved ions, which can have significant and often contradictory effects. For instance, dissolved lead ions, originating from mineral dissolution, can induce a "self-activation" of the galena surface by increasing the number of cationic sites available for subsequent anionic xanthate adsorption(20). Conversely, these same lead ions can cause the inadvertent activation of other sulfide minerals present in the ore, such as sphalerite, leading to poor selectivity and the loss of zinc to the lead concentrate(21,22). The role of an activating ion

is highly specific; copper ions, while being an effective activator for galena, can act as a depressant for other minerals like malachite by engaging in competitive adsorption for reagent sites(23)

An alternative or complementary strategy to activation is the chemical cleaning of the mineral surface prior to collector addition. Chelating agents, particularly ethylenediaminetetraacetic acid (EDTA), have been identified as powerful reagents for this purpose. EDTA is effective at dissolving and removing inhibitory oxidation products, such as metal oxides and hydroxides, from mineral surfaces without solubilizing the underlying sulfide mineral (12). By stripping away these passivating layers, EDTA treatment can expose a fresh, more reactive sulfide surface, thereby enhancing the efficiency of subsequent collector adsorption (12).

A review of the literature reveals that while copper activation and EDTA-based surface cleaning are both established as effective individual techniques for addressing the challenges of galena flotation, their combined, synergistic application has not been systematically investigated. A critical research gap exists concerning the potential benefits of a sequential strategy involving surface cleaning to remove inhibitory oxidation layers, followed by controlled activation to create highly receptive sites for collector attachment. Therefore, the rationale for the present study is to investigate the hypothesis that a sequential EDTA cleaning and copper activation strategy—examining the comparative effects of both copper sulfate and copper nitrate as activators—can lead to a more complete and robust xanthate adsorption, resulting in significantly improved flotation performance compared to activation alone.

I.2. Fundamentals of Froth Flotation

Froth flotation is a critical physicochemical separation process used extensively in the mineral processing industry to selectively recover valuable minerals from mined ore. The process is founded on the principle of manipulating the surface properties of minerals in an aqueous slurry to induce selective attachment to air bubbles (20,24,25) The fundamental property governing this separation is wettability, which describes the affinity of a mineral surface for water. Minerals that are naturally or chemically rendered non-wettable, or hydrophobic, will preferentially attach to air bubbles and be carried to the surface of the flotation cell, figure I.1, forming a mineral-rich froth that can be collected(15)

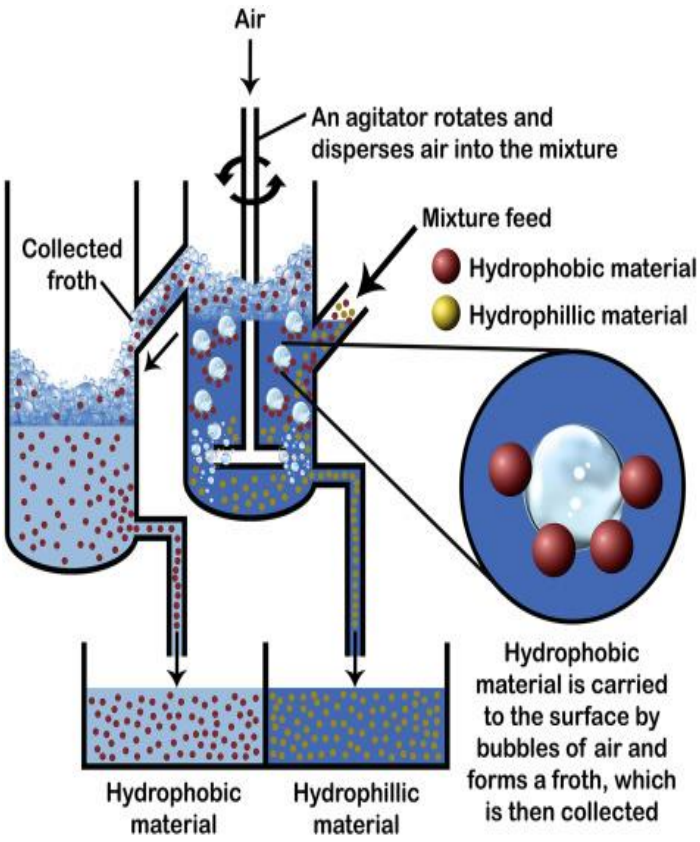


Figure I.1: The process of froth flotation.

Conversely, minerals that are readily wetted by water, or hydrophilic, remain suspended in the pulp (20,24).

I.3. Flotation type

I.3.1. Column flotation

Column flotation is a key mineral processing technology used to separate various metals and industrial minerals. It utilizes tall, vertical columns where mineral pulp is introduced from the top and air is injected from the bottom, creating bubbles. Hydrophobic particles attach to these bubbles and rise to the top. A washing system at the top of the column uses water to clean the froth, removing unwanted particles and improving concentrate purity. Industrial columns are typically large, with the collection zone forming the majority of their height, and feature systems for air bubble generation and froth washing.

I.3.2. Natural flotation

Natural flotation, often employed in primary separation, occurs when density differences alone are sufficient for separation. This process can sometimes be preceded by a step where droplets coalesce. It can also be initiated by the natural release of gas, such as during fermentation, exemplified by digester scum with high suspended solids content (20-40%) despite a density of

only 0.7-0.8 kg/L. While a natural phenomenon, injecting air bubbles into the liquid can enhance natural flotation. Assisted flotation, on the other hand, is specifically utilized for removing grease from highly turbid liquids.

I.3.3. Assisted flotation

Power-assisted flotation is an enhanced form of natural flotation, achieved by injecting air bubbles into a liquid. This method is especially effective for separating dispersed fats, as these hydrophobic solid particles readily capture air on their surfaces. For more comprehensive oil removal, mechanical aerators are employed to generate and diffuse fine air bubbles. The buoyant force of these bubbles carries the particles to the liquid surface, promoting their accumulation and subsequent removal. provides a comprehensive overview of various flotation types. We find the different types of flotation in Table I.1.

Table I.1 : flotation type.

Natural Flotation	Assisted Flotation	Induced Flotation
Used when the natural density difference is sufficient for separation	External aids are used to facilitate the separation of particles that would naturally float.	The density of particles is artificially reduced to promote flotation. This process relies on certain liquids or solids binding with gas bubbles, forming gaseous particles less dense than the liquid.

I.4. contact angle

The flotation process operates within a three-phase system where the selective attachment of solid mineral particles to gaseous air bubbles occurs within a liquid aqueous medium

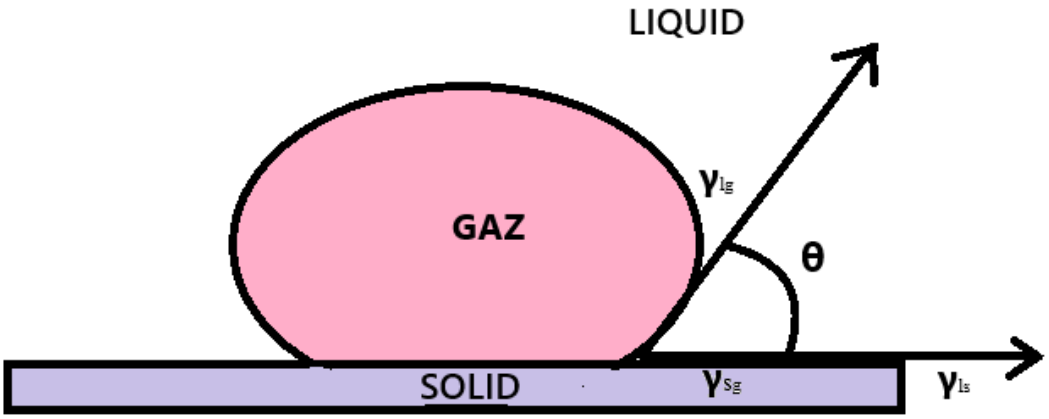


Figure I.2: Shematic of 3-phase system.

, figure I.2, The degree of this attachment is governed by the mineral's hydrophobicity, which is quantified by the contact angle (θ) formed at the solid-liquid-gas interface. A higher contact angle signifies greater hydrophobicity and a higher probability of stable bubble-particle attachment(26) .

However, the role of the contact angle extends beyond a simple qualitative indicator into the core physics that dictates the limits of flotation. The feasibility of flotation is determined by a balance between the upward-acting flotation force (Ff), which seeks to lift the particle, and the downward-acting gravitational or centrifugal force (Fc), which seeks to detach it. As demonstrated in the analysis by Z. Nedjar, D. BarkatStudies of Activation of Sphalerite by Copper and Xanthate Adsorption(27,28), the flotation force is directly proportional to the sine of the contact angle, as given by the relationshi

$F_f = P_m \cdot \gamma_{lg} \cdot \sin(\theta)$

$F_c = \rho_s . V_m . \gamma_c$

P_m : the particle perimeter

γ_{lg} : the liquid-gas surface tension.

V_m: Maximum volume of the particle (cm^3).

ρ_s: Particle density (g/cm^3)

γ_c: Acceleration (cm/s^2).

θ: Contact angle (°).

For a particle to be successfully floated, this upward force must equal or exceed the opposing downward force ($F_f \geq F_c$).

By establishing this force equilibrium, $F_f = F_c$

a direct physical relationship emerges that defines the maximum flotable particle size (Dm). (Let 's consider the cubic particle).

$$d_m = \sqrt[3]{\frac{4 \cdot \gamma_{lg} \cdot \sin\theta}{g \cdot (\rho_s - \rho_l)}}$$

This mathematical link shows unequivocally that increasing the contact angle directly increases the maximum size of a particle that can be recovered under constant hydrodynamic conditions.Nedjar et al. (2011) quantified this critical relationship, calculating that for galena, a contact angle of 40° corresponds to a maximum flotable diameter of 0.3705 mm. They further contextualize this by noting that for practical industrial applications, achieving a contact angle

in the range of 30° to 40° is essential for maintaining the favorable kinetics required for efficient separation in turbulent flotation cells(29) .Therefore, controlling pulp chemistry to maximize the contact angle is a primary engineering objective, as this single parameter directly governs the upper size limit and, consequently, the overall potential recovery of the valuable mineral.

I.5. Flotation Reagents

Flotation reagents are categorized based on their specific properties and functions.

I.5.1. Frothers

A frother is a surface-active reagent that fundamentally acts at the liquid-gas interface, where it serves three primary, interrelated functions. Its principal role is the creation and modification of bubbles; by adsorbing at the interface, frothers reduce surface tension and impart high elasticity, which promotes the formation of smaller, more uniformly sized, and nearly spherical air bubbles (typically 0.1 to 1 mm) in contrast to the large, unstable, and elongated bubbles found in their absence. This modification leads to a lower bubble rise rate, consequently increasing the total liquid-gas interfacial area available for particle collection. Furthermore, frothers enhance the attachment of collector-coated particles to this newly created interface through a mechanism of co-adsorption with the collector molecules, which is evidenced by an increase in the particle's contact angle and results in a more firmly adsorbed hydrophobic layer on the particle surface. The culmination of these effects is the formation of a pseudostable froth—a particle-laden foam—at the top of the flotation cell, which is crucial for the physical separation of the desired solids from the pulp. The mechanical stability of this froth is paramount, although turbulence within the cell can cause the undesirable mechanical entrainment of hydrophilic particles. However, under conditions of low turbulence, these entrained particles are effectively drained back into the pulp by the downward flow of water originating from the rupture of the water films surrounding the air bubbles within the froth(19)

I.5.2. Collectors or Surfactants

I.5.2.1. Characteristic Properties of a Surfactant

A collector or surfactant is a surfactant, formed from a heteropolar organic molecule consisting of at least one hydrocarbon chain and a polar head, which may contain one or more easily ionizable salt-forming groups. If the charge of the polar head (after dissociation in water) is negative, the collector is anionic, and if it is positive, the collector is cationic. The surfactant character is conferred by the affinity of the chain for the gas phase and of the polar head for the

liquid phase. The surfactant molecule is therefore oriented at the air-water interface.For sulfides, the most widely used surfactants belong to the thiol family.

These are mainly alkyldithiocarbonates and alkyldithiophosphates.(17,30). For oxides, silicates, and salts, the most commonly used surfactants are fatty acids, amines and their salts, alkyl sulfates, and alkyl sulfonates, FigureI.3.

I.5.2.2. Classification

Surfactants are classified into the following four broad categories:

I.5.2.2.1. Neutral Surfactants

These compounds are typically polyethylene or polyoxypropylene oxides, characterized by an alcohol or polyethylene-6 dodecanol functional group. A representative example is the substance with the empirical formula $CH_3 – (CH_2)_{11}O(CH_2CH_2O)_6$ H.

I.5.2.2.2. Cationic Surfactants

these are quaternary ammonium halides possessing lengthy hydrocarbon chains. Among them, n-hexadecyltrimethylammonium bromide (CTAB or HTMA) is particularly prevalent. Its chemical formula can be represented as $[n\text{-}C_{16}H_{33}N(CH_3)_3]^+,Br^-$.

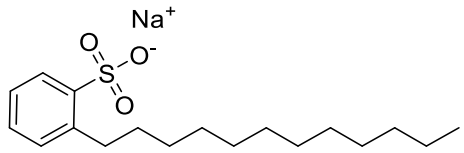
I.5.2.2.3. Anionic Surfactants

Defined by a substantial hydrophobic chain linked to an anionic group such as a sulfate, sulfonate, or carboxylate. For instance, $n\text{-}C_{12}H_{25}OSO_3^-Na^+$ serves as an illustrative example.

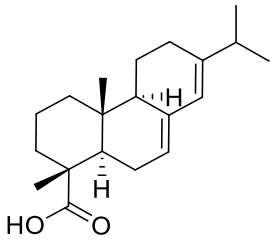
I.5.2.2.4. Zwitterionic Surfactants

This class of surfactants features both a cationic moiety, most frequently a quaternary ammonium group, and an anionic group like a sulfate or carboxylate. An example of such a

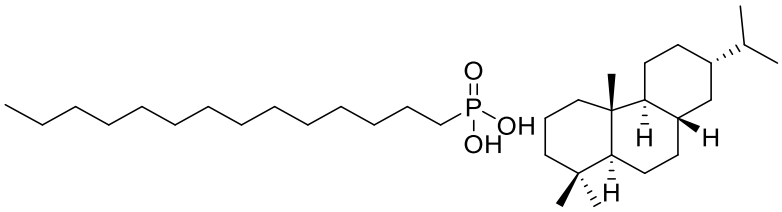
compound is CH_3-$(CH_2)_{11}N^+$ $(CH_3)_2$–CH_2–CH_2 – $CH_2SO_3^-$.



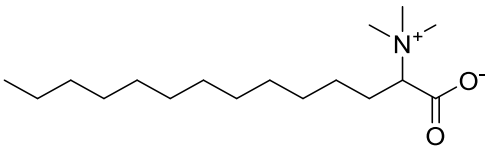
Sodium Dodecyl Benzene Sulfonate



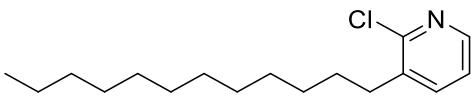
Abietic acid



AbietDimethyl ether of tetradecyl phosphonic acid



dodecyl betaine



N Dodecyl pyridine chloride

Figure I.3: Structural formula of some common surfactants[1]

I.5.3. pH-Modifying Agents

Because surface phenomena are frequently pH-sensitive, pH-adjusting agents (e.g., sulfuric acid, sodium hydroxide, hydrochloric acid) are commonly introduced.

I.5.4. Activators and Depressants(Modifiers)

Modifiers are a diverse group of chemical reagents added to control the flotation environment and enhance the selectivity and efficiency of the separation. They are crucial for navigating the complexities of multi-mineral ores.

I.5.4.1. Activators

Activators are reagents that modify a mineral's surface to facilitate or enhance collector adsorption, often by creating more favorable sites for the collector to bind. This is particularly important for minerals that are passivated or have a low affinity for a specific collector.

A classic and industrially vital example is the copper activation such as the activation of sphalerite with copper ions (18), And for galena Research by Popov and Vučinić (1990)(31), they demonstrated the complex dual role of copper ions. While dissolved copper ions were found to significantly depress the collectorless flotation of galena, they had a pronounced activating effect on flotation when the xanthate(KEX) was used as a collector.

In fact, flotation recovery was significantly better for galena treated with copper sulfate prior to KEX addition than for galena treated with KEX alone(31,32). The mechanism for this activation involves the creation of new adsorption sites on the galena surface. The formation of this stable copper xanthate species is responsible for the enhanced hydrophobicity and improved flotation performance(31–33).

Activation is not limited to foreign ions. A form of "self-activation" can occur, as demonstrated by the influence of lead ions on galena. Dissolved lead ions (Pb^{2+} and $Pb(OH)^{+}$), which can be present in the pulp water from mineral dissolution, were found to adsorb onto the galena surface. This adsorption increases the number of available cationic sites, leading to a significant increase in the subsequent adsorption of anionic xanthate. This was observed as an increase in the intensity of the infrared band corresponding to the monolayer form of lead ethyl xanthate, confirming an enhanced collector coverage(10).

I.5.4.2. Depressants

Depressants function in the opposite manner to activators, rendering unwanted (gangue) minerals hydrophilic to prevent their flotation and improve the selectivity of the process For example, sodium sulfide can act as a depressant by removing adsorbed collector products from mineral surfaces(30) .

Interestingly, an activating ion can also act as a depressant under different conditions. The work of Popov and Vučinić (1990) showed that in the absence of a collector, dissolved copper ions act as a potent depressant for galena(32). This depressing effect, observed in the pH range of 6.5 to 9.5, is attributed to the surface precipitation of hydrophilic copper(II) hydroxide ($Cu(OH)_2$) compounds. This newly formed hydrophilic layer passivates the naturally hydrophobic sites on the galena surface, thereby preventing its flotation(31). This example highlights how a single reagent can have opposing effects depending on the overall chemical conditions of the pulp.

I.5.4.3. The Role of the Aqueous Environment as a Modifier

Beyond added reagents, the aqueous environment itself, particularly the presence of water molecules at the mineral surface, acts as a critical modifier that can influence selectivity. A Density Functional Theory (DFT) study by Long et al. (2016) provided atomic-level insight into this phenomenon for the galena-sphalerite system(34). Their simulations revealed that the pre-adsorption of a water molecule has opposing effects on the two minerals. For sphalerite (ZnS), water adsorption was found to reduce the reactivity of the surface Zn atoms towards thiol collectors. Conversely, for galena (PbS), the presence of an adsorbed water molecule was shown to improve the reactivity of the surface Pb atoms, favoring the subsequent reaction with xanthate(34) .This suggests that water itself plays a fundamental role in the inherent selectivity of the system by effectively "depressing" the sphalerite surface while simultaneously "activating" the galena surface for collector interaction.

I.6. The Chemistry of Sulfide Mineral Surfaces

Sulfide minerals, such as galena (PbS) , FigureI.4, and pyrite (FeS_2)are the primary sources for many base metals, and their behavior in flotation is dictated by their unique crystal structures and surface chemistry (25).

Figure I.4:Galena

Among these, galena stands out as the principal ore of lead. Macroscopically, galena is characterized by its distinct metallic luster, high density, and a cubic crystal , figure I.5. It often forms well-defined cubes with perfect cleavage along three mutually perpendicular planes, a physical property that is a direct manifestation of its internal atomic arrangement.

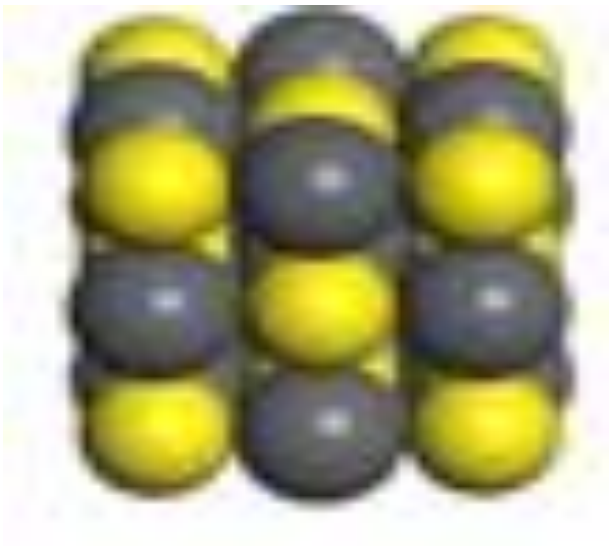


Figure I.5: galena structur

At the atomic level, the chemical properties of galena are governed by its crystal lattice. Galena crystallizes in the rock-salt structure, which is a simple face-centered cubic (FCC) lattice where lead (Pb^{2+}) and sulfur (S^{2-}) ions occupy alternating positions in a highly ordered, figure I.6, repeating three-dimensional array(35). This structure, with its specific lattice parameters and ionic bonding, defines the mineral's fundamental characteristics. The perfect cleavage observed macroscopically occurs along the (100) crystallographic planes, as these planes have the weakest bonding forces within the lattice. The behavior of galena in flotation is thus fundamentally dictated by the properties of this crystal structure and its resulting surface chemistry.

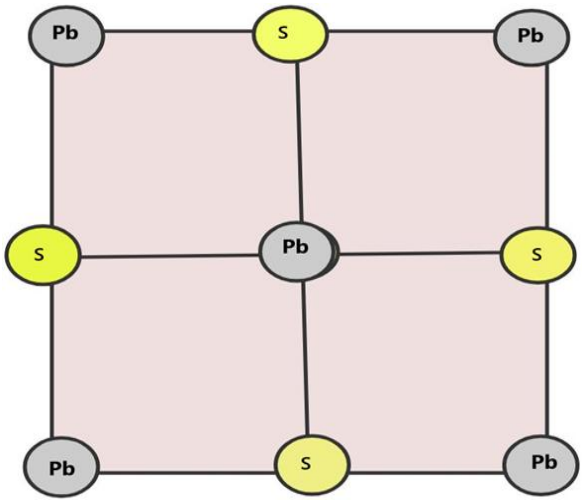


Figure I.6: Face-centered cubic unit cell of galena

While a freshly cleaved surface, exposing an ideal termination of this lattice, is inherently hydrophobic and can float without collectors, this property is ephemeral and quickly

compromised by surface oxidation (24). When exposed to atmospheric or aqueous environments, the sulfide mineral surface readily oxidizes, leading to the formation of a variety of surface species, including metal oxides, hydroxides, sulfates, and carbonates(27,36). Specifically for galena, this process transforms the hydrophobic PbS surface into hydrophilic layers composed of compounds such as lead sulfate ($PbSO_4$), lead carbonate ($PbCO_3$), and lead hydroxide ($Pb(OH)_2$) (26,37,38). This alteration, often termed passivation, renders the mineral surface more hydrophilic and can significantly hinder the adsorption of thiol collectors, thereby depressing its flotation (26,39). The extent and nature of this oxidation are influenced by numerous factors, including pH, electrochemical potential (Eh), and exposure time, making it a critical variable in sulfide flotation systems.

I.7. Thiol Collectors: Chemistry and Adsorption Mechanisms

In the flotation of sulfide minerals, thiol-based surfactants are the most prevalent class of collectors, with xanthates being preeminent due to their proven effectiveness and economic viability.

I.7.1. Definition and Structure

Xanthates are a class of organosulfur compounds defined as salts of O-esters of dithiocarbonic acid. Their general chemical formula is $ROCS_2M$, where R is an alkyl group, and M is typically an alkali metal such as potassium (K) or sodium (Na).

I.7.2. Types of xanthate

- ✓ Potassium ethyl xanthate (KEX).
- ✓ Potassium amyl xanthate (KAX.
- ✓ Potassium butyl xanthate (KBX).
- ✓ Potassium isobutyl xanthate (KIBX).
- ✓ Potassium propyl xanthate (KPX).
- ✓ Potassium isopropyl xanthate (KIPX).
- ✓ Potassium isoamyl xanthate (KIAX)(40).

I.7.3. Characteristics of Xanthate

I.7.3.1. Structural and Molecular Properties

A prime example used extensively in industry is Potassium Ethyl Xanthate (KEX), figure I.7, with the formula $CH_3CH_2OCS_2K$. Structurally, xanthates are amphiphilic molecules, featuring a polar dithiocarbonate head group responsible for chemical interaction with the mineral

surface, and a nonpolar hydrocarbon tail (the alkyl "R" group) that imparts hydrophobicity (24,41). This dual character is fundamental to their function as flotation collectors.

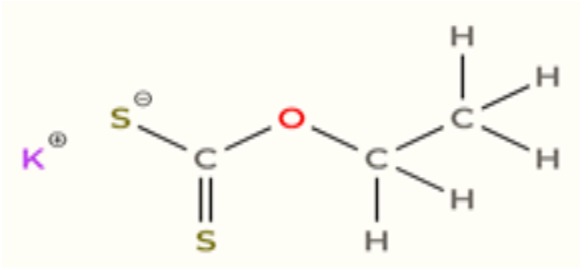


Figure I.7: Chmeical structure of Potassium Ethyl Xanthate (KEX)

I.7.3.2. Physical and Chemical Properties

Physically, xanthate salts are typically crystalline solids that are soluble in water. In an aqueous solution, the xanthate salt readily dissociates to release the active collector species, the xanthate anion ($ROCS_2^-$), as shown in Equation 1.

$CH_3CH_2OCS_2K\ (aq) \rightarrow CH_3CH_2OCS_2^-\ (aq) + K^+\ (aq)$ (Equation 1)

The primary chemical property exploited in flotation is the ability of this anion to adsorb onto sulfide mineral surfaces. This adsorption can proceed via two principal mechanisms. The first, and most relevant for galena, is chemisorption, where the xanthate anion forms a direct, often covalent, bond with metal cations on the mineral surface(42). In the case of galena, this leads to the formation of lead xanthate species, which precipitate on the surface and render it hydrophobic (Equation 2). This adsorbed layer can exist in various forms, from a monolayer to a precipitated multilayer, depending on collector concentration and surface conditions (27,43).

$Pb^{2+}(surface) + 2\ CH_3CH_2OCS_2^-(aq) \rightarrow Pb(OCS_2CH_2CH_3)_2(surface)$ (Equation 2)

The polar heads bind to the lead sites, orienting the hydrophobic tails away from the surface, thereby inducing hydrophobicity and promoting flotation.

The second mechanism is the electrochemical oxidation of two xanthate anions to form a neutrally charged dimer known as dixanthogen (Equation 3), figure I.8.

$2\ CH_3CH_2OCS_2^-(aq) \rightarrow (CH_3CH_2OCS_2)_2(aq) + 2e^-$(Equation 3)

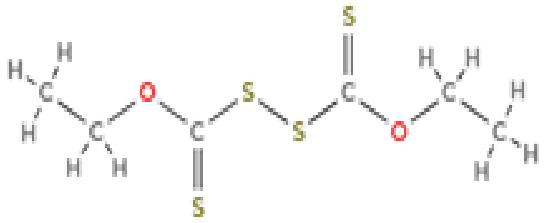


Figure I.8: Molecular structure of Dixanthogene(X2)

While dixanthogen is a strongly hydrophobic product and a key species in the flotation of minerals with higher rest potentials like pyrite(21,44), its formation on galena is significantly less favored under typical, less-oxidizing flotation conditions(18,45,46). Therefore, in the galena-xanthate system, lead xanthate species are considered the dominant hydrophobic product.

I.7.4. Advantages of Using Xanthate

The primary advantages of using xanthates as collectors in mineral flotation are well-established and include:

- ✓ High Collecting Power and Cost-Effectiveness: Xanthates are recognized for their strong ability to induce hydrophobicity on sulfide mineral surfaces and are widely employed due to their proven effectiveness and economic viability (44).
- ✓ Tunable Performance: The effectiveness and hydrophobicity imparted by xanthates can be tailored for specific applications. The collecting power generally increases with the length of the hydrocarbon (R) group, allowing for the selection of an appropriate xanthate for specific ore characteristics(47). This principle is evidenced by the use of different alkyl xanthates, such as butyl, ethyl, and amyl xanthates, across various flotation studies to optimize performance for different mineral systems(16,19,44).

I.7.5. Disadvantages of Using Xanthates

Despite their widespread use, the application of xanthates presents several challenges that require careful management:

- ✓ Sensitivity to Physicochemical Conditions: The effectiveness of xanthates is highly dependent on the conditions of the pulp, particularly the electrochemical potential (Eh) and pH. Research has extensively documented

that adsorption maxima and flotation recovery can vary significantly across different pH ranges, making process control crucial.

- ✓ Variable Adsorption Products: The specific chemical species formed on the mineral surface—whether it is a metal xanthate or dixanthogen—is contingent on the prevailing conditions and the mineral substrate itself. For example, dixanthogen is often the primary product on pyrite, whereas a mixture of metal xanthate and dixanthogen is typically observed on chalcopyrite and galena, complicating process control and optimization(16,19).
- ✓ System-Specific Limitations: In the galena-xanthate system, the flotation process relies heavily on the formation of lead xanthate, as the formation of the highly hydrophobic dixanthogen can be thermodynamically unfavorable under typical conditions. This necessitates precise control over reagent dosage to avoid collector over-addition, which is detrimental to selectivity and process economics.
- ✓ Limited Reagent Stability: Xanthates have a relatively short shelf life (approximately 7 days), which can present logistical challenges for storage and consistent performance in industrial operations.

Despite these challenges, the robust performance of xanthates has solidified their role as a foundational collector in the global mineral processing industry.

I.8. Activation in Sulfide Flotation

While some sulfide minerals readily interact with collectors, others, such as sphalerite, or those with passivated surfaces, require **activation** to enhance collector adsorption (45). Activation involves the use of specific metal ions to modify the mineral surface, creating more favorable sites for the collector to bind(18). For sulfide minerals, the most common and industrially significant activation process involves the use of copper(II) sulfate ($CuSO_4$)(48).

The mechanism of copper activation is an electrochemical process. When $CuSO_4$ is added to the pulp, aqueous Cu^{2+} ions interact with the sulfide mineral surface. Studies on pyrite and galena have shown that the surface reduces Cu^{2+} to Cu^{+}, which is the true activating species (48) (31). This newly formed Cu(I) site has a high affinity for xanthate, leading to the formation of a stable copper(I)-xanthate complex on the surface, which is more robust than the corresponding lead- or iron-xanthate (39,43) The work of Yin et al. (2020) on malachite showed that Cu^{2+} can also engage in competitive adsorption, depressing sulfidization flotation by occupying sites that would otherwise be available for collector (11). Consequently, a mineral

surface wich was previously passive or non-reactive toward a collector was expected to become strongly hydrophobic and floatable.Therefore The effectiveness of activation is dependent on several factors. The pH of the pulp dictates the speciation of both the copper ions and the mineral surface, while the concentrations of the activator and collector must be carefully balanced for optimal performance. Furthermore, conditioning time is crucial for allowing the ion exchange and surface transformation reactions to proceed (31). The use of $CuSO_4$ as an activator for various sulfide flotation systems is well-documented, highlighting its central role in modern mineral processing(31,45,49).

I.9. Surface Cleaning and Chelation Chemistry

The performance of both direct collector adsorption and activation can be severely compromised by pre-existing oxidation layers on the mineral surface. When galena (PbS) is exposed to oxygenated water, its surface readily oxidizes to form insoluble, hydrophilic passivating species such as lead hydroxide ($Pb(OH)_2$) and lead sulfate ($PbSO_4$), (as shown in Equations 4 and 5).

$PbS_{(s)} + 2\ O_{2(g)} \rightarrow PbSO_4$ (surface) (Equation 4)

$PbS_{(s)} + 2H_2O_{(l)} + ½\ O_{2(g)} \rightarrow Pb(OH)_2$(surface) + $S_{(s)} + H_2O$ (Equation 5)

These layers inhibit the interaction between the underlying sulfide mineral and the collector molecules. This has led to the concept of surface cleaning, where a chemical pre-treatment step is used to remove these inhibiting species and expose a fresh, more reactive mineral surface(46). One promising class of reagents for this purpose are chelating agents. Ethylenediaminetetraacetic acid (EDTA) is a powerful and well-known chelating agent.

I.9.1. Characteristics of Ethylenediaminetetraacetic Acid (EDTA)

Ethylenediaminetetraacetic acid (EDTA) is a versatile chelating agent with extensive applications across numerous industrial sectors, including water treatment, detergents, textiles, photography, paper pulp, food processing, cosmetics, and agriculture.

I.9.1.1. Structural and Molecular Properties

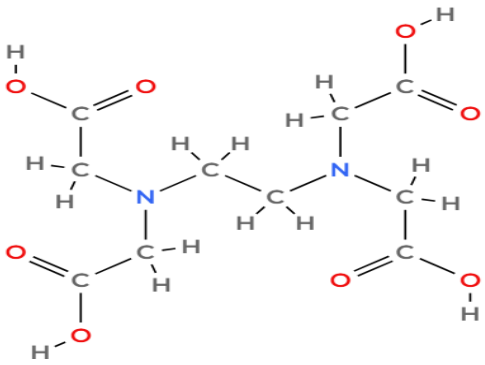


Figure I.9:Chemical Formul of EDTA ($C_{10}H_{16}N_2O_8$).

Its molecular structure, in its fully protonated form (Y^{4-}), contains multiple donor atoms (two amine nitrogens and four carboxylate oxygens), making it a hexadentate ligand ,Figure I.9.

I.9.1.2. Physical Properties(99)

- ✓ Physical State: At standard temperature and pressure, EDTA exists in a solid state.
- ✓ Appearance: The appearance of EDTA varies with its form; the pure acid is typically observed as colorless crystals, whereas its tetrasodium salt is a white powder.
- ✓ Density: 0.86 g/cm³.
- ✓ Solubility: The solubility of EDTA is highly dependent on its chemical form:
- ✓ The acid is sparingly soluble in water, with a reported solubility of 0.5 g/L at 20 °C, and is generally insoluble in most organic solvents.
- ✓ The tetrasodium salt of EDTA, in contrast, is highly soluble in water, dissolving at a concentration of 500 g/L at 20 °C.

I.9.1.3. Chemical Properties(99)

- ✓ Stability: Both the acid and salt forms of EDTA are chemically stable compounds under normal conditions of use and storage.
- ✓ Reactivity with Non-Metals: EDTA can react with strong oxidizing agents and strong bases.
- ✓ Reactivity with Metals: The compound is known to react with certain metals, notably copper, nickel, and their alloys.
- ✓ Complexing Ability: EDTA is recognized as a powerful complexing agent, a property that makes it highly effective in the extraction of metal oxides from surfaces.

Due to these properties, EDTA has proven effective in dissolving and removing metal oxides and hydroxides from various mineral surfaces, including oxidized galena. By removing these

passivated layers, EDTA treatment can reveal a purer sulfide surface, enhancing the effectiveness of subsequent adsorption or activation steps in the complex(39).

I.10. Conclusion

This literature review has systematically established the central challenge underpinning the efficient froth flotation of galena: the inherent and dual-natured propensity of its surface to oxidize. The existing body of research confirms that while a minimal degree of surface oxidation is a prerequisite for the chemisorption of xanthate collectors, excessive oxidation leads to the formation of hydrophilic passivation layers—composed of lead sulfates, carbonates, and hydroxides—that severely inhibit collector attachment and depress flotation. This dichotomy necessitates a sophisticated approach to surface chemistry modification that goes beyond simple collector addition.

The literature extensively documents two primary, yet largely separate, strategies to mitigate this issue. The first, and most industrially prevalent, is chemical activation, predominantly using copper salts like copper sulfate. The mechanism is well-understood as an electrochemical process wherein copper ions create new, highly reactive Cu(I) sites on the mineral surface that exhibit a strong affinity for xanthate. The second strategy involves the chemical cleaning of the mineral surface with chelating agents, particularly EDTA, which effectively dissolves the inhibitory passivation layers to expose a more pristine and reactive underlying sulfide surface.

The critical synthesis of these findings reveals a significant and compelling research gap. While both copper activation and EDTA-based cleaning are established as effective techniques in their own right, the literature lacks a systematic investigation into their combined, synergistic application. The potential benefits of a sequential strategy—whereby the oxidized surface is first chemically cleaned to remove inhibitory species after being intentionally activated to create optimal sites for collector adsorption—have not been explored. However, the relative efficacy of different activators, such as copper sulfate versus copper nitrate, within such a combined treatment regime remains unknown.

Therefore, this study is strategically positioned to address this gap. It builds upon the established principles of galena surface chemistry, activation, and chelation to investigate the hypothesis that a sequential EDTA cleaning and copper activation strategy can facilitate a more complete and robust xanthate adsorption than activation alone. By systematically characterizing

the surface at each treatment stage, this research will provide empirical evidence to either validate or refute this hypothesis, thereby contributing new and fundamentally important insights into the optimization of sulfide mineral flotation.

CHAPTER II:

COPPER NITRATE FOR GALENA ACTIVATION: A SURFACE CHEMISTRY STUDY OF XANTHATE ADSORPTION

II.1. Introduction

The global demand for lead and other base metals has driven the need for efficient and sustainable mineral processing techniques (50–52). Galena (PbS) is the primary ore of lead and is often associated with other sulfide minerals such as sphalerite (ZnS) and pyrite (FeS_2) (52,53). The selective flotation of galena from these minerals is essential for the recovery of lead and the production of high-quality concentrates (52,54–56). However, the inherent hydrophobicity of galena is often insufficient for effective flotation (53,54), necessitating the use of activators to modify its surface properties and enhance the adsorption of collectors (50,55,57,58).

Copper activation is a well-established method for improving the flotation of galena (35,59). The addition of copper ions, typically in the form of copper sulfate ($CuSO_4$), promotes the formation of copper sulfide species on the galena surface, which in turn facilitates the adsorption of xanthate collectors (20,60). This process enhances the hydrophobicity of the mineral surface, leading to improved flotation performance (35,50). Despite the widespread use of $CuSO_4$, the underlying mechanisms of copper activation and its impact on xanthate adsorption are still not fully understood (35,61). Furthermore, the influence of different copper salts on the activation process and flotation efficiency remains largely unexplored (61).

Moreover, the mineral processing industry is increasingly under pressure to adopt more environmentally sustainable practices (51). While highly toxic reagents like cyanides (used as depressants) draw significant criticism (51,55,57), the extensive use of metal salts, including activators like copper sulfate, also contributes to the overall chemical load in process water and tailings. There is a continuous drive for alternative reagents and processes that are not only effective but also more ecologically benign and economically viable (55,57). This includes optimizing reagent consumption and exploring activators that may offer improved performance or a reduced environmental footprint.

Driven by the continuous demand for enhanced efficiency, cost-effectiveness, and environmental sustainability in mineral beneficiation, this study explores copper nitrate ($Cu(NO_3)_2$) as a novel activator in galena flotation. Specifically, the primary objective is to provide a systematic evaluation of the activation capabilities of $Cu(NO_3)_2$, focusing on its effectiveness in enhancing the adsorption of potassium ethyl xanthate (KEX) on galena (PbS) surfaces. Given the importance of activators for collector adsorption in mineral flotation, such an investigation is essential for identifying alternative activators that can improve the flotation

performance of galena, optimizing flotation efficiency while maintaining environmental and economic viability.

Despite extensive research on copper sulfate ($CuSO_4$) as an activator for sulfide minerals, the activation performance of copper nitrate ($Cu(NO_3)_2$) has remained largely unexplored. To our knowledge, the only study that has addressed $Cu(NO_3)_2$ in the context of mineral activation was conducted by Nedjar and Barkat (62), which focused on its use as an activator for sphalerite (ZnS) flotation. No studies have systematically investigated the activation of galena (PbS) by $Cu(NO_3)_2$, leaving a critical gap in the understanding of its surface interactions, activation mechanisms, and flotation efficiency. This study is the first to directly address this gap, providing a comprehensive evaluation of $Cu(NO_3)_2$ as an activator for galena.

To achieve this objective, a suite of advanced surface characterization techniques will be employed. X-ray diffraction (XRD) confirmed the structural integrity of galena post-activation, while Fourier-transform infrared spectroscopy (FTIR) identified chemisorbed xanthate species (e.g., Pb–X and Cu–X complexes) on the mineral surface. Scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS) provided spatial and elemental evidence of $Cu(NO_3)_2$-induced surface modification, corroborating enhanced xanthate adsorption. These analytical methods align with established protocols for studying sulfide mineral activation (e.g., Nedjar and Barkat, 2013), ensuring accurate and reproducible results.

Moreover, to establish the practical relevance of $Cu(NO_3)_2$, its activation efficiency will be benchmarked against that of copper(II) sulfate ($CuSO_4$), a widely recognized activator in galena flotation (63). Through this direct comparative analysis, the study seeks to determine whether $Cu(NO_3)_2$ offers a more effective and sustainable alternative to $CuSO_4$. By providing a detailed, evidence-based assessment of the activation potential of $Cu(NO_3)_2$, this research addresses the ongoing demand from the mineral processing community for improved and alternative flotation reagents.

II.2. Materials and methods

II.2.1. Samples, Reagents, and Sample Preparation

The galena (PbS) samples used in this study were obtained from the Shaibet El Hamra mine in Algeria.The raw ore was manually separated, then crushed and ground in an agate mortar , figure II.1.

Figure II.1: Galena crushind and ground in an agate mortar

For adsorption tests, a galena fraction of -208 + 108 µm (i.e., particles passing a 208 µm sieve and retained on a 108 µm sieve) was utilized. For scanning electron microscopy (SEM) examination, a ground product sieved to -74 + 38 µm was used. For Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Diffraction (XRD) analyses, a portion of the -108 µm powder (i.e., particles passing a 108 µm sieve) was further ground to a particle size of approximately less than 2 µm.

Potassium ethyl xanthate (KEX, purity 96%), copper (II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$, purity 98.5%), and copper (II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$, analytical grade) were procured from Sigma-Aldrich Co. (St. Louis, MO, USA). Sodium hydroxide (NaOH, analytical grade), also from Sigma-Aldrich Co., was used for pH adjustment. All solutions were prepared using distilled water.

II.3. Methods and instrumentation

II.3.1. Scanning electron microscopy with energy dispersive spectrometer (SEM-EDS) analysis

The surface morphology and elemental composition of galena were analyzed before and after reagent treatments using a Bruker Nano GmbH scanning electron microscope (SEM) equipped

with an Xflash Detector 610M energy-dispersive X-ray spectrometer (EDS), figure II.2. The EDS analysis area corresponded to the SEM observation region, typically ranging between 1 and 100 µm². The accuracy of the EDS spectral analysis was approximately 1%. The SEM was operated at an accelerating voltage of 20 kV to determine the atomic concentrations of elements such as lead, sulfur, copper, carbon, and oxygen on the sample surfaces. Analyses were performed at the PTLA laboratory, part of the University of Biskra's research laboratories.

Figure II.2: Bruker Nano GmbH scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectrometer (EDS).(Biscra univercity)

II.3.2. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

FTIR spectra were collected using a Perkin-Elmer Spectrum Two spectrometer (PerkinElmer Inc., Waltham, MA, USA), figure II.3, with a resolution of 8 cm^{-1}. The analysis was performed in transmission mode across the wavenumber range of 400–4000 cm^{-1}. For every sample, 120 scans were accumulated. Prior to analysis, approximately 100 µg of the powder sample was mixed with 23±2 mg of KBr, and compressed using a cold isostatic press (CIP) at 150 MPa to form a pellet with a thickness of 200–250 µm. The IR spectra display transmittance (T) as a function of the incident wavenumbers. Analyses were performed at the Laboratory of Structures, Properties and Inter-Atomic Interactions (LAPI2A), part of the University of Khenchela's research laboratories.

Figure II.3: Perkin-Elmer spectrometer(Khenchela univercity).

II.3.3. X-Ray diffraction (XRD)

X-ray powder diffraction (XRD) analysis was employed to qualitatively identify the crystalline mineral phases present in the samples. XRD patterns were obtained using a Rigaku MiniFlex 600 benchtop diffractometer (Rigaku Corporation, Tokyo, Japan) equipped with a CuKα radiation source (λ=1.542 Å), figureII.4. Data were collected at a scan rate of 0.03°/s over a 2θ range of 5° to 90°. Phase identification was performed by comparing experimental diffraction patterns with reference data from the JCPDS (International Center for Diffraction Data) database. Analyses were performed at the PTLA laboratory, part of the University of Biskra's research laboratories.

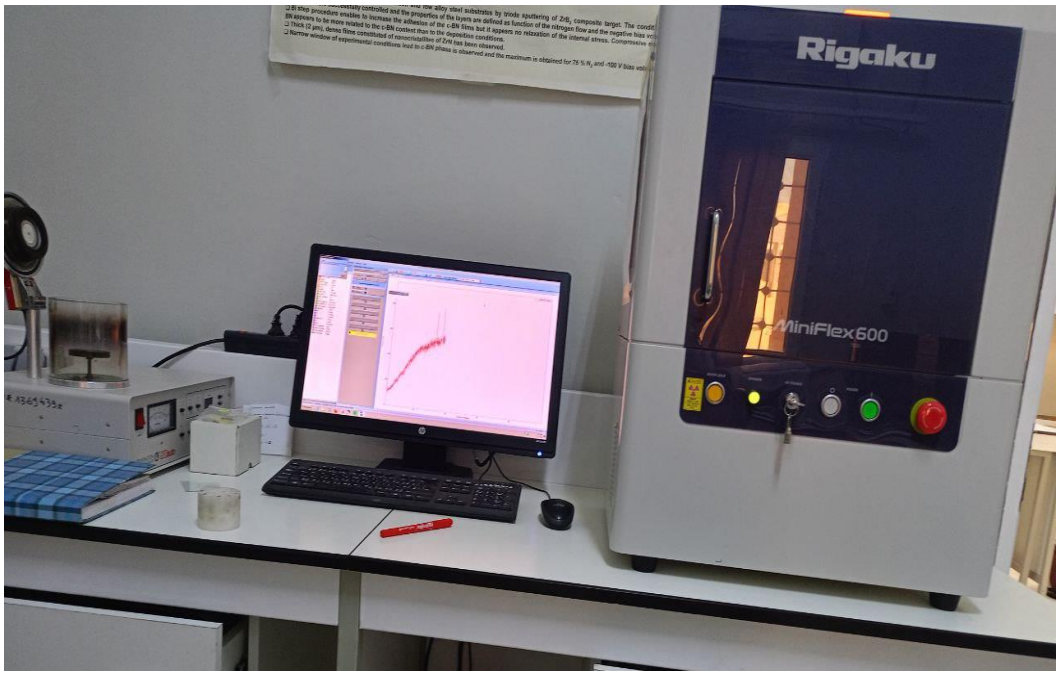


Figure II.4 : Rigaku MiniFlex 600 benchtop X-Raydiffractometer (Biscra univercity).

II.4. Adsorption and Activation Procedure

The experimental conditions for KEX adsorption and copper activation (pH, reagent concentrations, contact times) were selected based on a review of established literature for galena flotation, aiming to ensure relevant conditions for comparing the effects of $CuSO_4$ and $Cu(NO_3)_2$ on surface chemistry rather than performing a comprehensive optimization study. The rationale for each specific parameter is detailed below.

pH Conditions: The pH of the galena suspension was adjusted to and maintained between 9.0 and 10.0 using NaOH (10^{-1} mol/L). This moderately alkaline range is consistent with optimal conditions reported for galena flotation, particularly when using xanthate collectors and copper activators. Studies such as Özün & Ergen (24) found the highest galena recoveries at pH 9-9.5, correlating this with favorable surface chemistry for xanthate chemisorption. Similarly, Nedjar & Barkat (64–66) consistently employed pH values around 9-9.5 for their studies on copper activation and xanthate adsorption on galena, noting that basic pH is generally favorable. Popov & Vucinic (63) also found optimal flotation with KEX between pH 8 and 10 after copper activation.

KEX Concentration: Potassium ethyl xanthate (KEX) was used at a concentration of 5 x 10^{-2} mol/L. While specific collector dosages vary, this concentration ensures sufficient collector availability for surface coverage and is within the range of concentrations explored in fundamental adsorption studies, allowing for clear detection of surface species. For comparison,

Nedjar & Barkat (64,65) used xanthate concentrations in the order of 10^{-3} M for their surface characterization work.

Activator Dosage: For activated samples, copper sulfate ($CuSO_4$) or copper nitrate ($Cu(NO_3)_2$) was used at a concentration of 10^{-3} mol/L. This dosage is consistent with concentrations reported in literature for effective copper activation of sulfide minerals (e.g., Nedjar & Barkat) , (Nedjar and Barkat, 2015; (65), used 10^{-4} M $CuSO_4$; Popov & Vucinic, (63), used $3x10^{-5}$ M $CuSO_4$ for flotation tests, with higher concentrations for zeta potential). The 10^{-3} M concentration was chosen to ensure significant activation for clear comparative analysis of the surface modifications. An equivalent molar concentration of Cu^{2+} ions was used for both $CuSO_4$ and $Cu(NO_3)_2$ to allow for a direct comparison of the counterion effects.

Contact Time: A contact time of 10 minutes was employed for the activation step (when activators were used) and subsequently for the KEX adsorption step. This duration was selected to allow suficient time for the respective surface reactions to proceed towards equilibrium, as indicated by studies monitoring rest potential stabilization or observing adsorption kinetics (e.g., Nedjar & Barkat), (64), reported activation times around 8-30 minutes based on rest potential; Özün & Ergen, (67), used 5-10 minutes for xanthate conditioning.

II.4.1. Experimental Protocol for Sample Preparation

Three types of samples were prepared for surface characterization. For each preparation, 3 g of galena powder was added to 30 ml of distilled water. The suspension was then subjected to the following treatments, with adequate agitation during each reagent addition and conditioning period , Scheme II-1 :

Sample 1 (KEX alone): The pH of the galena suspension was adjusted to 9 -10 using NaOH (10^{-1} mol/L). KEX solution was then added to achieve a final concentration of 5 x 10^{-2} mol/L, and the suspension was conditioned for 10 minutes.

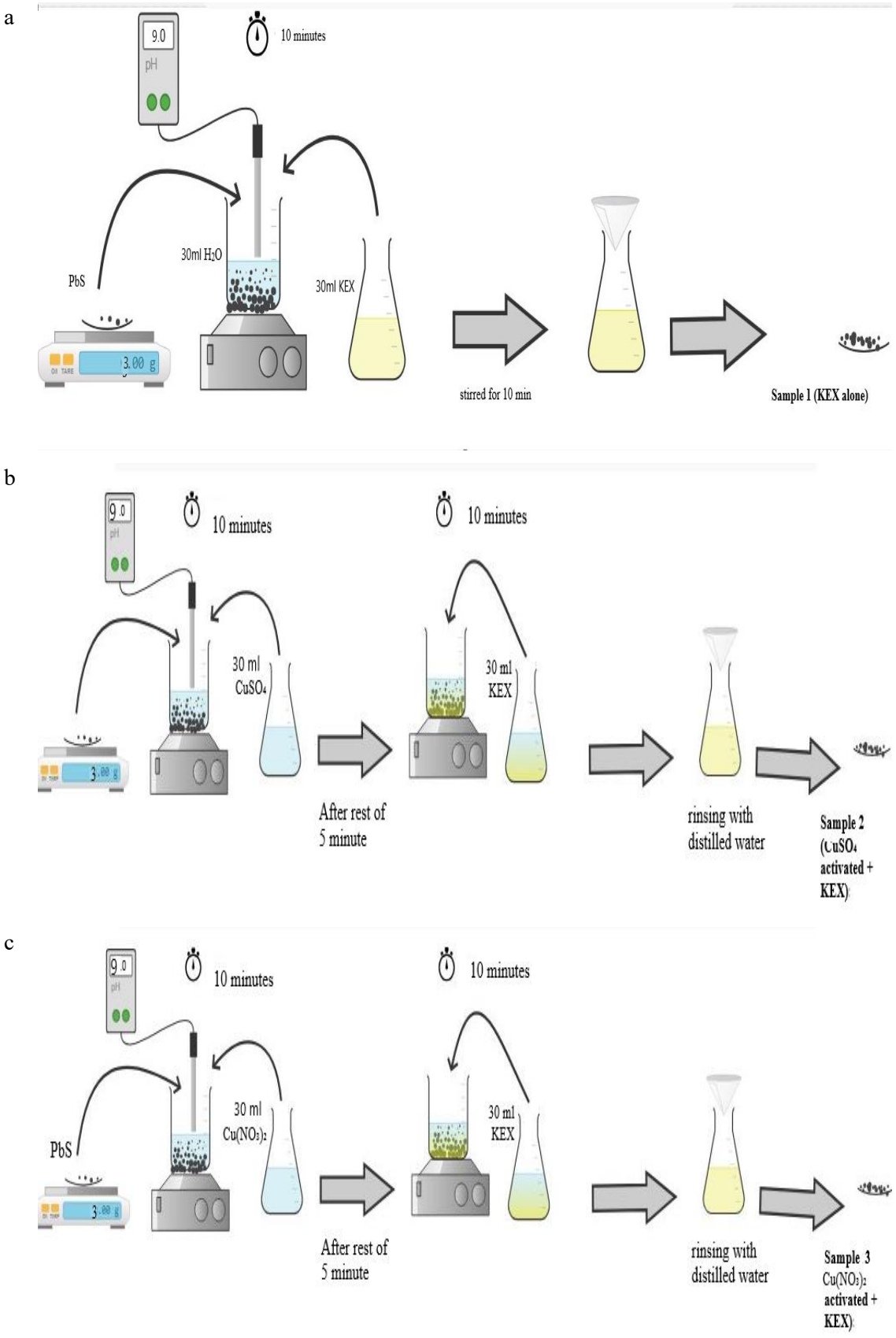


Schéma II.1: Adsorption Procedure of KEX on Galena

Note:(a):sample 1; (b) sample 2 ;(c) sample 3.

Sample 2 ($CuSO_4$ activated + KEX): The pH of the galena suspension was adjusted to 9.0-10.0. $CuSO_4$ solution was added to achieve a final concentration of 10^{-3} mol/L, and the suspension was conditioned for 10 minutes (activation step). Subsequently, KEX solution was added to a final concentration of 5 x 10^{-2} mol/L, and the suspension was conditioned for an additional 10 minutes.

Sample 3 ($Cu(NO_3)_2$ activated + KEX): The pH of the galena suspension was adjusted to 9-10$Cu(NO_3)_2$ solution was added to achieve a final concentration of 10^{-3} mol/L, and the suspension was conditioned for 10 minutes (activation step). Subsequently, KEX solution was added to a final concentration of 5 x 10^{-2} mol/L, and the suspension was conditioned for an additional 10 minutes.

After the final treatment step, each sample mixture was allowed to rest for 5 minutes. The solids were then separated by repeated rinsing with distilled waterand filtration to remove unadsorbed reagents prior to surface characterization analyses, Figure II.5.

Figure II.5: Drying samples in open air.

II.5. Results and Discussion

This section presents and discusses the experimental findings from our investigation into the comparative effects of copper sulfate (CuSO4) and copper nitrate (Cu(NO3)2) as activators for galena. In line with our study's primary aim to elucidate the surface modifications and their impact on xanthate adsorption, we first detail the baseline characterization of the pristine galena mineral and the potassium ethyl xanthate (KEX) collector. Subsequently, we present the results obtained from X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and Energy Dispersive X-ray Spectroscopy (EDS)analyses. These analyses systematically examine the galena surface chemistry and morphology after interaction with KEX alone, and then after activation with $CuSO_4$ or

$Cu(NO_3)_2$ prior to KEX treatment. The ensuing discussion interprets these findings in the context of existing literature, focusing on the mechanisms of copper activation, xanthate adsorption, and the differential impacts of the two copper salts, thereby providing insights relevant to optimizing galena flotation processes.

II.5.1. Galena Characterization

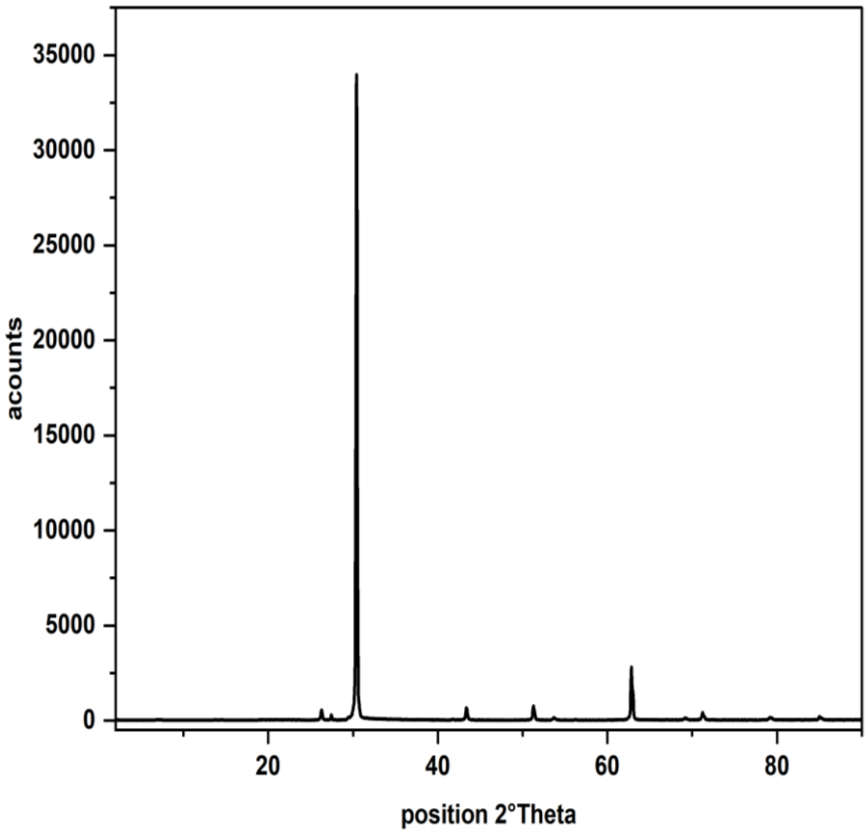
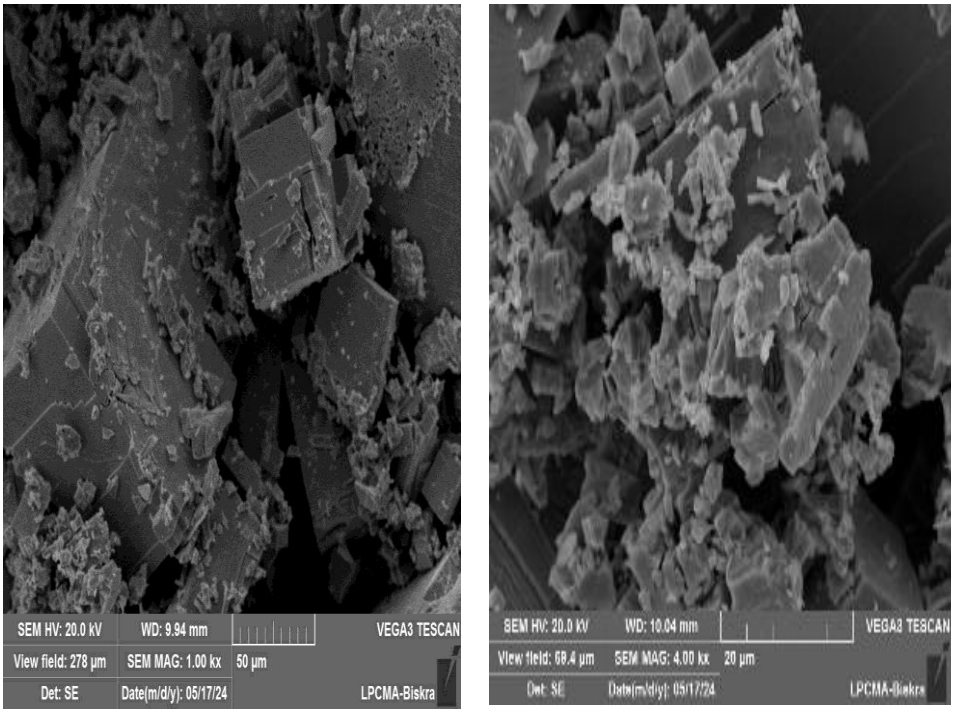


Figure II.6: X-ray diffraction pattern of galena

The XRD analysis of the galena, Figure II.6, revealed distinct diffraction peaks at 2θ angles of 26.07°, 30.02°, 43.23°, 51.18°, 53.64°, and 62.6, corresponding to d-values of 3.41 Å, 2.95 Å, 2.09 Å, 1.78 Å, 1.70 Å, and 1.47 Å, respectively. These peaks are consistent with the reference JCPDS file No. 96-901-3401 for galena (PbS), confirming the presence of galena as the primary phase in the sample. The most intense peak at 2θ = 30.2° (d = 2.95 Å) indicates the preferred orientation of the galena crystals, which is typical for this mineral. The relative peak intensities suggest a well-crystallized structure; the peak at 2θ = 26.07° (d = 3.41 Å), also exhibiting significant intensity (92.6%), further supports the dominance of galena in the sample. These findings are consistent with the XRD patterns of galena reported across multiple studies. For instance, the characteristic diffraction peaks of galena were similarly observed by Basilios

et al.(68). Similarly, Nedjar and Barkat (60) and Leppinen JO et al. (50) also observed the main characteristic peaks of galena in their XRD analyses, confirming its crystalline nature. Although the specific peak intensities in our study differ slightly from some of these studies, such variations can be attributed to differences in the origin and processing of the samples, as well as the experimental conditions used for XRD analysis (60,68). The high intensity of the peak at $2\theta = 30.2°$ in our study is also in agreement with the findings of Nedjar et al. (69), who reported this peak as the most intense in their XRD analysis of galena. This consistency across various studies confirms the reliability of our XRD analysis in identifying galena as the primary mineral phase.

The SEM images, Figure II.7, of galena at magnifications of 1000 × (a), and 4000× (b) reveal the granular and crystalline nature of the galena. The images show well-defined crystal faces and a relatively uniform particle size distribution, which is characteristic of galena. These observations are consistent with the morphological features of galena described in various studies. For instance, Nedjar et al. (69) observed similar granular morphology with well-defined crystal faces in their SEM analyses. Additionally, the findings align with Leppinen JO et al. (50), who found that galena samples exhibited well-defined cubic crystal morphology, which they attributed to the cubic crystal structure of PbS. The consistency in morphological features across these studies underscores the typical characteristics of galena.



(a) (b)

Figure II.7: SEM images of galena showing magnification of 1000× (a), and 4000× (b).

The EDS analysis, Figure II-8, confirmed the elemental composition of the sample, with lead (Pb) and sulfur (S) being the predominant elements, accounting for 77.81% and 16.64% by weight, respectively. Trace amounts of oxygen (O) and carbon (C) were also detected, likely due to surface oxidation or contamination during sample preparation. The absence of copper (Cu) in the EDS analysis suggests that the galena sample is relatively pure, with no significant copper-bearing phases. This is consistent with the findings of Basilios et al. (68) and Özün et al. (47), who also reported the absence of copper in their galena samples. The presence of trace amounts of oxygen and carbon in our EDS analysis is likely due to surface oxidation, which is a common phenomenon in galena samples exposed to air (70); (71).

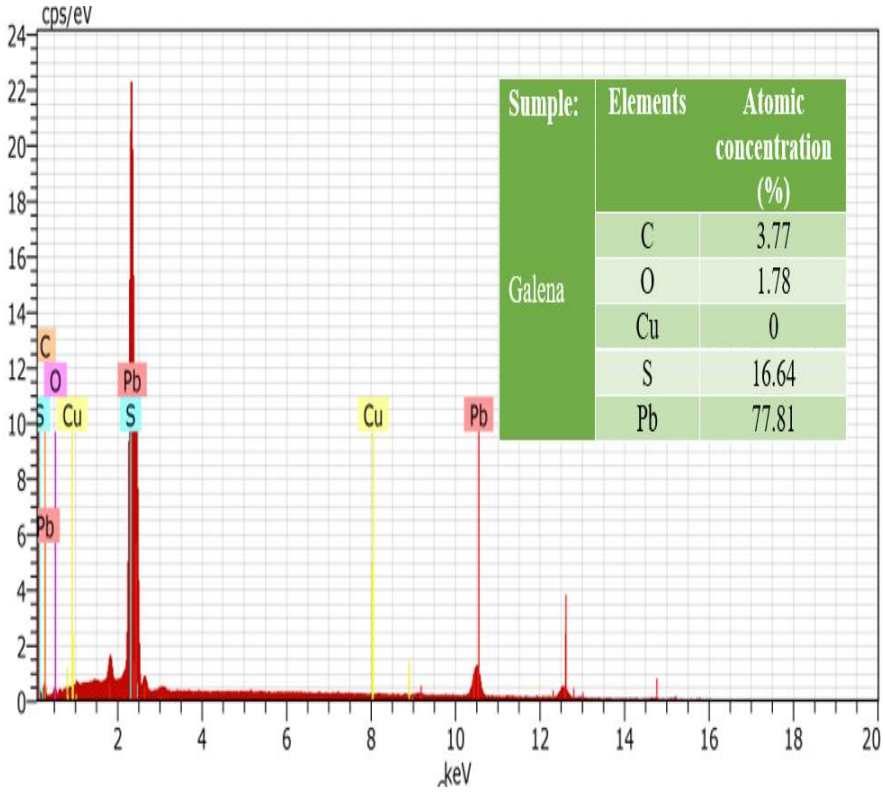


Figure II.8: EDS spectrogram of galena.

The Fourier Transform Infrared Spectroscopy (FTIR) spectrum of galena, Figure II.9, exhibits a characteristic absorption band at approximately 1415 cm^{-1}, which is attributed to the stretching vibrations of Pb-S bonds. This confirms the presence of lead sulfide in the sample. Minor peaks at higher wavenumbers (e.g., around 1385 cm^{-1} and 1622 cm^{-1}) may be associated with surface hydroxyl groups or adsorbed water molecules, suggesting a relatively clean galena surface with minimal organic or inorganic contamination. These findings are in line with the FTIR spectra reported by Xie et al. (26) and Vucinic et al. (72), where similar absorption bands were observed and attributed to Pb-S vibrations and surface species. The presence of minor peaks related to surface species in our FTIR spectrum is a common observation in mineral analysis and is

consistent with similar findings in the literature, where such peaks are often attributed to surface oxidation or adsorbed water (72,73). While some studies like Leppinen et al. (50) do not focus on the FTIR analysis of pure galena, they present FTIR spectra of galena after interaction with other reagents and also detect peaks corresponding to Pb-S vibrations.

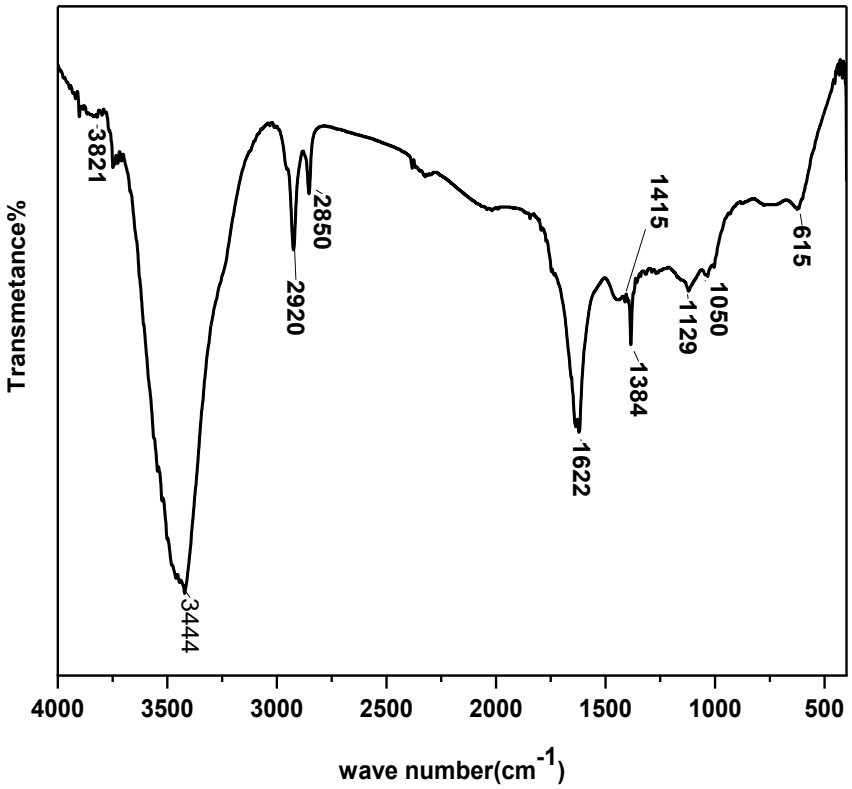


Figure II.9: FTIR Spectrum of Galena

II.5.2. Potassium Ethyl Xanthate (KEX) Characterization

The XRD analysis of potassium ethyl xanthate (KEX), Figure II.10, revealed several diffraction peaks at 2θ angles of 7.90°, 8.25°, 24.44°, 26.28°, 29.19°, and 33.13°, corresponding to d-values of 11.17 Å, 10.70 Å, 3.637 Å, 3.38 Å, 3.065 Å, and 2.70 Å, respectively. These peaks are consistent with the reference JCPDS file No. 00-009-0700 for KEX, confirming the identity of the compound.

The most intense peak at 2θ = 7.908° (d = 11.17 Å) indicates a highly ordered crystalline structure, which is typical for KEX. The relative intensities of the peaks suggest a well-defined crystalline phase, with the peak at 26.28° (d = 3.38 Å) also showing significant intensity (78%).

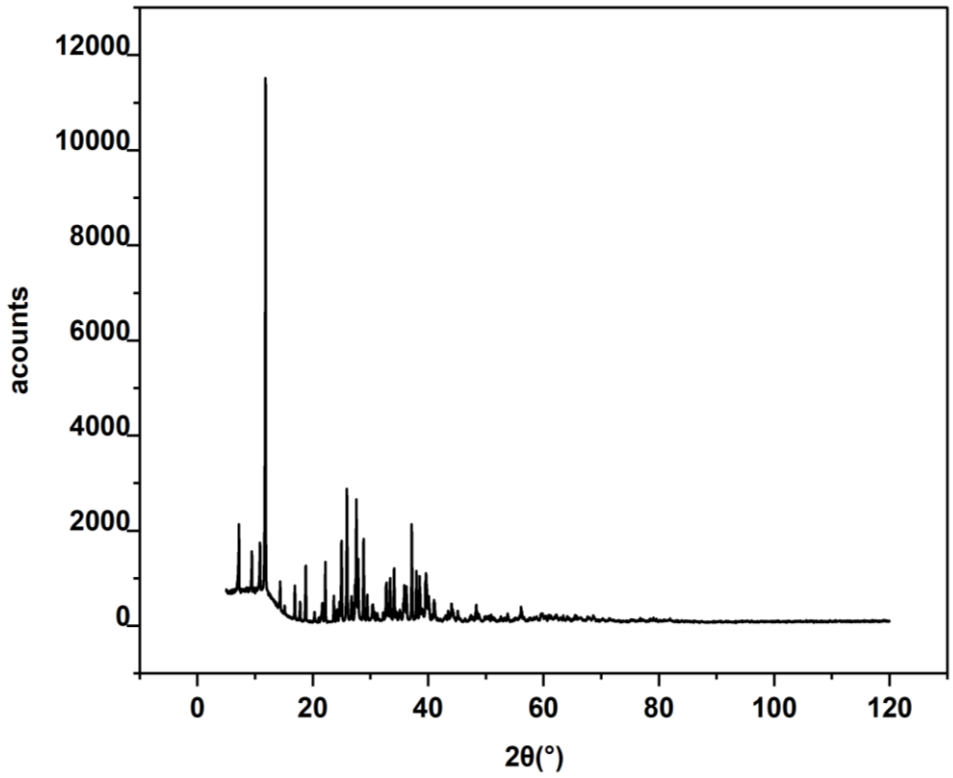
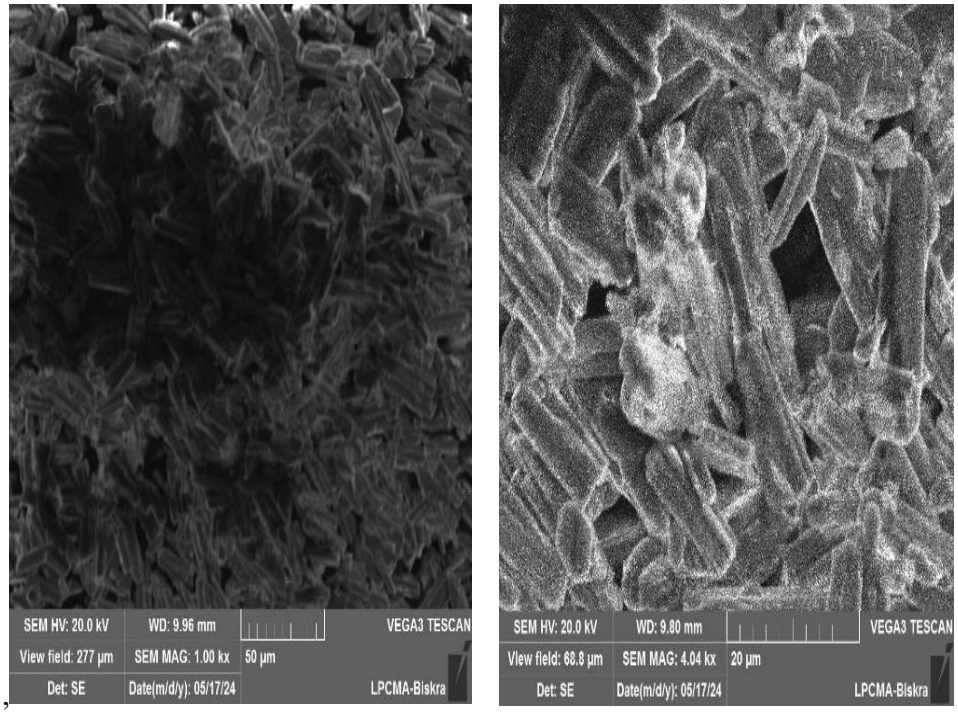


Figure II.10: X-ray diffraction pattern of KEX

The observed diffraction patterns align with the expected crystalline nature of xanthates used in flotation processes, as discussed in multiple studies. Although none of the reviewed studies specifically address the XRD analysis of pure KEX, the crystalline nature of xanthates is well-acknowledged (50,74). Nedjar et al. (14) note that xanthates are commonly used as thiol collectors in flotation, underscoring their well-defined structure.

The SEM images of KEX, Figure II-11, at magnifications of 1000× and 4000× reveal a flaky and layered morphology, which is consistent with the crystalline nature of the compound. The images show a relatively uniform particle size distribution, with some agglomeration observed at higher magnifications. This morphology is typical for KEX, which is known to form layered structures due to its molecular arrangement. Similar morphological features have been described for xanthates in other studies. For instance, (74) and (4) mention the layered structures of xanthates in their studies. The observed morphology aligns with the descriptions of KEX's physical appearance in the literature. Prestidge et al. (46) describe the purification and characterization of KEX, providing a basis for understanding the physical properties of the compound. Furthermore, the flaky and layered morphology observed in our study is consistent with the general behavior of xanthates, as described by Nedjar et al. (14), who noted that the morphology of the products is influenced by the structure of the xanthate molecules.



(a) (b)

Figure II.11: SEM images of KEX showing magnification of 1000× (a), and 4000× (b).

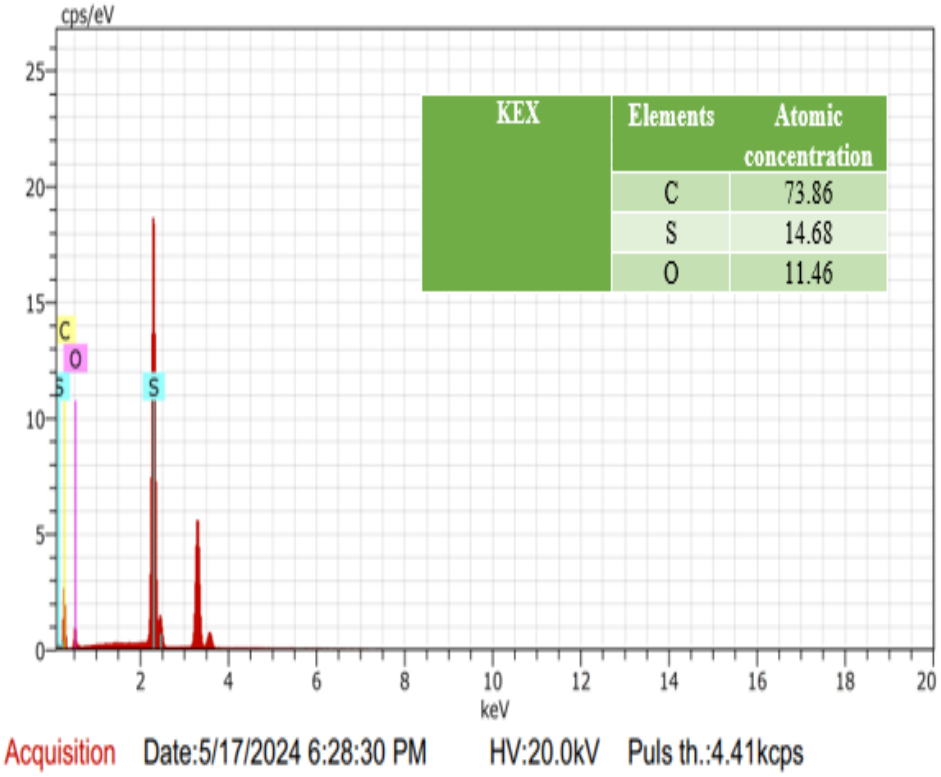


Figure II.12: EDS spectrum of KEX.

The EDS spectrogram for pure Potassium Ethyl Xanthate (KEX),figure II.12, acts as a crucial reference, confirming the elemental signature of the collector reagent before its application to the mineral surface. The analysis reveals dominant peaks for Carbon (73.86%), Sulfur (14.68%), and Oxygen (11.46%), which are the constituent elements of the xanthate molecule itself. The complete and expected absence of any signal for Lead (Pb) or Copper (Cu) is the most significant finding, as it provides a definitive baseline. This control spectrum confirms that any detection of carbon and sulfur on the treated galena samples can be confidently attributed to the adsorption of the KEX collector, allowing for a clear distinction between the elements originating from the mineral, the activator, and the collector.

The FTIR spectrum of KEX, Figure II.13, exhibits characteristic absorption bands associated with the functional groups of the compound. The strong absorption band at approximately 1050 cm^{-1} corresponds to the C-O stretching vibrations of the xanthate group. Additionally, the spectrum shows absorption bands at 2850 cm^{-1} and 2920 cm^{-1}, which are attributed to the C-H stretching vibrations of the ethyl group. These findings confirm the molecular structure of KEX and its suitability for use in the adsorption experiments. The presence of the ethyl group vibrations is consistent with the known structure of potassium ethyl xanthate.

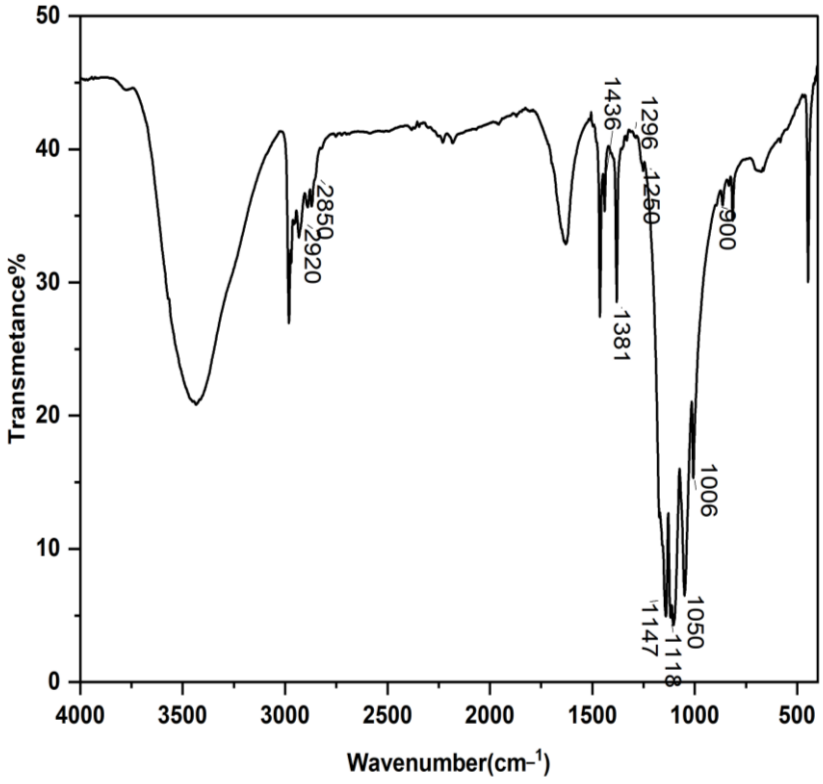


Figure II.13: FTIR Spectrum of KEX.

The FTIR results are in agreement with the findings reported in several studies, such as [30] and [34], who identified similar absorption bands for xanthate compounds. The identification of these characteristic bands confirms the successful synthesis of KEX and its suitability for use in the subsequent adsorption experiments. Additionally, the comprehensive review of xanthate adsorption mechanisms by Rao et al. [35] provides additional context for interpreting the FTIR spectrum of KEX, supporting the identification of the characteristic absorption bands. The FTIR spectrum of KEX is also consistent with the findings reported by Nedjar and Barkat [12], where the characteristic peaks of xanthates were identified and used to analyze their adsorption on mineral surfaces.

II.5.3. Adsorption and Surface Modifications Induced by Copper Activation

II.5.3.1. XRD Analysis

The XRD patterns of galena samples treated with KEX (5.10^{-2} mol/L) and activated with either $CuSO_4$ (10^{-3} mol/L) or $Cu(NO_3)_2$(10^{-3} mol/L) revealed significant differences in the extent of surface interactions and complex formations. For galena treated with KEX (5×10^{-2} mol/L) alone, as shown in Figure II-14, the characteristic PbS peaks (JCPDS No. 96-901-3401) dominated. Minor, low-intensity peaks at 2θ values of 27.569°, 27.304°, and 22.78°, attributed to the formation of lead-xanthate complexes, were also observed and found to be consistent with phases indexed under JCPDS file No. 96-901-1805. However, these peaks were faint (<5% intensity), indicating a limited interaction between KEX and the galena surface in the absence of copper activation. This observation is consistent with studies where minimal xanthate adsorption was noted on galena without activation (1,69,75,76). The limited formation of lead-xanthate complexes in the absence of copper ions can be attributed to the relatively low solubility of PbS, which restricts the availability of Pb^{2+} ions for reacting with xanthate (20). This aligns with findings suggesting that lead xanthate formation is limited without activators (77).

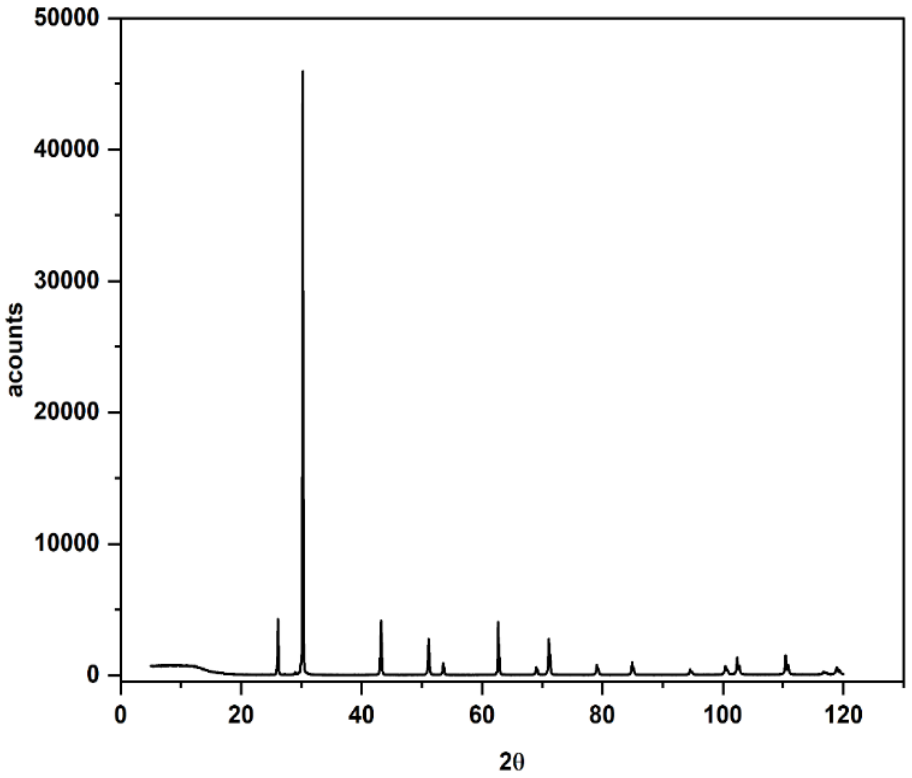


Figure II.14: X-ray diffraction pattern of galena sample treated with KEX (5.10^{-2}mol/L)

In contrast, samples activated with $CuSO_4$ (Sample 2) exhibited, in addition to the main galena peaks (JCPDS No. 96-901-3401), additional peaks at 2θ values of 19.63°, 28.35°, and 18.31° , Figure II.15. These peaks correspond to copper-xanthate complexes and are consistent with phases indexed under JCPDS file No. 96-711-7190. The intensities of these copper-xanthate peaks were significantly higher than those of lead-xanthate in Sample 1, suggesting that $CuSO_4$ effectively modifies the galena surface, facilitating robust copper-xanthate complex formation. This finding is well-supported by research demonstrating that copper activation enhances the formation of metal-xanthate complexes on sulfide mineral surfaces (47,59,72,78). The presence of distinct copper-xanthate peaks in our study supports the notion that copper activation plays a crucial role in promoting xanthate adsorption (79,80). The effectiveness of $CuSO_4$ in promoting complex formation is further supported by studies indicating that copper ions enhance xanthate adsorption on mineral surfaces (25,34).

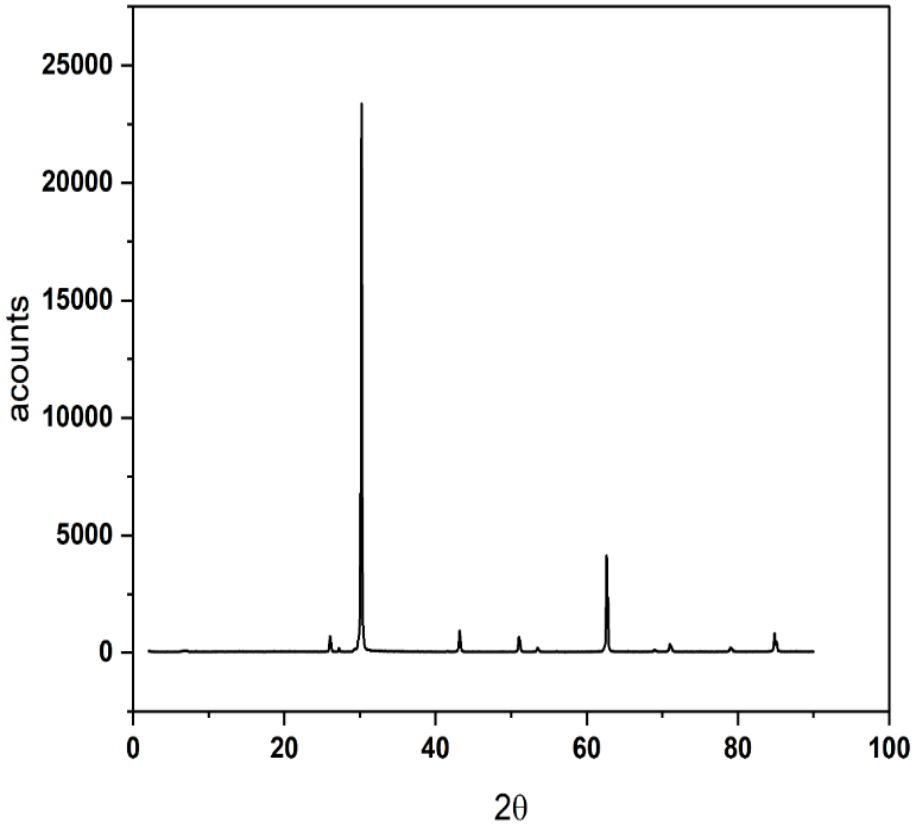


Figure II.15: X-ray diffraction pattern of galena sample activated with CuSO4(10^{-3}mol/L) and treated with KEX (5.10^{-2}mol/L)

Samples activated with $Cu(NO_3)_2$ (10^{-3} mol/L) (Sample 3) also displayed, alongside the main galena peaks (JCPDS No. 96-901-3401), peaks indicative of copper-xanthate complexes at 2θ values of 24.37°, 24.38°, and 18.40° , Figure II.16. These peaks, consistent with phases indexed under JCPDS file No. 96-711-7190, exhibited lower intensities compared to those from $CuSO_4$ activation, reflecting less extensive surface modifications.

This difference in peak intensities between the $CuSO_4$- and $Cu(NO_3)_2$-activated samples could be related to the different counterions (SO_4^{2-} vs. NO_3^-) in the activating agents, similar to observations made in studies involving different ionic species in flotation systems (38,70,77,79). The lower intensity of copper-xanthate peaks in the case of $Cu(NO_3)_2$ activation suggests that the nitrate counterion may not promote complex formation as effectively as sulfate ions (50,81). This observation is consistent with research indicating that different copper salts result in varying degrees of surface activation and subsequent xanthate adsorption (34,76,82).

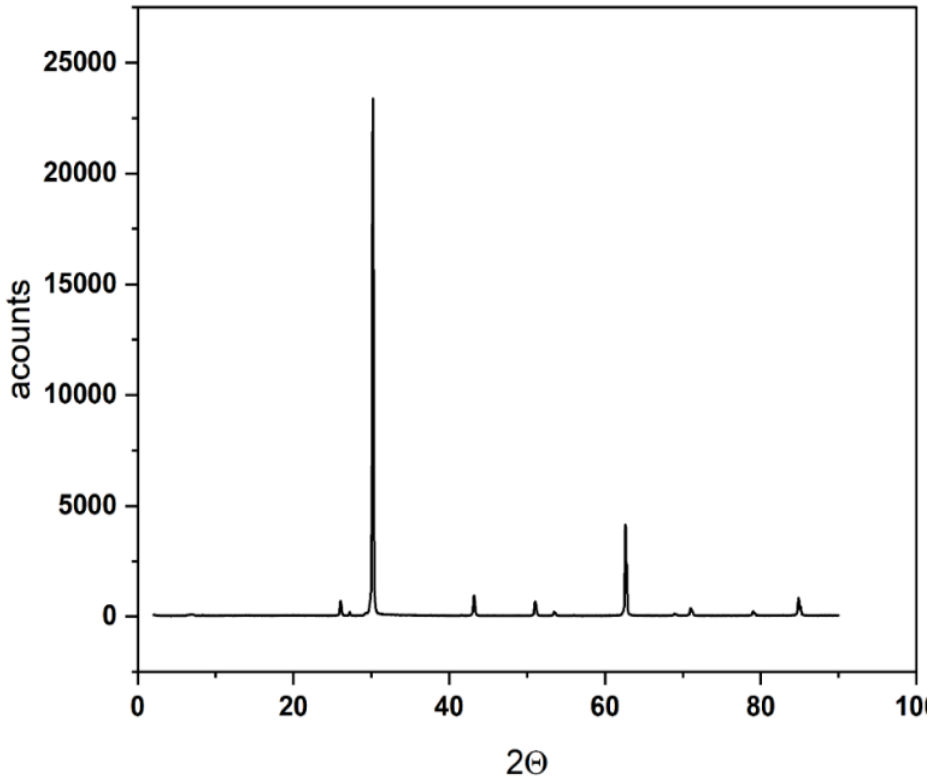


Figure II.16: X-ray diffraction pattern of galena sample activated with $Cu(NO_3)_2$ (10^{-3}mol/L) and treated with KEX (5.10^{-2}mol/L).

II.5.3.2. FTIR Analysis

Fourier Transform Infrared (FTIR) spectroscopy, figure II-17, was utilized to further investigate the adsorption mechanisms and the influence of different copper activation treatments on the galena surface. The FTIR spectra of untreated galena, KEX ($5x10^{-2}$ mol/L)-treated/unactivated galena (Sample 1), $CuSO_4$ (10^{-3} mol/L)-activated galena subsequently treated with KEX (Sample 2), and $Cu(NO_3)_2$ (10^{-3} mol/L)-activated galena subsequently treated with KEX (Sample 3) are comparatively analyzed.

The spectrum for untreated galena displays a characteristic broad absorption band centered around 3444 cm^{-1}. This feature is attributed to O-H stretching vibrations arising from surface hydroxyl groups or adsorbed water molecules, a common occurrence on mineral surfaces (83,84). A distinct peak at 1622 cm^{-1} corresponds to the O-H bending vibration of adsorbed water, often associated with physisorbed water or water within the crystal lattice (65). The band appearing at 1415 cm^{-1}, previously suggested as Pb-S stretching, is more accurately assigned to the stretching vibrations of lead carbonate (cerussite-like) species. Cerussite is a known oxidation product of galena, and its characteristic absorptions are found in the 1407-1435 cm^{-1} range (84,85). It is important to emphasize that Pb-S stretching vibrations for galena are typically observed in the Far-IR region, below 400 cm^{-1}, due to the heavier atomic masses

involved (84). A weaker feature around 1385 cm^{-1} may also be related to carbonate species, either as a component of the broader lead carbonate absorption or from minor atmospheric CO_2 interaction (85).

For the galena sample treated with KEX ($5x10^{-2}$ mol/L) alone (Sample 1), without prior copper activation, very weak new absorption features are discernible in the 1200-1220 cm^{-1} region. These bands are attributable to C-O stretching vibrations of adsorbed xanthate species (86,87). The extremely low intensity of these signals indicates minimal interaction and adsorption of KEX onto the galena surface in the absence of an activator. This observation is consistent with findings suggesting limited xanthate adsorption on unactivated galena surfaces (85).

Upon activation with $CuSO_4$ (10^{-3} mol/L) followed by KEX treatment (Sample 2), a significant transformation in the FTIR spectrum is evident. A strong and well-defined absorption band appears at approximately 1197 cm^{-1}, often accompanied by a smaller shoulder or distinct peak near 1190 cm^{-1}. These prominent peaks arise from C-O bond vibrations and are characteristic of the formation of copper-xanthate complexes on the galena surface (64,75,82). The intensity of these bands, markedly greater than those in Sample 1, confirms a substantial increase in xanthate adsorption facilitated by copper ions. The broad O-H stretching band around 3463 cm^{-1} persists, indicating the continued presence of surface water or hydroxyl groups.

Finally, for the sample activated with $Cu(NO_3)_2$ (10^{-3} mol/L) and subsequently treated with KEX (Sample 3), peaks are again observed at approximately 1197 cm^{-1} and 1190 cm^{-1}. These positions are similar to those identified in the $CuSO_4$-activated sample, confirming the formation of copper-xanthate species. However, the intensity of these bands in the Sample 3 spectrum is notably less than that observed for Sample 2. This suggests that while $Cu(NO_3)_2$ also facilitates xanthate adsorption, the extent of copper-xanthate formation or the stability/orientation of the surface complex may be less pronounced compared to activation with $CuSO_4$ under these experimental conditions. The O-H stretching vibration is observed around 3469 cm^{-1}.

In summary, the FTIR spectra provide direct spectroscopic evidence for the enhancing effect of copper activation on xanthate adsorption onto galena. While untreated galena shows negligible evidence of xanthate adsorption, and KEX treatment alone results in minimal interaction, both $CuSO_4$ and $Cu(NO_3)_2$ activation clearly promote the formation of surface copper-xanthate complexes. The data suggest that $CuSO_4$ activation leads to a more substantial

presence of these copper-xanthate species compared to $Cu(NO_3)_2$ activation under the investigated conditions. This spectroscopic evidence directly supports and complements conclusions drawn from XRD, SEM, and EDS analyses regarding the surface chemistry transformations during these flotation-related processes.

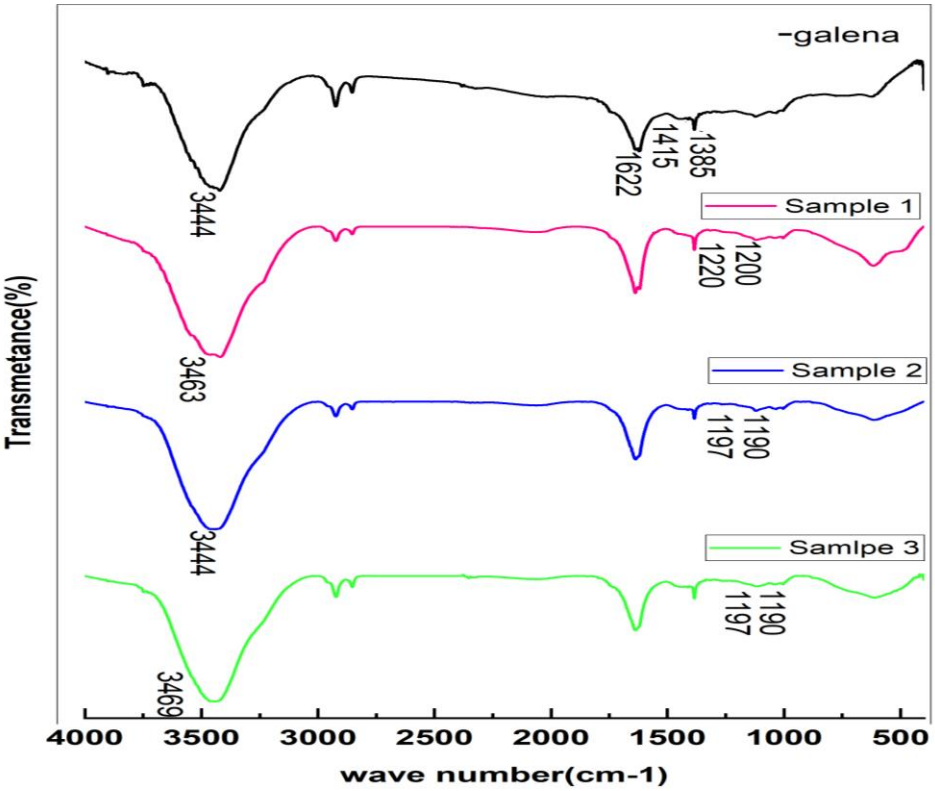
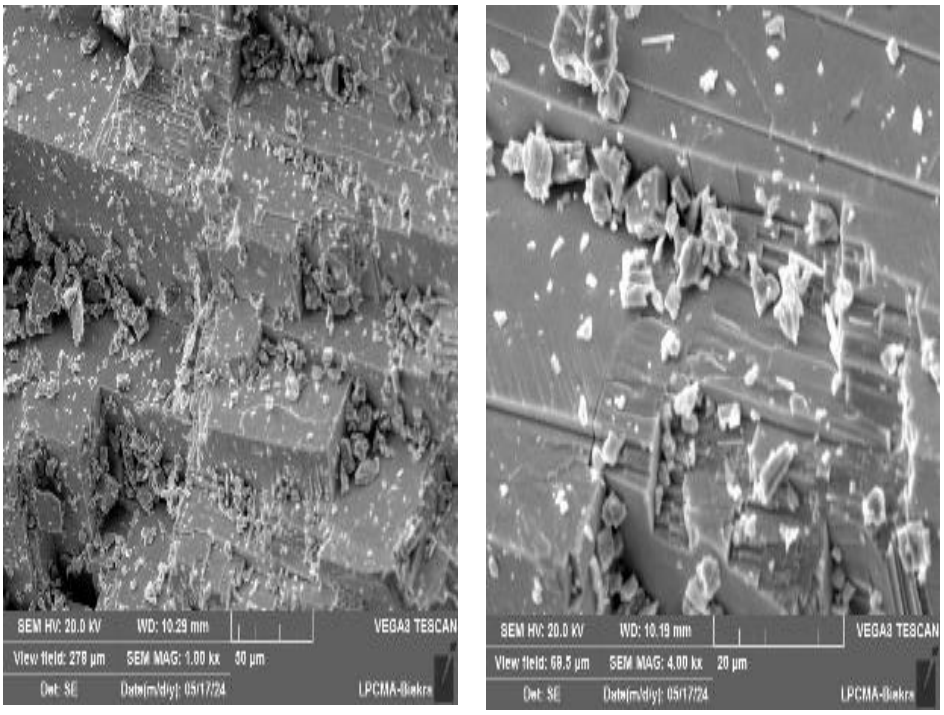


Figure II.17: FTIR spectra of galena's surfaces before and after reagents treatment

Note: Samlpe 1:galena treated by KEX (5.10^{-2}mol/L) ; sample 2 galena activated by $CuSO_4$(10^{-3}mol/l) and KEX (5.10^{-2}mol/l) treated ; sample 3 galena activated by $Cu(NO_3)_2$(10^{-3}mol/L) and KEX (5.10^{-2}mol/L) treated ^{2}mol/L

II.5.3.3. SEM and EDS Analysis

SEM images of galena treated solely with KEX (5.10^{-2}mol/L) at pH 9-10, Figure II.18, revealed minimal alterations to the surface morphology. At 1000× magnification, in Figure II.18(a), the surface appeared relatively smooth with only a few scattered particles. While slight roughness was observed at higher magnifications (4000×) in Figure 18(b), the overall surface remained largely intact. These observations suggest a limited interaction between KEX and the galena surface under these conditions, which is consistent with the findings of Arnaud et al.(88) , who reported a relatively unaltered surface morphology for galena treated with ethyl xanthate in the absence of an activator. They attributed this to the weak interaction between xanthate and the galena surface in alkaline conditions.



(a) (b)

.Figure II.18: SEM images of galena surfaces after KEX(5.10-2mol/L) treatment showing magnification of 1000× (a), and 4000× (b)

EDS analysis of the KEX-treated galena ,Figure II.19, confirmed the presence of carbon and oxygen, consistent with xanthate adsorption and minor surface species, alongside lead and sulfur from the native galena composition. This finding aligns with the work of Basilio et al. (68), who observed negligible xanthate adsorption on sphalerite in the absence of copper ions. The limited interaction between KEX and galena at pH 9-10 without an activator can be attributed to insufficient adsorption of the collector, emphasizing the necessity of heavy metal ions for effective xanthate adsorption on sulfide minerals.

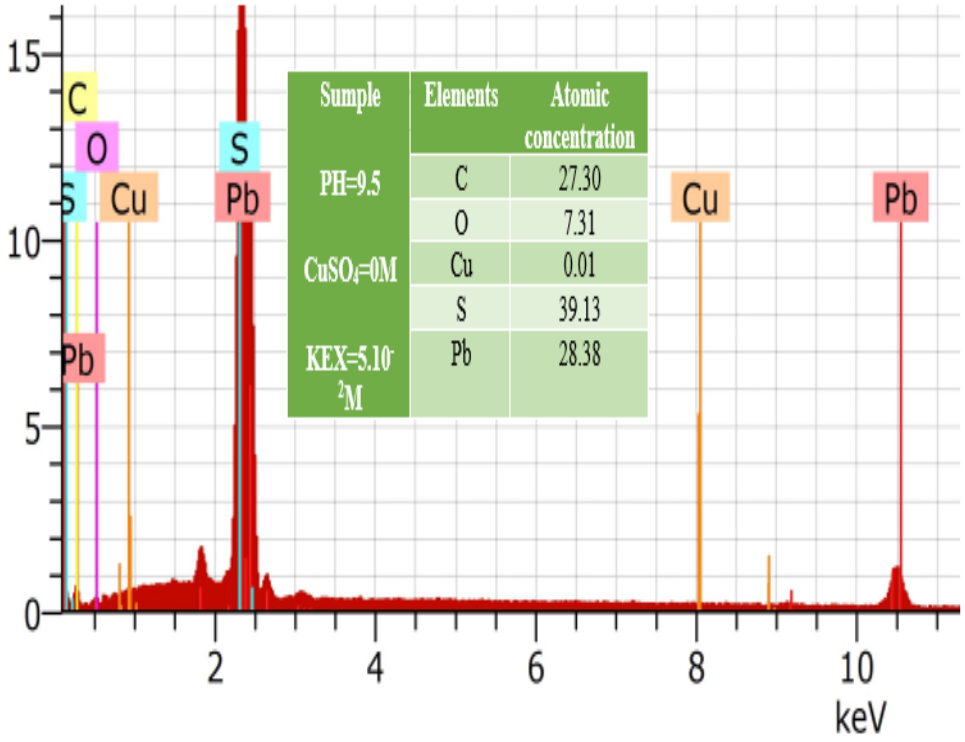
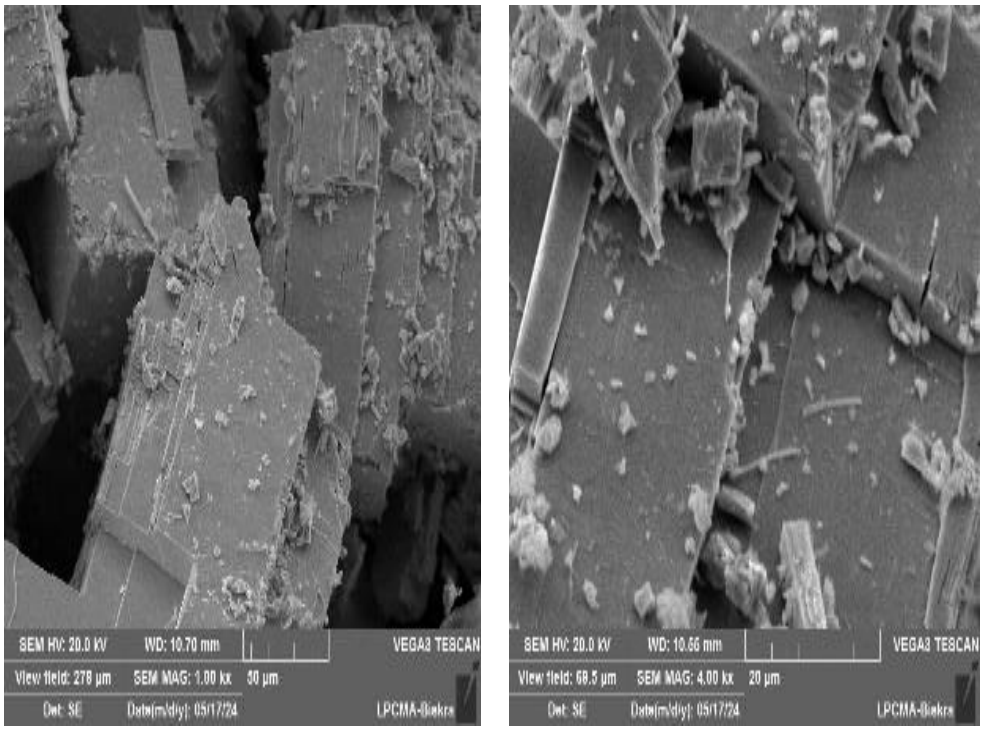


Figure II.19: EDS spectrogram of the Galena surface after KEX (5.10^{-2}mol/l) treatment.

In stark contrast to the unactivated samples, SEM images of galena activated with $CuSO_4$(10^{-3}mol/L), Figure II.20, revealed significant surface modifications. The activated surfaces exhibited pronounced roughness and dense particle aggregation, indicative of strong surface interactions and robust copper-xanthate complex formation. These morphological changes align with previous studies that have linked increased surface roughness and particle aggregation to enhanced reagent adsorption (47,59,69,72,78).



(a) (b)

Figure II.20: SEM images of galena activated by $CuSO_4$ (10^{-3} mol /L) surface after KEX (5.10^{-2}mol/L) treatment showing magnification of 1000× (a), and 4000× (b).

EDS analysis of these samples confirmed a higher copper atomic concentration (0.39%) and an increase in sulfur content, Figure II.21, further supporting the formation of sulfur-rich (50.70%), copper-xanthate complexes (34,50,76,89).

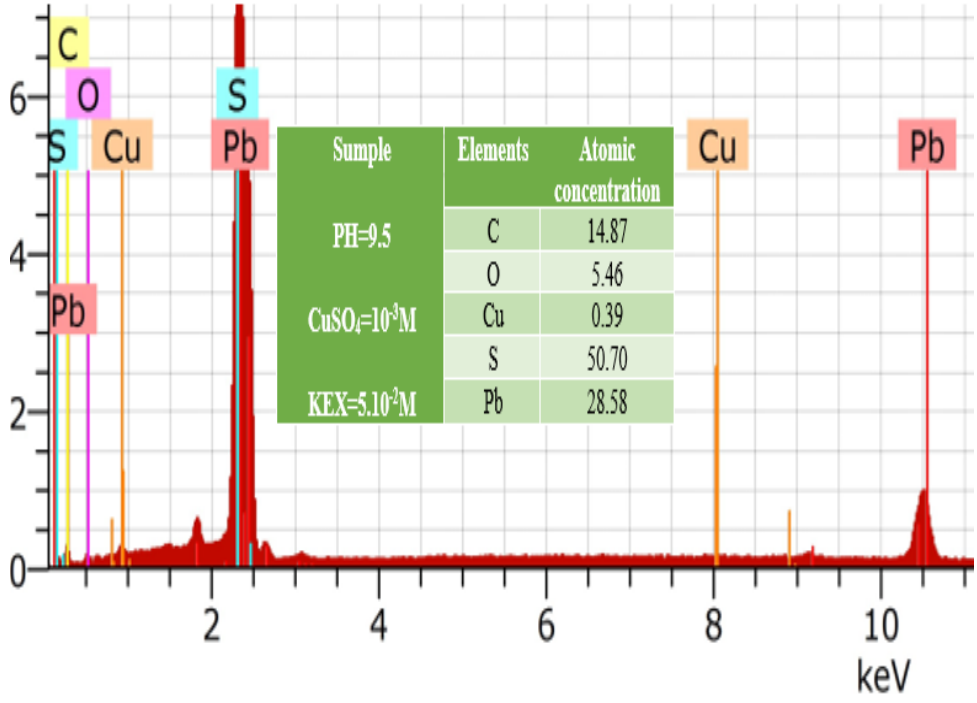
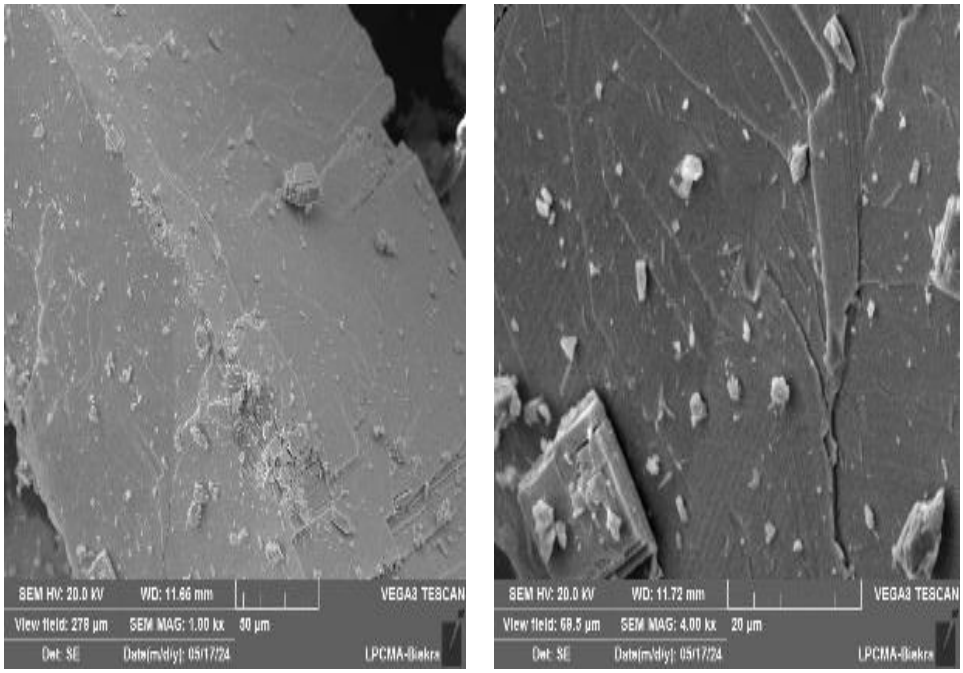


Figure II.21: EDS spectrogram of of galena activated by $CuSO_4$ (10^{-3}mol/L) surface after KEX (5.10^{-2}mol/L) treatment.

Galena samples activated with $Cu(NO_3)_2(10^{-3}mol/L)$ showed moderate surface roughness and less particle aggregation in SEM images compared to $CuSO_4$ activated samples, Figure II.22.



(a) (b)

Figure II.22 SEM images of galena activated by $Cu(NO_3)_2$ (10^{-3}mol/L) surface after KEX(5.10^{-2}mo/L) treatment showing magnification of 1000× (a), and 4000× (b)

EDS analysis revealed a lower copper atomic concentration (0.11%) on the $Cu(NO_3)_2(10^{-3}mol/L)$activated samples, Figure II.23, indicating less effective activation.

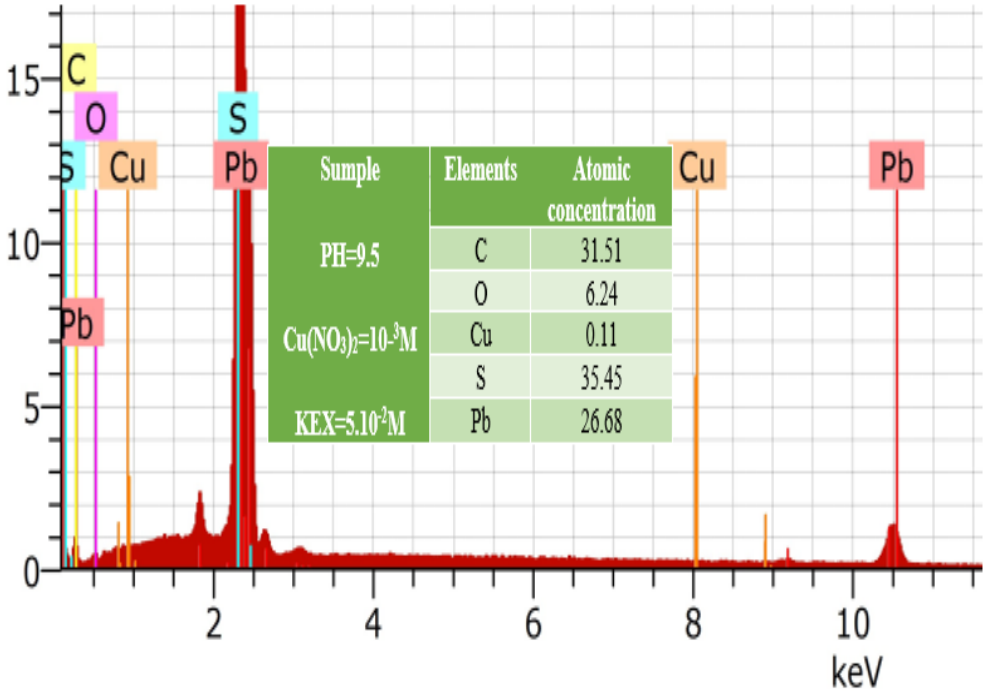


Figure II.23: EDS spectrogram of galena activated by $Cu(NO_3)_2$ (10^{-3}mol/L)surface after KEX (5.10^{-2}mol/L)treatment.

These findings are consistent with previous research demonstrating that different activators can have varying degrees of effectiveness in modifying mineral surfaces(38,42,46,75,77,90). The reduced effectiveness of $Cu(NO_3)_2$ might be attributed to the different chemical behavior of the nitrate counterion compared to sulfate, potentially leading to less extensive surface modifications (34,80).

II.5.4. Proposed Adsorption Mechanism

Based on the comprehensive surface characterization results obtained from XRD, FTIR, SEM, and EDS analyses, a proposed mechanism for the adsorption of potassium ethyl xanthate (KEX) onto the galena (PbS) surface in the presence of copper activators is illustrated schematically in Figure II-24. This process, supported by established literature on copper activation of galena (63,64), can be described in two primary stages:

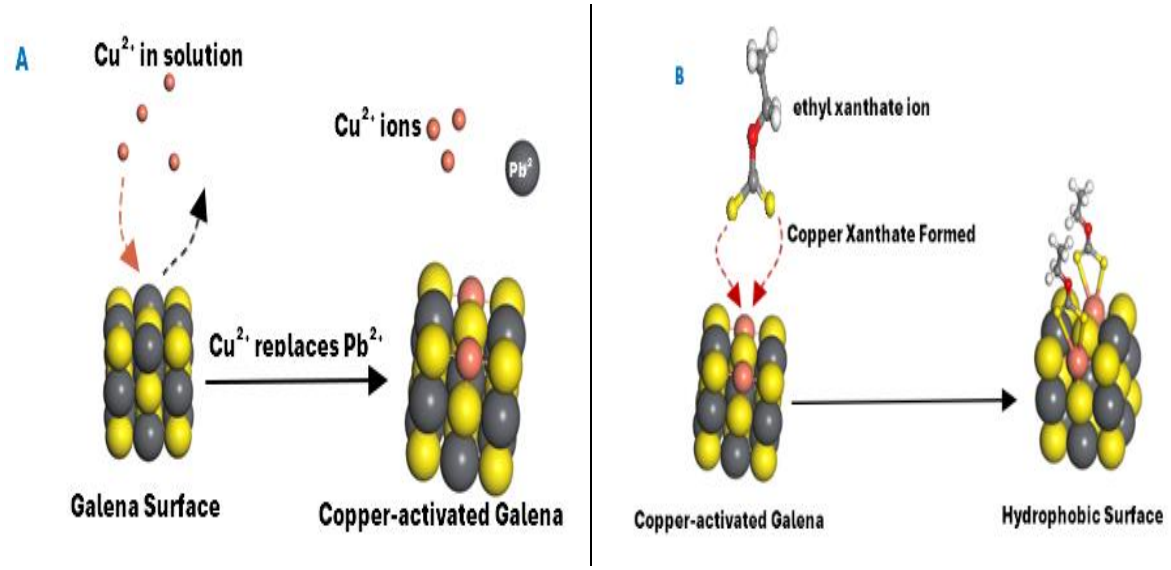


Figure II.24: Schematic illustration of the proposed adsorption mechanism of KEX on copper-activated galena

A. Copper Activation of the Galena Surface

Initially, the galena surface is predominantly composed of lead (Pb^{2+}) and sulfide (S^{2-}) sites (Figure II.24A, left). Upon introduction of copper ions (Cu^{2+}) into the solution (e.g., from the dissolution of $CuSO_4$ or $Cu(NO_3)_2$), these Cu^{2+} ions interact with the galena surface. A key activation mechanism involves an ion-exchange process where Cu^{2+} ions replace Pb^{2+} ions at the mineral surface, or through the formation of copper sulfide (CuS-like) species (63,64) . This results in the formation of a copper-rich layer, effectively creating copper sulfide-like sites (e.g., CuS or Cu_2S) on the galena, as depicted in Figure II-24B (right). This "copper-activated galena" surface is more amenable to subsequent collector adsorption compared to the original PbS surface (63). Its formation is confirmed by the presence of copper in EDS analysis (Figure II.21

and II.23) and by the identification of copper-xanthate species via XRD (Figures II.15 and II.16) and FTIR (Figure II.17, Samples 2 and 3). Displaced Pb^{2+} ions are released into the aqueous phase.

B. Adsorption of Ethyl Xanthate onto the Activated Surface

Following copper activation, the ethyl xanthate ions (EX^-, $CH_3CH_2OCS_2^-$, from KEX dissociation) present in the solution interact with the newly formed copper sites on the galena surface (Figure 18A, right, and 18B, left). The polar head group of the xanthate ion (specifically the sulfur atoms in the $-OCS_2^-$ group) chemisorbs onto these copper sites, leading to the formation of copper ethyl xanthate complexes (e.g., Cu(EX) or $Cu(EX)_2$) (63,64) . This adsorption is strongly supported by the XRD peaks corresponding to copper-xanthate phases (Figures II.15 and II.16) and the characteristic C-O stretching vibrations of adsorbed xanthate observed in the FTIR spectra of activated samples (Figure II.17, Samples 2 and 3). As shown in Figure 18B (right), the adsorption of multiple xanthate molecules, with their non-polar ethyl groups (CH_3CH_2-) oriented outwards from the mineral surface, imparts hydrophobicity to the galena particles. The morphological changes observed by SEM, such as increased surface roughness and particle aggregation on activated surfaces (Figures II.20 and II.22), are consistent with extensive collector adsorption and surface species formation. This increased hydrophobicity is essential for the attachment of the mineral particles to air bubbles during the froth flotation process, facilitating their recovery.

Table II.1 : Contextual Comparison of the Current Investigation with Previous Studies on Copper Activation of Galena and Xanthate Adsorption.

Authors, [ref]	Activator Used	Target Mineral(s)	Effectiveness/Key Surface Species Formed (with Xanthate)	Experimental Methods (brief)	Key Findings Relevant to Activated Galena-Xanthate System	Notes/Remarks
Koriche, I. & Nedjar, Z. (2025). (Current Study)	$Cu(NO_3)_2$ (primary); $CuSO_4$ (benchmark)	Galena (PbS)	$Cu(NO_3)_2$: Copper-xanthate complexes (less intense than $CuSO_4$). $CuSO_4$: More extensive copper-xanthate complex formation.	XRD, FTIR, SEM-EDS	$Cu(NO_3)_2$ activates galena for KEX adsorption via a similar mechanism to $CuSO_4$, but is less effective. Both lead to copper-xanthate surface species. Counter-ion (NO_3^- vs. SO_4^{2-}) influences activation extent.	First systematic study directly comparing $Cu(NO_3)_2$ and $CuSO_4$ as activators for KEX adsorption on galena.
Popov & Vučinić, [16]	$CuSO_4$	Galena (PbS)	$Pb(EX)_2$ and Cu(I)EX identified. $CuSO_4$ enhances KEX flotation.	Flotation, Zeta-potential, ATR-IR.	$CuSO_4$ activates galena for KEX flotation. Co-existence of Pb and Cu xanthate species on the surface. Adsorption mechanism is pH-dependent.	Excellent benchmark for $CuSO_4$ activation mechanism and resulting surface species on galena with ethyl xanthate.
Nedjar & Barkat, [12]	$CuSO_4$	Galena (PbS)	Colloidal Pb-IAX, dixanthogen, Cu(I) isoamyl xanthate.	Electrochemical potential, FTIR, SEM.	$CuSO_4$ activates galena for KIAX adsorption. Detection of Cu(I) isoamyl xanthate and dixanthogen on the surface, alongside Pb-IAX, depending on Cu addition levels.	Focuses on isoamyl xanthate (KIAX). Provides SEM evidence and confirms formation of various xanthate-derived species after copper activation.
Nedjar & Barkat, [18]	$CuSO_4$	Galena (PbS)	$Pb(IPX)_2$, $(IPX)_2$, and Cu-IPX identified. CuS formation on the surface.	Rest potential, FTIR, SEM.	$CuSO_4$ activates galena for potassium isopropyl xanthate (PIPX) adsorption. CuS formation is implicated. Surface species include lead, copper xanthates, and dixanthogen.	Uses isopropyl xanthate (PIPX). Reinforces the general mechanism of copper activation leading to mixed metal-xanthate and dixanthogen species.

II.6. Conclusion

This study addressed a critical gap in galena flotation by systematically evaluating copper nitrate ($Cu(NO_3)_2$) as a novel activator, benchmarked against the conventional copper sulfate ($CuSO_4$). The investigation focused on the comparative effects of these activators on the surface chemistry of galena and their efficacy in enhancing potassium ethyl xanthate (KEX) adsorption, aiming to determine if $Cu(NO_3)_2$ offers a viable alternative. Through comprehensive analysis using X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and Energy-Dispersive X-ray Spectroscopy (EDS), distinct differences in their activation mechanisms and outcomes were elucidated.

The findings clearly establish that while both activators promote KEX adsorption, $CuSO_4$ activation leads to a more substantial enhancement of xanthate interaction with the galena surface. This is evidenced by the more extensive formation of copper-xanthate complexes observed through stronger XRD and FTIR signals, more pronounced surface roughening and particle aggregation seen in SEM images, and a significantly higher deposition of copper (0.39%) as determined by EDS. In contrast, $Cu(NO_3)_2$ also facilitated KEX adsorption, but its impact on surface modification and copper-xanthate formation was consistently less pronounced (0.11% Cu via EDS) under the investigated conditions. These differences are likely attributable to the distinct roles of the sulfate versus nitrate counterions in the activation mechanism and subsequent complex formation.

The insights gained from this research have significant application prospects. Firstly, they provide practical guidance for mineral processing operations: while $Cu(NO_3)_2$ is confirmed as a viable activator, $CuSO_4$ remains more effective under conditions similar to those tested, potentially leading to improved lead recovery and optimized reagent usage. This systematic evaluation helps in informed decision-making. Secondly, this work contributes to a deeper fundamental understanding of counterion effects in mineral activation, which is crucial for predicting the behavior of various activators and can inform the rational design of more selective or environmentally benign reagent schemes. A detailed comparison with prior studies, presented in Table 1, further highlights the specific advancements and novelty contributed by this investigation. Thirdly, the detailed surface characterization provides a valuable benchmark for future research, which could explore the optimization of $Cu(NO_3)_2$ (e.g., concentration, pH, synergistic effects) or investigate a broader range of alternative activators and counterions, aiming to enhance both efficiency and sustainability in sulfide mineral flotation.

Ultimately, by providing a detailed, evidence-based assessment of the activation potential of $Cu(NO_3)_2$ relative to $CuSO_4$, this study underscores the critical role of activator selection in galena flotation and contributes to the ongoing efforts to improve the efficiency and sustainability of lead ore processing.

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CHAPTER III:
ENHANCED XANTHATE ADSORPTION ON GALENA THROUGH COPPER ACTIVATION AND EDTA TREATMENT .

III.1. Intruduction

Building upon the foundational literature review presented in Chapter I, which established the theoretical basis and identified a critical research gap, this chapter transitions to the empirical core of the thesis. The preceding review highlighted that while copper activation and EDTA-based surface cleaning are recognized as effective individual strategies for managing galena's surface oxidation, their combined, synergistic effect has not been systematically investigated.

A principal challenge in galena flotation is the propensity for surface oxidation. Extensive research has demonstrated that exposure to air and aqueous environments leads to the formation of various surface species, including lead sulfate ($PbSO_4$), lead carbonate ($PbCO_3$), and lead hydroxide (21,91). This hydrophilic oxide layer fundamentally alters the subsequent interaction with flotation reagents. The adsorption of xanthate onto unactivated, oxidized galena is often a subtle phenomenon, typically understood as a reaction with these surface oxidation products rather than with the pristine PbS surface itself.

To improve collector uptake on sulfide minerals that respond poorly to direct xanthation, such as sphalerite, activation with metal ions—most commonly copper (Cu^{2+})—is a standard industrial practice (92,93). This process creates a new, copper-rich surface that facilitates robust xanthate adsorption. While also applied to galena, the efficacy of copper activation can be hindered by the pre-existing oxide layers that may limit the access of activator ions to the underlying mineral. While surface modification strategies such as deliberate passivation with sulfuric acid have been explored to selectively depress galena (94), an approach focused on cleaning the surface to enhance subsequent activation remains less characterized.

This chapter, therefore, investigates the hypothesis that pre-treatment with a powerful chelating agent, Ethylenediaminetetraacetic acid (EDTA), can significantly enhance the copper-activated adsorption of xanthate on galena. We posit that EDTA functions as a surface "cleaning" agent, dissolving inhibitory oxide species. This action is expected to expose a more pristine and reactive mineral surface, thereby enabling a more complete and uniform copper activation. Consequently, this should lead to the formation of a more stable and extensive copper-xanthate complex layer, ultimately improving the hydrophobicity and flotation potential of galena.

To test this hypothesis, a systematic investigation was conducted to characterize the morphological and compositional changes on the galena surface at progressive stages of treatment: (i) with potassium ethyl xanthate (KEX) alone, (ii) following activation with copper

sulfate or copper nitrate, and (iii) after the complete sequential treatment involving a copper activator and EDTA. The mineral surfaces were analyzed using Scanning Electron Microscopy (SEM), Energy-Dispersive X-ray Spectroscopy (EDS), Fourier-Transform Infrared Spectroscopy (FTIR), and X-ray Diffraction (XRD) to elucidate the underlying mechanism of the EDTA-enhanced xanthate adsorption.

III.2. Techniques and Equipment

The same techniques and equipment described in Chapter III were used, with the sole modification being the order of reagent addition.

III.3. Adsorption and Activation Procedure

This section details the experimental protocol for the adsorption and activation of galena surfaces. The study was structured into two parallel parts to systematically investigate and compare the efficacy of two different copper activators: copper sulfate ($CuSO_4$) and copper nitrate ($Cu(NO_3)_2$).The overall experimental methodology, including pH conditions, reagent contact times, and post-treatment procedures (agitation, filtration, rinsing), remains consistent across all tests to ensure a valid basis for comparison. The primary variable between the two parts is the counter-anion (SO_4^{2-} vs. NO_3^-) of the copper salt. The rationale for the maintained parameters is detailed below.

- **pH Conditions:** The pH of the galena suspension was adjusted to and maintained between 9.0 and 10.0 using NaOH (10^{-1} mol/L). This moderately alkaline range is consistent with optimal conditions reported for galena flotation, particularly when using xanthate collectors and copper activators, ensuring a relevant and comparable chemical environment across all tests(47,95).
- **Reagent Concentrations:** The concentrations of the key reagents were adjusted for this specific comparative study:
    - **Potassium ethyl xanthate (KEX)** was used at a concentration of 5 x 10^{-3} mol/L. This concentration is highly relevant for fundamental surface chemistry studies, allowing for clear detection of adsorbed species without causing excessive bulk precipitation.
    - **Copper sulfate ($CuSO_4$) and Copper Nitrate ($Cu(NO_3)_2$)**, when used as activators, were maintained at a concentration of 10^{-3} mol/L to ensure effective activation.

- **Ethylenediaminetetraacetic acid (EDTA)** was utilized in protocols at a concentration of 0.1 mol/L. This concentration was selected for its proven efficacy as a strong chelating agent capable of removing surface oxidation layers to prepare the mineral surface for subsequent reactions.
- **Contact Time:** A standard contact time of 10 minutes was employed for each sequential reagent addition step.

III.3.1. Experimental Protocol for Sample Preparation

III.3.1.1. Part 1: Surface Treatment with Copper Sulfate ($CuSO_4$)

This first part of the study focuses on the conventional use of copper sulfate as the activator. Three types of samples were prepared to establish a baseline and evaluate the effects of activation and subsequent EDTA treatment. For each preparation, 3 g of galena powder was added to 30 ml of distilled water.

- **Sample 1 (KEX alone - Baseline**): The pH of the galena suspension was adjusted. KEX solution was then added to a final concentration of 5×10^{-3} mol/L, and the suspension was conditioned for 10 minutes. This sample serves as the reference for both parts of the study.
- **Sample 2 ($CuSO_4$ activated + KEX):** The pH was adjusted. First, $CuSO_4$ solution was added to a final concentration of 10^{-3} mol/L and conditioned for 10 minutes. Subsequently, KEX solution was added to a final concentration of 5×10^{-3} mol/L and conditioned for an additional 10 minutes.
- **Sample 3 ($CuSO_4$ + EDTA + KEX):** The pH was adjusted. The following sequential treatment was performed, Scheme III 1:
  - $CuSO_4$ solution (10^{-3} mol/L) was added and conditioned for 10 minutes.
  - EDTA solution (0.1 mol/L) was then added and conditioned for 10 minutes.
  - Finally, KEX solution (5×10^{-3} mol/L) was added and conditioned for a final 10 minutes.

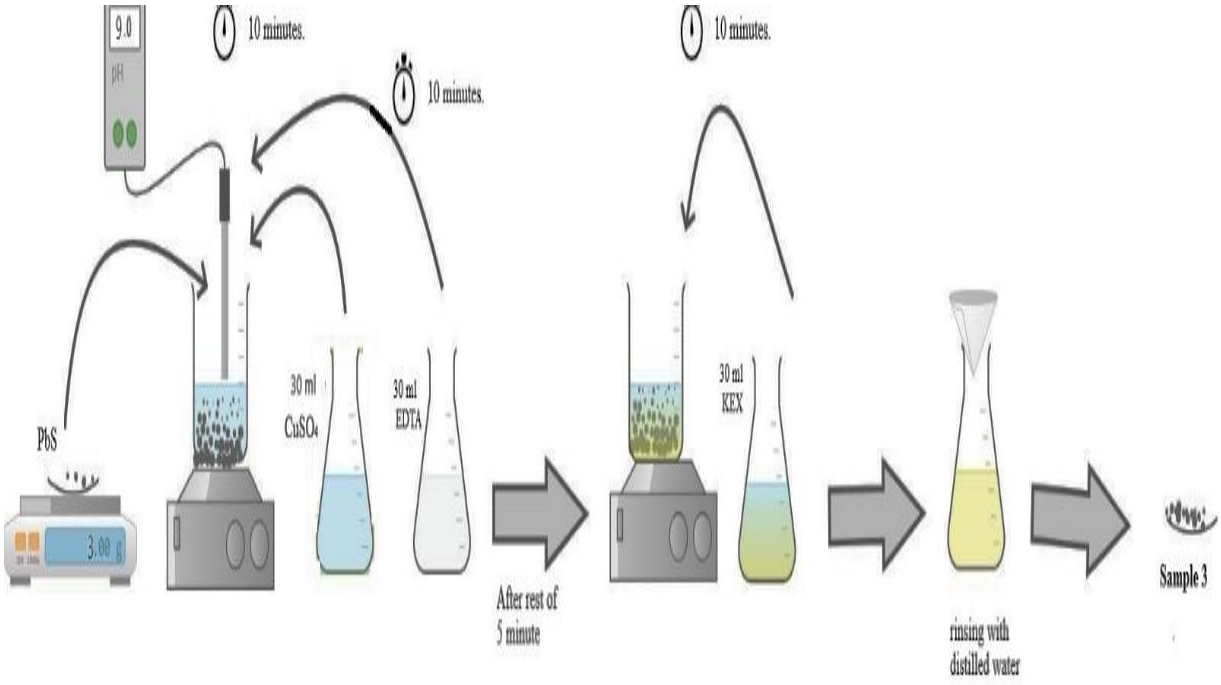


Schéma III.1: Adsorption Procedure of KEX on copper sulfate activated Galena after EDTA treatment

III.3.1.2. Part 2: Surface Treatment with Copper Nitrate ($Cu(NO_3)_2$)

This second part of the study mirrors the protocol of Part 1 precisely, with the sole exception of substituting copper sulfate with copper nitrate. This allows for a direct investigation into the influence of the counter-anion on the activation and cleaning mechanisms. Sample 1 (KEX alone) serves as the common baseline. Two additional samples were prepared

- **Sample 4 ($Cu(NO_3)_2$ activated + KEX):** The pH was adjusted. First, $Cu(NO_3)_2$ solution was added to a final concentration of 10^{-3} mol/L and conditioned for 10 minutes. Subsequently, KEX solution was added to a final concentration of 5 x 10^{-3} mol/L and conditioned for an additional 10 minutes.
- **Sample 5 ($Cu(NO_3)_2$ + EDTA + KEX):** The pH was adjusted. The sequential treatment was as follows , Scheme III-1:

➢ $Cu(NO_3)_2$ solution (10^{-3} mol/L) was added and conditioned for 10 minutes.

➢ EDTA solution (0.1 mol/L) was then added and conditioned for 10 minutes.

- Finally, KEX solution (5 x 10^{-3} mol/L) was added and conditioned for a final 10 minutes.

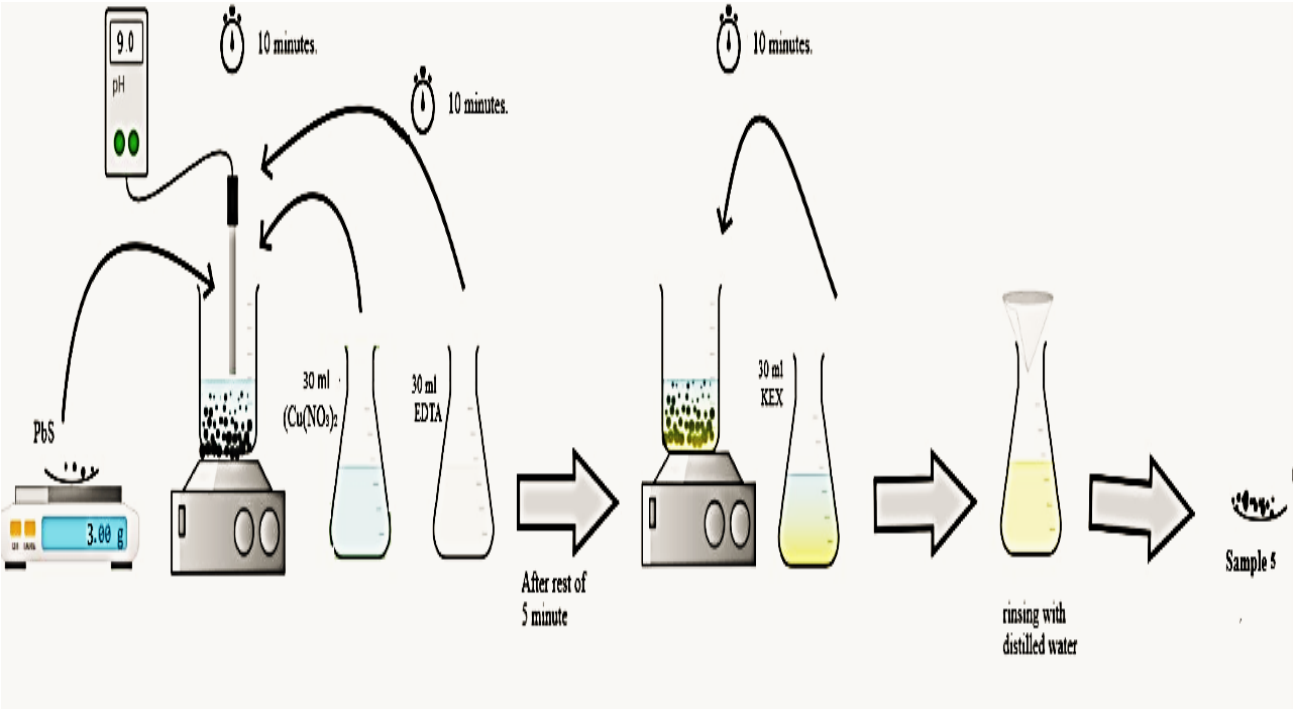


Schéma III.2: Adsorption Procedure of KEX on copper Nitrate activated Galena after EDTA treatment.

III.3.1.3. Post-Treatment and Analysis

After the final conditioning step for each of the five samples, the solids were separated by filtration and repeated rinsing with distilled water to remove unadsorbed reagents. The prepared solids were then preserved for subsequent surface characterization analyses.

After the final conditioning step, each sample was processed as previously described (settling, rinsing, and filtration) to prepare the solids for subsequent surface characterization. The following analyses will be used to compare the surface chemistry resulting from these three distinct treatment paths.

(a) SEM,and EDS analysis.

(b)XRD analysis.

(c)FTIR analysis.

III.4. Results and Discussion

Unlike the experiments conducted in chapter II, which utilized high reagent dosages to establish baseline interactions, the analyses presented in this chapter employ a reduced collector concentration (5×10^{-3} mol/L). This shift in experimental design is intended to evaluate the 'reagent-saving' potential of EDTA-mediated surface cleaning. Consequently, the following

XRD, FTIR, and SEM/EDS data are interpreted through a comparative lens, benchmarking the efficiency of this optimized system against the high-concentration results previously documented.

III.4.1. Galena with Copper Sulfate Activation and enhaced adsoption with EDTA(low concentration)

III.4.1.1. XRD analysis

X-ray diffraction (XRD) patterns revealed distinct surface interactions and complex formations , as showes as figure III.1, between galena samples treated with KEX (5×10^{-3} mol/L) alone, samples terated with $CuSO_4$(10^{-3} mol/L) and KEX (5×10^{-3} mol/L) versus those treated with a mixture of $CuSO_4$(10^{-3} mol/L) , EDTA (0.1 mol/L), and KEX (5×10^{-3} mol/L). The use of EDTA resulted in significant differences in diffraction patterns.

The X-ray diffraction of the studied samples shows a pattern similar to the Galena spectrum , with some differences. Its lines along the crystal planes of (040), and (020) of the previous samples, Figure III.2.a and b are not identical and increase in deflection across the three curves, indicating that the crystal pattern is not symmetrical, According to Bragg's law ($n\lambda = 2d \sin\theta$), these angular shifts directly reflect changes in the distance between crystal planes (d) resulting from the lattice stress induced on the surface during the reaction of the reactants.

The XRD analysis of the untreated galena sample confirms its structural integrity and phase purity, aligning with the fundamental characteristics established in section II.5.1. The diffraction patterns revealed primary peaks at 2θ angles of 26.07°, 30.2°, 43.23°, 51.18°, 53.64°, and 62.79°, corresponding to d-spacings of 3.41 Å, 2.95 Å, 2.09 Å, 1.78 Å, 1.70 Å, and 1.47 Å, respectively. These results are in strict accordance with the JCPDS reference file (96-901-3401) and the cubic crystal system (space group $F_{m\bar{3}m}$, a = 5.93 Å) discussed previously. The strong agreement between these core peak positions and those reported in literature for natural galena—specifically the peaks at 26.04°, 30.16°, 43.16°, 51.04° and 62.6°—verifies the high purity of the PbS phase used in this study, providing a reliable baseline for the subsequent surface interaction analysis.(89).

The sample treated with KEX alone showed some noticeable peak shifts at angles of 62.42°, and 30.12°. This observation is consistent with Nedjar s article(96). that the interaction between KEX and the Galena surface under these conditions is primarily a surface phenomenon, such as adsorption(97), which does not induce significant changes in the bulk crystallographic structure.

In contrast, Galena activated with Copper sulfate prior to Xanthate treatment showed a more pronounced shift in the XRD pattern, with diffraction angles of 62.74° and 30.30. This increased shift indicates a greater degree of structural modification compared to the sample treated with xanthate alone(31). This result strongly suggests that copper sulfate activation promotes the subsequent adsorption of Xanthate onto the Galena surface, leading to a fundamental change in the surface structure. This observation confirms Najjar's findings(96). Interestingly, the Galena sample activated with $CuSO_4$, and treated with a complexing agent EDTA exhibited the largest peak shifts at angles of 30.49°, and 62.81°. This remarkable difference indicates a fundamental change in the surface structure of the Galena crystal upon interaction with the complexing agent EDTA. The observation of more pronounced shifts indicates the formation of a potentially more organized and stable surface layer compared to the other samples , indicating that surface cleaning is more determinant of lattice rearrangement than bulk reagent dosage. These results should be confirmed by further analyses such as Fourier transform infrared spectroscopy (**FTIR**), scanning electron microscopy (**SEM**), and energy-dispersive X-ray spectroscopy (**EDS**

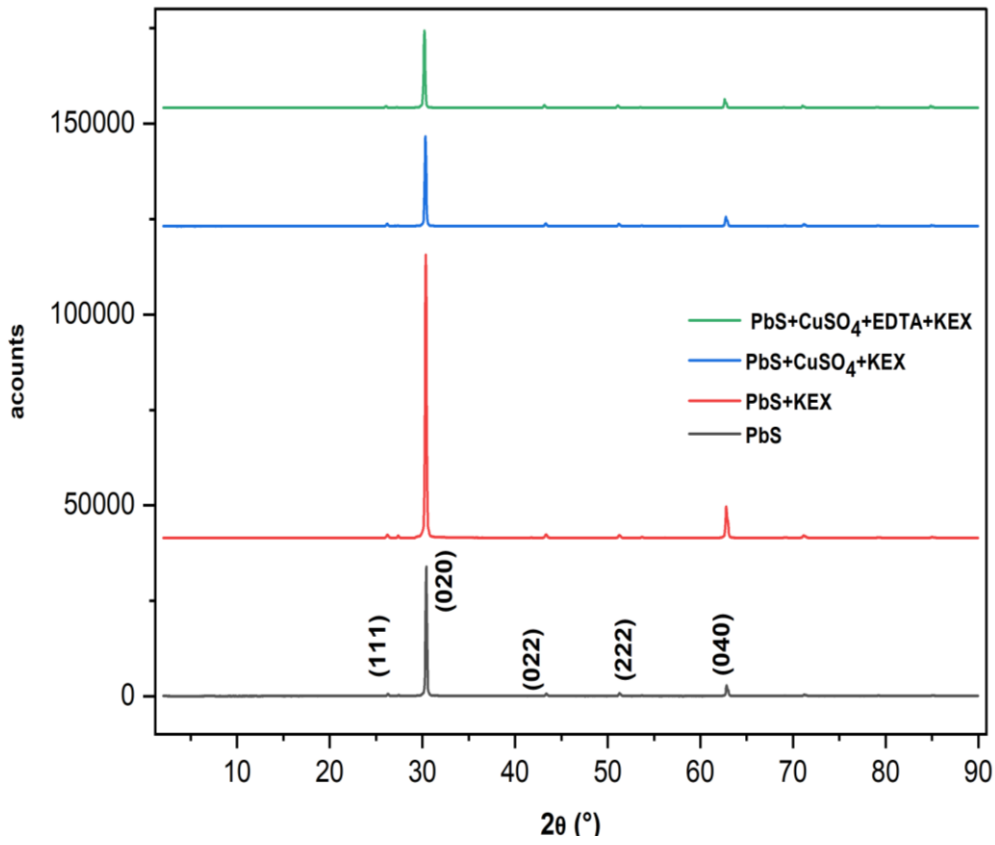


Figure III.1: XRD spectra of the the galena's surfaces before and after reagents treatment(Copper Sulfate activation).

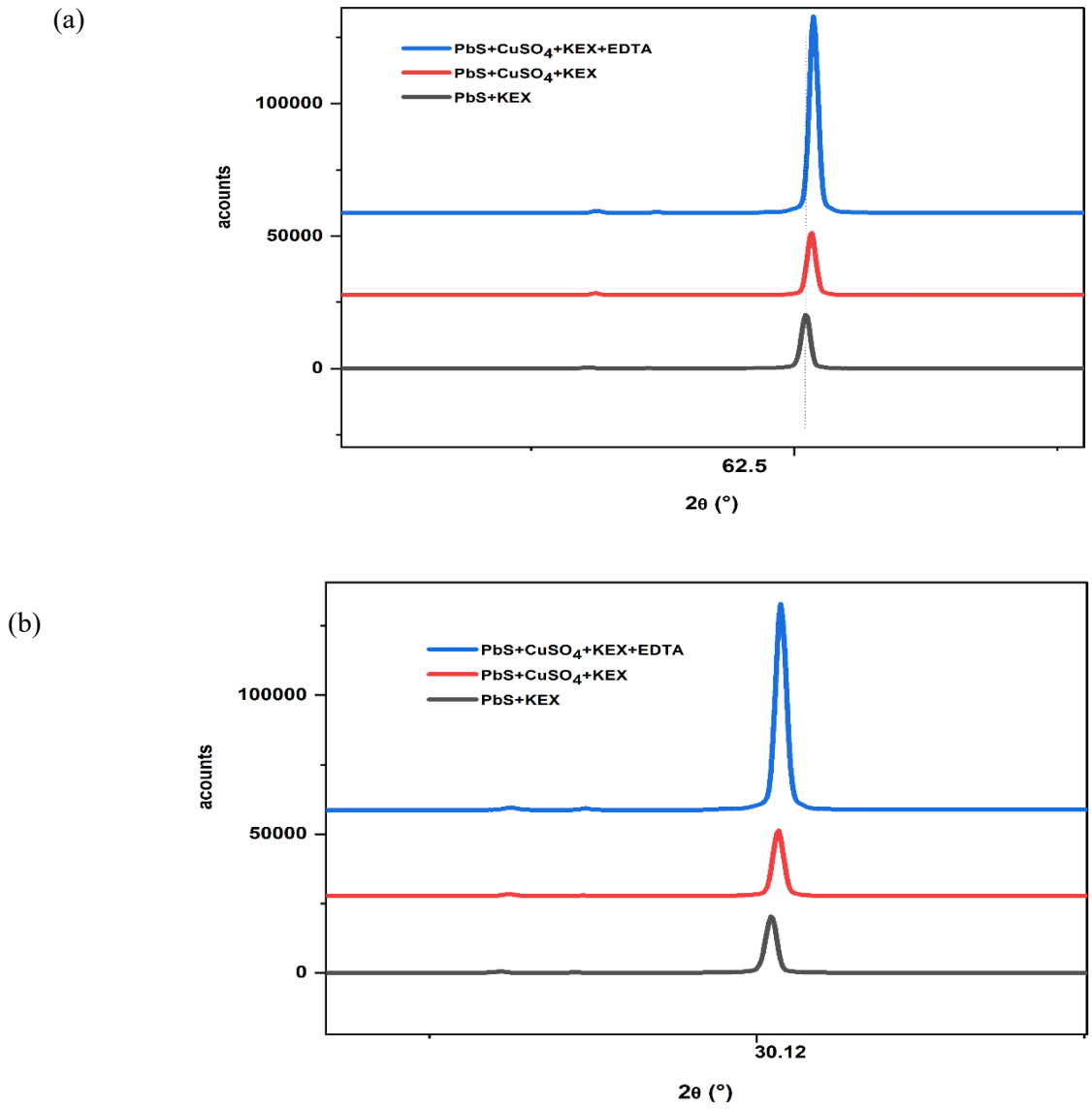


Figure III.2 : Magnification of the diffraction line (a)(040), and (b)(020) for nanoparticles of galena's surfaces before and after reagents treatment (Copper Sulfate activation).

III.4.1.2. FTIR analysis

.Fourier-Transform Infrared (FTIR) spectroscopy was used to identify the molecular functional groups on the galena surfaces after each treatment, as shown in Figure III.3, which contains the spectra of the samples (galena samples treated with KEX (5×10^{-3} mol/L) alone (black line), samples trated with $CuSO_4$(10^{-3} mol/L) and KEX (5×10^{-3} mol/L) (red line) versus those treated with a mixture of $CuSO_4$(10^{-3} mol/L) , EDTA(0.1 mol/L), and KEX(5×10^{-3} mol/L) (blue line)). providing definitive chemical evidence of the adsorbed species. The key focus was on the characteristic peaks of xanthate molecules.

The FTIR spectrum for Sample 1 (Galena treated with KEX alone) showed distinct absorption bands at 1024 cm^{-1} and 1047 cm^{-1}. These peaks are characteristic of the C-S and C=S stretching vibrations in metal xanthates. Their presence confirms the successful formation and adsorption of a lead xanthate species on the galena surface.(98) . This finding is consistent with established literature, which has long used these specific vibrational frequencies as a fingerprint for the collector's interaction with the mineral (69).

For Sample 2 (Galena with $CuSO_4$ activation and KEX treatment), the FTIR spectrum showed a shift in the characteristic peaks to 1122 cm^{-1} and 1139 cm^{-1}. This spectral region is strongly associated with the C-S stretching or conjugated modes in copper ethyl xanthate (CuEtX) (4). The presence of these new bands, along with the consistent peak at 1047 cm^{-1}(69), confirms that the copper activation process was successful. This treatment effectively facilitated the adsorption of KEX in the form of a copper-based complex. Additionally, the slightly higher intensity of these peaks compared to the KEX-only sample indicates a greater surface concentration of xanthate, which is a direct result of the enhanced collector adsorption provided by the copper activation.

The FTIR spectrum of Sample 3 (Galena treated with $CuSO_4$) , EDTA, and KEX) revealed the most intense xanthate peak, located at approximately 1122 cm^{-1} (a frequency consistent with CuEtX) (15,69). This high intensity, which is significantly greater than in the other two samples, indicates the highest rate of xanthate absorption. This result is in perfect agreement with our XRD findings, which suggested a more extensive and robust xanthate layer on the EDTA-treated surface. This spectroscopic evidence provides strong support for the hypothesis that EDTA removes inhibitory surface species, thereby optimizing the Galena surface for copper activation and maximizing subsequent xanthate adsorption. These results confirm the X-ray diffraction analyses.

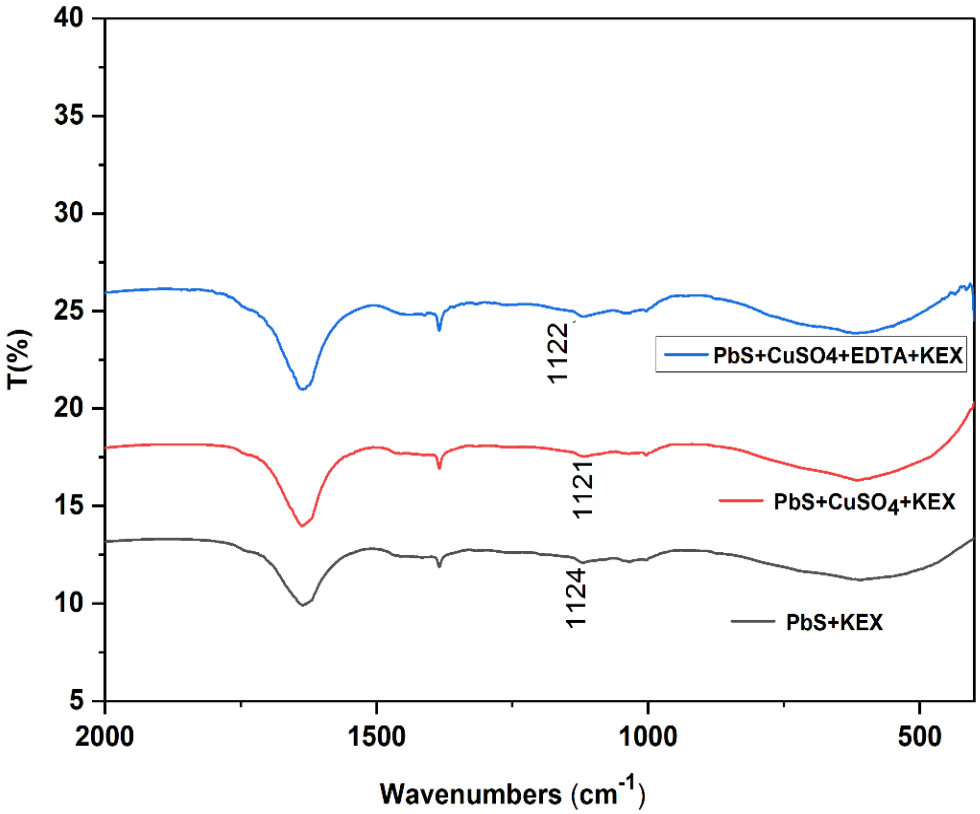


Figure III.3: FTIR spectra of the the Galena's surfaces before and after reagents treatment (Copper Sulfate activation).

III.4.1.3. SEM analysis

When Galena was treated with potassium ethyl xanthate (KEX) (5×10^{-3}mol/L) alone (Sample1), FigureIII.4, the SEM images showed only a subtle increase in surface roughness compared to the pristine, untreated mineral. This minor morphological change is significant, as it suggests the formation of a very thin, possibly monolayer, of lead xanthate species on the galena surface.

The limited extent of this change indicates that a simple collector adsorption process, without activation, does not dramatically alter the mineral's physical appearance. This observation is consistent with findings from other studies, which have described similar subtle changes as "white stains" or minor surface texturing rather than a complete surface coating. This phenomenon suggests that for galena, achieving substantial morphological transformation typically requires a more extensive surface reaction or the formation of a new, thicker phase. The true chemical nature of this thin layer, however, is best understood through complementary spectroscopic techniques. Similarly, Arnaud et al. (1989) (88)noted that at low concentrations, ethylxanthate adsorbs onto galena, forming a condensed phase, but substantial surface changes require higher concentrations leading to precipitation(98).

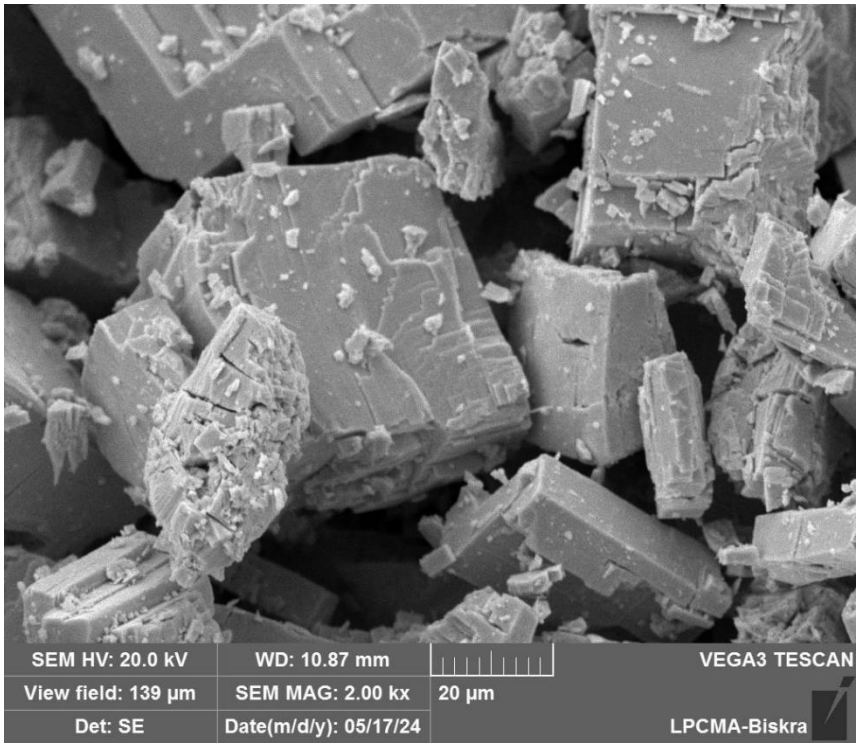


Figure III.4: SEM images of Galena + KEX (5×10^{-3}mol/l) .

The SEM analysis of the galena sample activated with $CuSO_4$(10^{-3}mol/L) and treated with KEX(5×10^{-3}mol/L) , figure III.5, revealed a significant surface modification, appearing as a thin, continuous layer that effectively masked the underlying mineral structure. This morphological change provides direct visual confirmation of successful copper activation, where the formation of a new, copper-rich surface creates highly favorable sites for the subsequent adsorption of xanthate to form stable copper-xanthate complexes (99); This observation is consistent with numerous studies establishing copper activation as an effective method for improving sulfide mineral flotation(45,49,100).

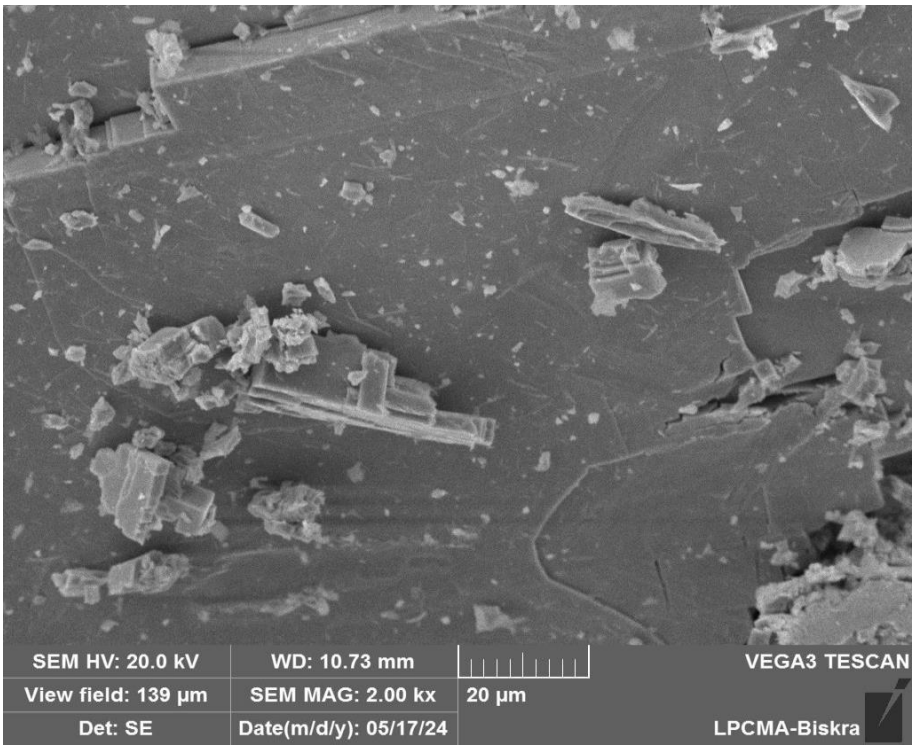


Figure III.5: SEM images of galena activated by $CuSO_4$ (10^{-3} mol /l) surface after KEX (5.10^{-3}mol/l) treatment

The SEM analysis of Sample 3, figure III.6, (Galena + CuSO4(10^{-3}mol/l)+KEX(5.10^{-3}mol/L)+ EDTA(0.1mol/L)) revealed the most significant morphological changes among all the samples. The images showed a notable increase in surface roughness and extensive particle agglomeration, a clear departure from the relatively uniform layer seen in Sample 2. This profound aggregation suggests that the addition of EDTA facilitated the formation of more stable, extensive, and possibly differently structured copper-xanthate complexes on the galena surface(99).

While other studies have noted similar phenomena, such as colloidal precipitates or hydrophobic aggregation under specific conditions (29,69), the pronounced effect here, in combination with EDTA, suggests a distinct mechanism. Our interpretation is that EDTA, acting as a powerful chelating agent, removes unwanted surface oxides and hydroxides that may have inhibited the copper activation process. This "cleaning" step exposes a more pristine and reactive galena surface, allowing for a more thorough copper activation. The result is a more robust and uniform layer of copper-xanthate complexes, leading to the observed enhanced particle aggregation. This finding is strongly supported by research showing EDTA's ability to dissolve such inhibitory species and improve collector performance (101); (72,77,90). Our results thus suggest that the sequential application of EDTA is an effective strategy for optimizing surface chemistry and enhancing flotation efficiency.

It is remarkable that the extent of aggregation and surface coverage observed in sample 3, even at this lower kex concentration, surpasses the results obtained in chapter II without EDTA. .

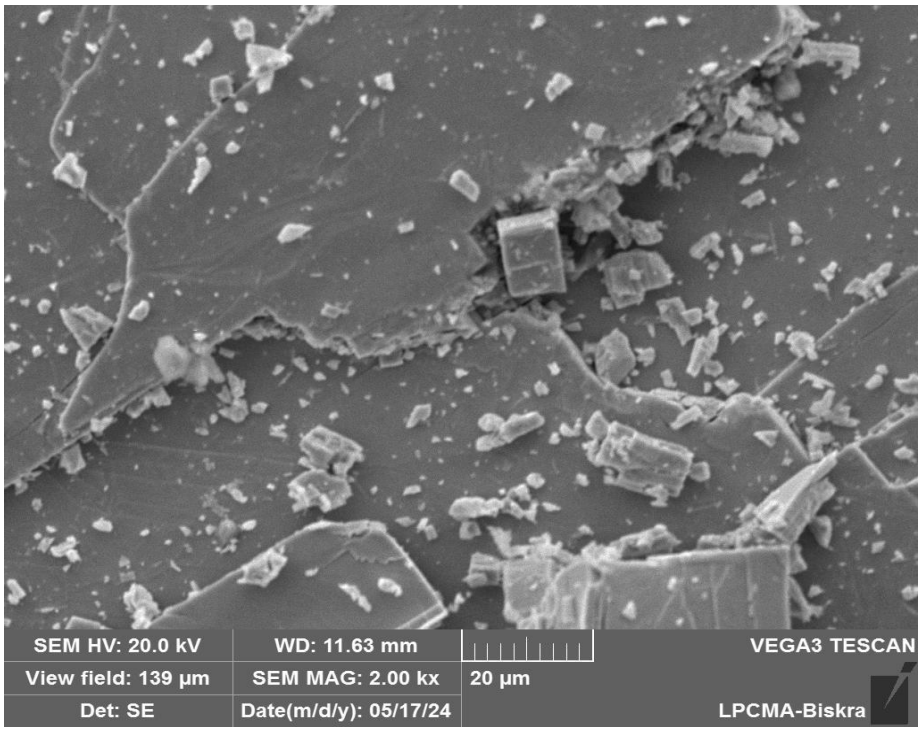


Figure III.6: SEM images of galena activated by $CuSO_4$ (10^{-3} mol /L) surface after KEX (5.10^{-3}mol/L) treatment in presence of EDTA(0.1mol/l).

III.4.1.4. EDS analysis

Energy-Dispersive X-ray Spectroscopy (EDS) was employed to determine the elemental composition of the treated galena surfaces. The EDS results for Sample 1 (Galena trated by KEX (5 10^{-3}mol/l) , figure III.7, confirmed the presence of Carbon (C), Oxygen (O), Sulfur (S), and Lead (Pb). This elemental profile is a key indicator of successful xanthate adsorption. The presence of carbon, oxygen, and additional sulfur confirms that the xanthate molecule, which contains these elements, has bonded to the galena surface. This finding is consistent with the well-established formation of lead xanthate species upon reaction with galena. This mechanism has been a cornerstone of flotation chemistry for decades and is supported by numerous studies (15,77).

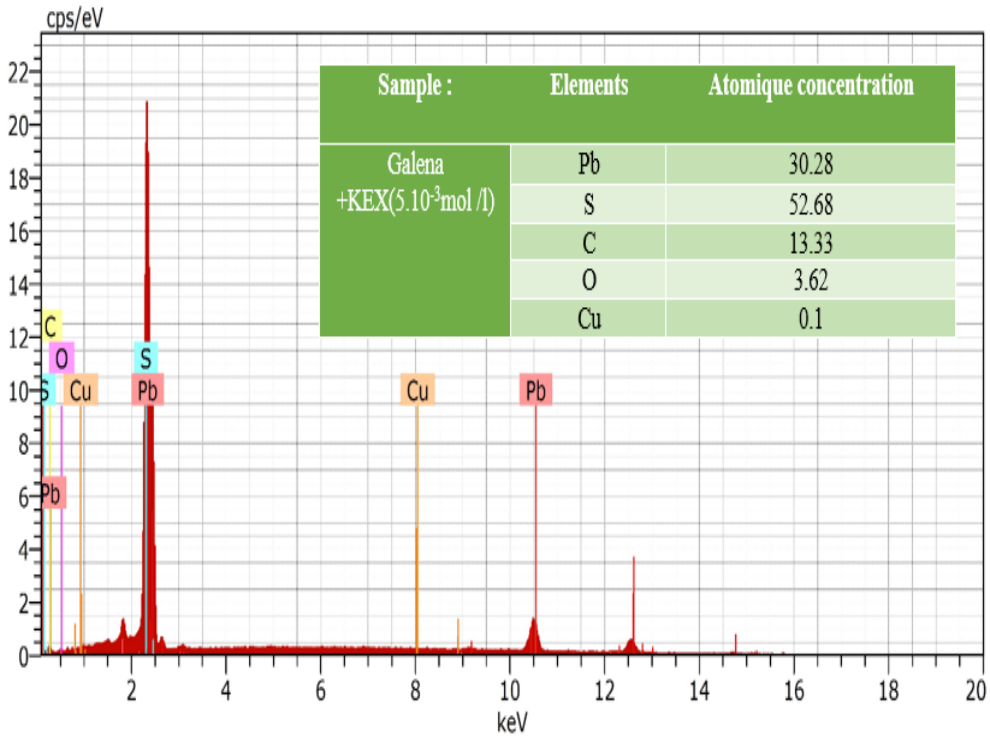
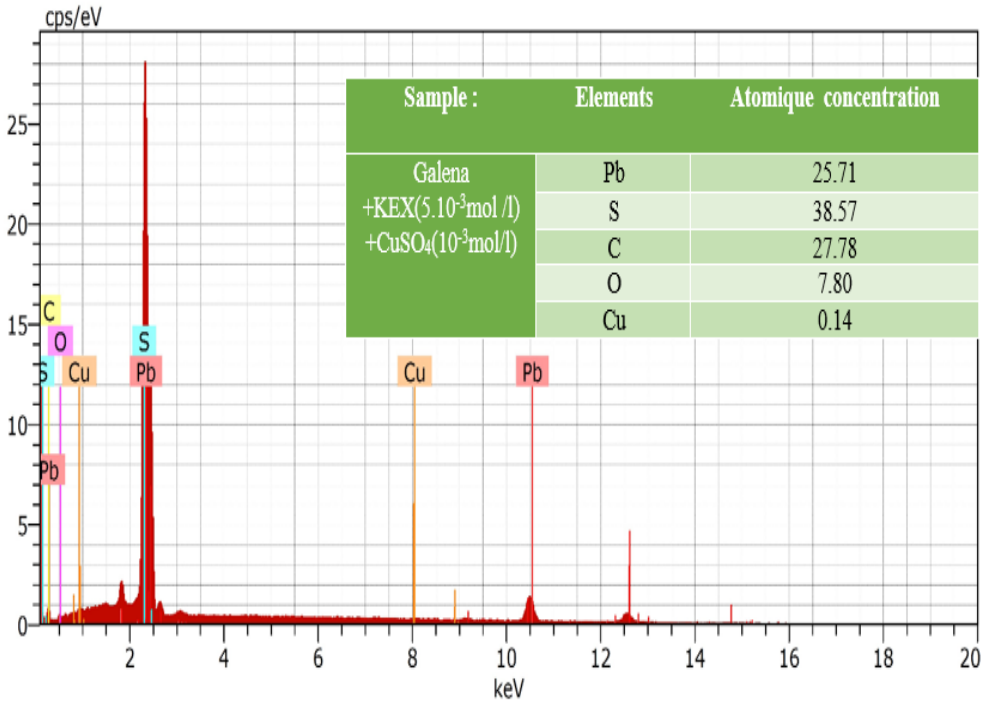


Figure III.7: EDS spectrogram of the Galena surface after KEX (5.10^{-3}mol/l) treatment.

As shown in Figure III.8, further EDS analysis of Sample 2 (galena activated with $CuSO_4$ before KEX(5×10^{-3}mol/l) treatment) provided crucial elemental data. The spectrum revealed a notable presence of copper (Cu) with an atomic concentration of 0.14%, in addition to an increased content of carbon (C) at 27.78%.

This elemental composition strongly supports the SEM findings and the proposed activation mechanism. The presence of copper confirms that the Cu^{2+} ions from the copper sulfate solution successfully adsorbed onto or reacted with the galena surface. The significant increase in carbon content, which originates from the KEX molecule, indicates that this copper-rich surface layer effectively promoted the adsorption of xanthate collectors. Together, these results provide compelling evidence for the formation of copper-xanthate complexes. This mechanism, where an activator ion facilitates collector adsorption, is a well-documented process in the flotation of other sulfide minerals like pyrite and sphalerite (49,100);



Sample :	Elements	Atomique concentration
Galena +KEX(5.10^{-3}mol /l) +$CuSO_4$(10^{-3}mol/l)	Pb	25.71
	S	38.57
	C	27.78
	O	7.80
	Cu	0.14

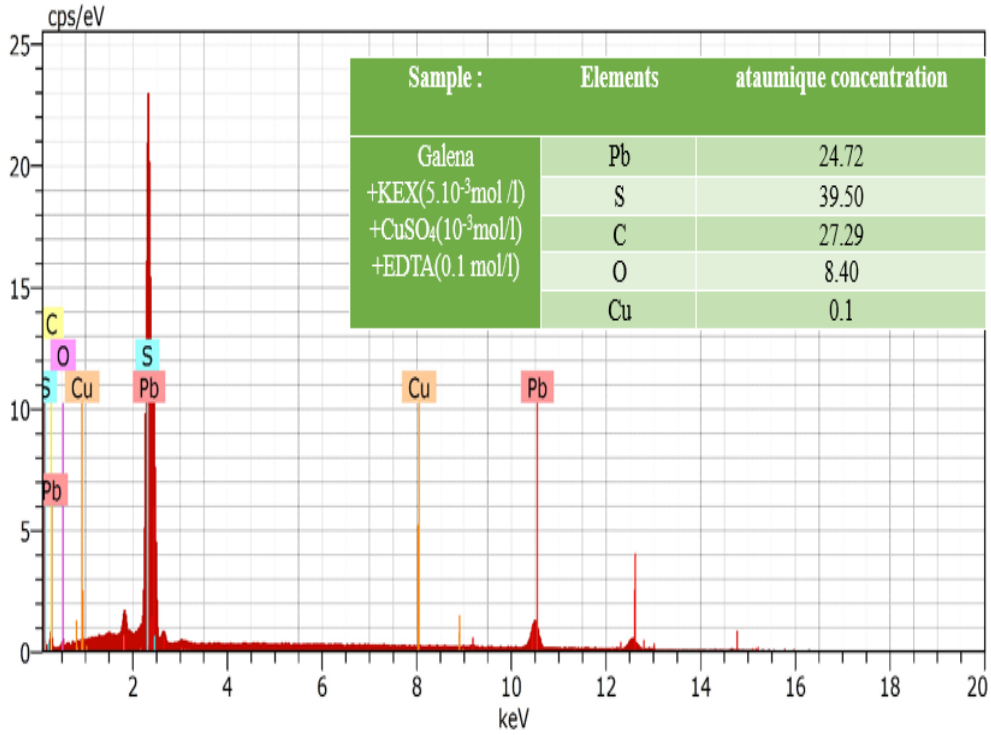
Figure III.8: EDS spectrogram of of galena activated by $CuSO_4$ (10^{-3}mol/l) surface after KEX (5×10^{-3}mol/l) treatment

Maintaining a high level of xanthate adsorption with EDTA treatment (Galena activated with ($CuSO_4$(10^{-3}mol/L) before KEX(5×10^{-3}mol/l) tratment in presence of EDTA(0.1mol/L)), figureIII.6, confirmed by the significantly increased atomic concentration of sulfur (39.50%), supports the hypothesis that EDTA enhances overall xanthate uptake.

The EDS analysis of Sample 3 (galena treated with $CuSO_4$(10^{-3}mol/L) , KEX(5×10^{-3}mol/l), and of EDTA(0.1mol/L)) provides the strongest evidence for the effectiveness of our proposed treatment. As shown in Figure III.9, the results confirmed a significantly increased atomic concentration of sulfur (39.50%). This finding is highly significant because sulfur is a key component of the xanthate molecule. The high concentration of sulfur, originating from the KEX, indicates a superior level of xanthate adsorption on the galena surface.

This result supports our central hypothesis that EDTA, by chelating and removing inhibitory surface species, creates a more favorable surface for both copper activation and subsequent xanthate adsorption. The concurrent increase in oxygen (8.40%) is likely a combination of two factors: a higher concentration of oxygen from the xanthate molecules themselves due to increased surface coverage and potentially some residual surface oxidation products, such as hydroxides or carbonates, that were not completely removed by the EDTA. This suggests that while EDTA is highly effective, the surface chemistry remains complex. However, the data clearly shows that the overall effect of the EDTA treatment is to significantly enhance the uptake

of sulfur from the xanthate, leading to a more robust and complete collector layer compared to galena treated only with copper activation(77,100,102).



Sample :	Elements	ataumique concentration
Galena +KEX(5.10^{-3}mol /l) +$CuSO_4$(10^{-3}mol/l) +EDTA(0.1 mol/l)	Pb	24.72
	S	39.50
	C	27.29
	O	8.40
	Cu	0.1

Figure III.9: EDS spectrogram of of Galena activated by $CuSO_4$ (10^{-3}mol/l) surface after KEX (5×10^{-3}mol/l) and treatment in presence of EDTA(0.1mol/l)

III.4.2. Galena with Copper Nitrate Activation and enhaced adsoption with EDTA(low concentration)

III.4.2.1. XRD analysis

X-ray diffraction patterns of galena samples treated with $Cu(NO_3)_2$ (10^{-3} mol/L) and KEX (5×10^{-3} mol/L) (blue line) or samples treated with $Cu(NO_3)_2$ (10^{-3} mol/L) , EDTA (0.1 mol/L) , and KEX (5×10^{-3} mol/L) (green line) showed marked differences in the range of surface interactions and complex formation.

For galena treated with KEX (5×10^{-3} mol/L) only (red line), as shown in Figure III.10, confirms the preservation of the cubic crystal system (space group $F_{m\bar{3}m}$) previously discussed(chapter III-4.1.4). However, a systematic comparison of the diffraction patterns reveals a gradual shift in the 2θ position of the (020), Figure III.11 (a) and (040), Figure III.11(b) planes of the same samples. While the sample treated with copper nitrate and KEX showed moderate peak shifts to 62.73° and 30.21°(from 62.42°and 30.12°), the use of EDTA as a complexing agent led to greater shifts to 62.79° and 30.42°. This maximum shift is a structural indicator of increased adsorption. By effectively removing the inhibited oxidation products

(following activation with copper nitrate), EDTA facilitates the formation of a denser and more uniform copper Xanthate layer despite the low Xanthate concentration, thus generating greater stress on the underlying crystal lattice. To address the radiation limits in X-ray diffraction (XRD), which often render very thin surface layers nearly invisible or amorphous, this study uses these micro-peak shifts as an indicator to determine the degree of surface modification. Furthermore, the X-ray diffraction results from both Guettaf (2015) and Debilou (2015) (104,105) or the treated galena and sphalerite also show only the peaks of the underlying mineral, supporting the conclusion that surface modifications are not usually visible with this technique. However, it is important to note that while these X-ray diffraction shifts provide significant structural evidence of enhanced adsorption, they are only a relatively accurate diagnostic tool. Therefore, these results are supportive, not definitive, and require further verification using complementary surface-sensitive techniques such as FTIR, SEM, and EDS to fully confirm the chemical composition and homogeneity of the adsorbed layers.(39)

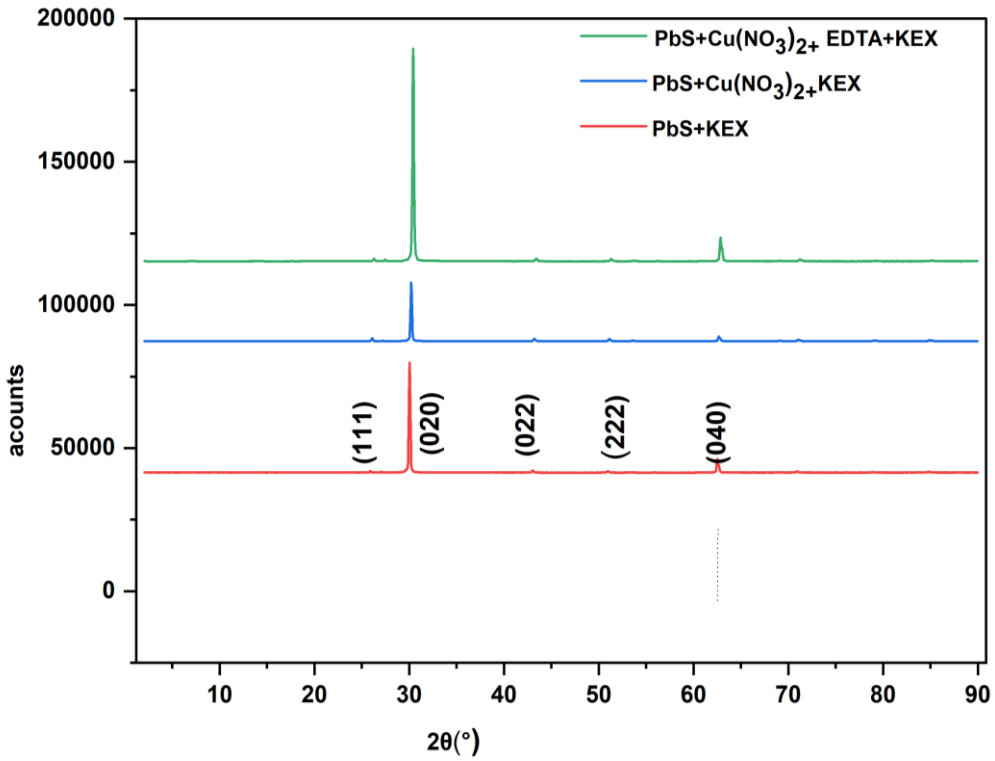


Figure III.10: XRD spectra of the the galena's surfaces before and after reagents treatment.

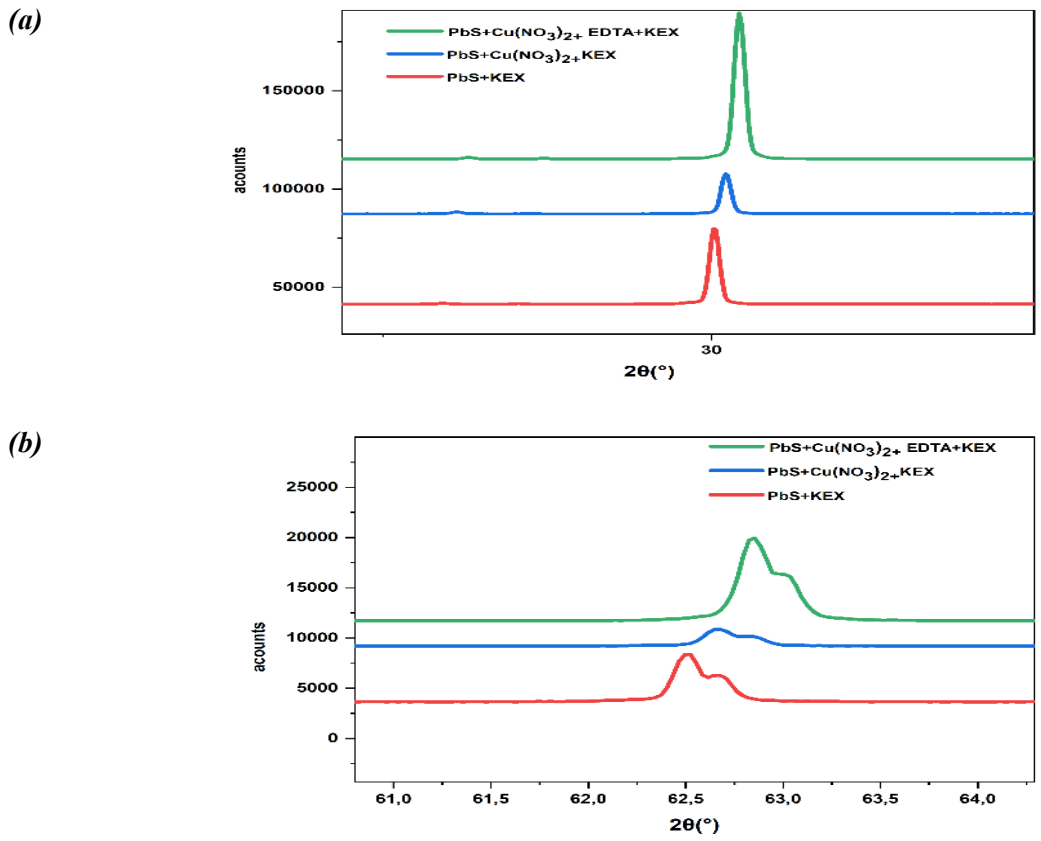


Figure III.11 : Magnification of the diffraction line (a) (020), and(b) (040) for nanoparticles of galena's surfaces before and after reagents treatment(Copper Nitrate activation).

III.4.2.2. FTIR analysis

Fourier Transform Infrared (FTIR) spectroscopy was employed to identify the molecular functional groups on the Galena surfaces following each chemical treatment. Figure III.12 provides a comparative analysis of the spectra, including the Galena samples treated with KEX(5×10^{-3} mol/L) alone, copper Nitrate (10^{-3} mol/L) and KEX(5×10^{-3} mol/L), and the / copper Nitrate (10^{-3} mol/L) /EDTA(0.1 mol/L) / KEX(5×10^{-3} mol/L) mixture.

For Galena sample trated with KEX and $Cu(NO_3)_2$ The distinct absorption bands observed at approximately 1200 cm^{-1} and 1122 cm^{-1} are characteristic of the stretching vibrations of the C-O-C and C-S bonds within a metal-xanthate complex.(103). The specific positions of these peaks are strongly indicative of copper ethyl xanthate, confirming that the copper ions successfully activated the mineral surface, creating sites for the subsequent chemical bonding of the xanthate collector. This analysis verifies the formation of a copper xanthate layer, and the intensity of these peaks can be used as a relative measure to compare the quantity of adsorbed collector against samples prepared under different conditions, such as with KEX alone , wich has least strongly absorbed intensity sample, and has lower adsorption rates, and the results of this sample have been explained previously(III.4.1.2).(103). Furthermore, Chandra et al. (2012)

utilized FTIR to identify Cu(I)-xanthate and diethyl dixanthogen on activated pyrite surfaces, demonstrating the technique's power in differentiating adsorbed collector species (49).

The Fourier Transform Infrared (FTIR) spectrum for the galena sample treated with copper nitrate, KEX, and EDTA provides crucial molecular evidence that supports the findings from the EDS analysis. The distinct absorption bands observed around 1191 cm^{-1} and 1124 cm^{-1} are the characteristic fingerprints for a copper-xanthate complex, confirming its presence on the mineral surface. Critically, the intensity of these peaks is visibly more pronounced compared to the spectrum of the sample treated without EDTA. This increased signal intensity directly indicates that a greater quantity of xanthate collector has adsorbed onto the surface, reinforcing the conclusion that EDTA's role in this specific system was to clean away inhibiting oxidation products, which in turn allowed for more effective activation and enhanced collector uptake.

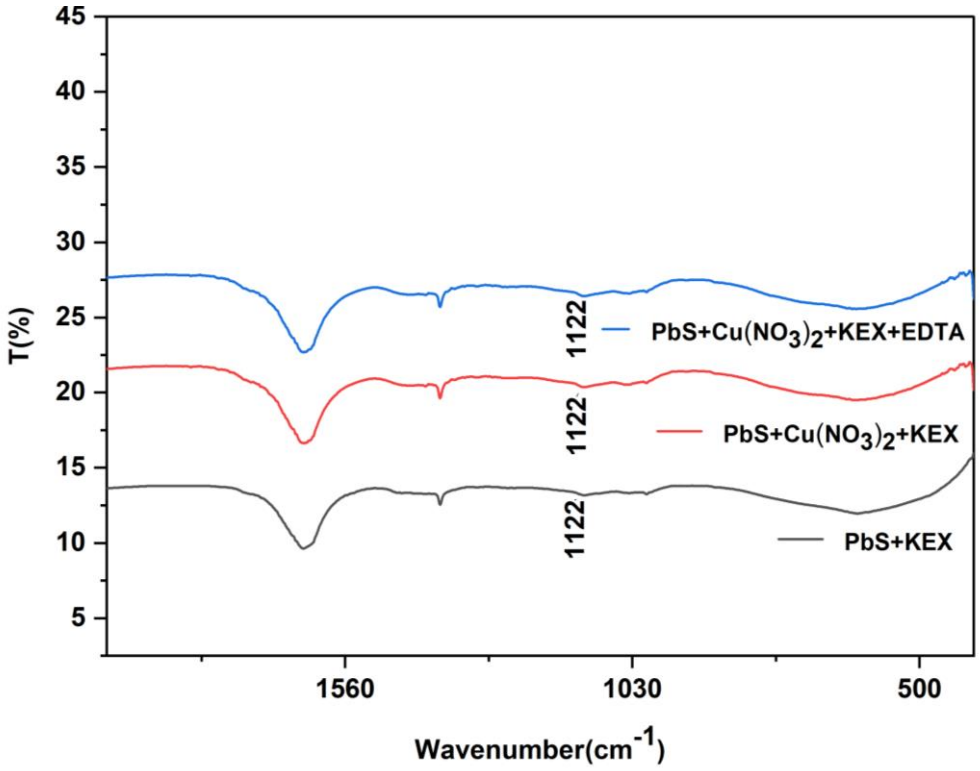


Figure III.12:FTIR spectrum of Galena galena's surfaces before and after reagents treatment.(Copper Nitrate activation).

III.4.2.3. SEM analysis

The provided SEM image , figure III.13, reveals the surface of a galena particle after activation with copper nitrate ($Cu(NO_3)_2$) at a concentration of 10^{-3} mol/L, followed by treatment with potassium ethyl xanthate (KEX) at 5.10^{-3} mol/L. The image displays a surface

with some degree of modification, characterized by the presence of fine, somewhat dispersed

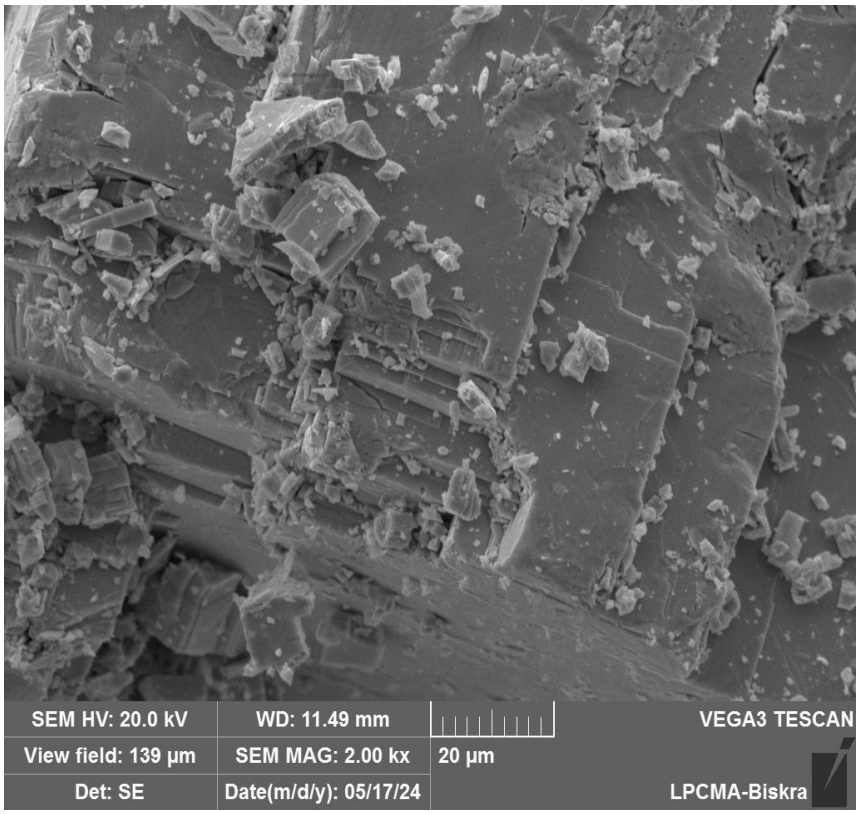


Figure III.13: SEM images of galena activated by $Cu(NO_3)_2$ (10^{-3} mol /l) surface after KEX (5.10^{-3}mol/l) treatment

precipitates overlying the typical crystalline structure of galena.

When comparing this to the previously described activation with copper sulfate, a noticeable difference in the extent and nature of the surface coverage emerges. Activation with copper sulfate resulted in a more pronounced and seemingly thicker layer covering the galena. In contrast, the activation with copper nitrate appears to yield a less extensive and more patchy adsorption layer. This visual evidence suggests that under the studied conditions at lower concentrations, copper sulfate is a more effective activator for promoting the subsequent adsorption of xanthate onto the galena surface(39) .

Figure III-14 shows the Galena surface after sequential treatment with Copper Nitrate (10^{-3} mol/L), then EDTA (0.1 mol/L), and finally Potassium Ethyl Xanthate (KEX, 5×10^{-3} mol/L). Visual evidence indicates that the Xanthate adsorption is slightly higher than that observed in the previous image (Figure III-13), which showed only the activated Galena without EDTA. Despite the lower concentration of KEX used here, adsorption is clearly improved in this region. Notably, the surface exhibits more distinct quantum dots, indicating that the addition of EDTA facilitated better organization of the adsorbed species. This improvement demonstrates that

EDTA effectively cleans the metal surface, removing obstructive deposits and allowing for better expansion of the aggregate. Consequently, the underlying crystal structure is more accessible, leading to improved adsorption efficiency compared to the previous sample (12)

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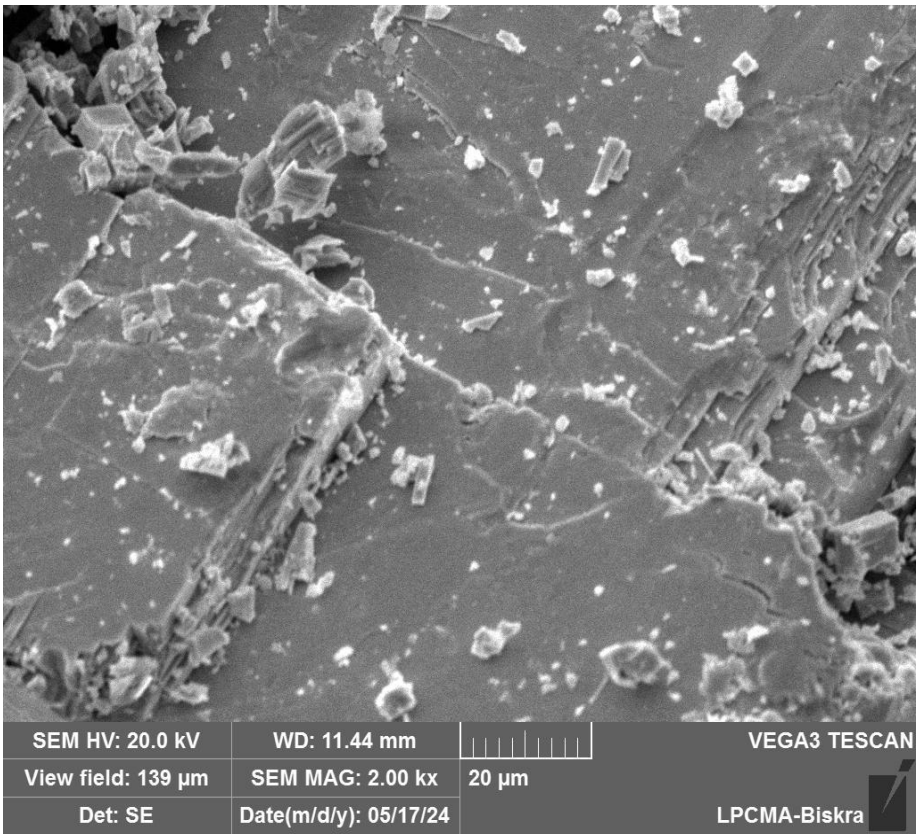

Figure III.14 : SEM images of galena activated by $Cu(NO_3)_2$ (10^{-3} mol /l) surface after KEX (5.10^{-3}mol/l) and EDTA (0.1 mol/l) treatment .

III.4.2.4. EDS analysis

EDS analysis of galena activated with copper nitrate (10^{-3} mol/L) and treated with KEX (5.10^{-3} mol/L), as shown in Figure III.15, reveals a less efficient adsorption process compared to activation with copper sulfate, forming an incomplete and discontinuous adsorption layer. This observation was confirmed by the successful activation with a 0.13% copper signal and the subsequent adsorption of the collector via a 23.64% carbon peak. However, it demonstrates that the total xanthane adsorption is significantly lower than that achieved with copper sulfate, a finding previously reported in Chapter 2 at higher concentrations(104).

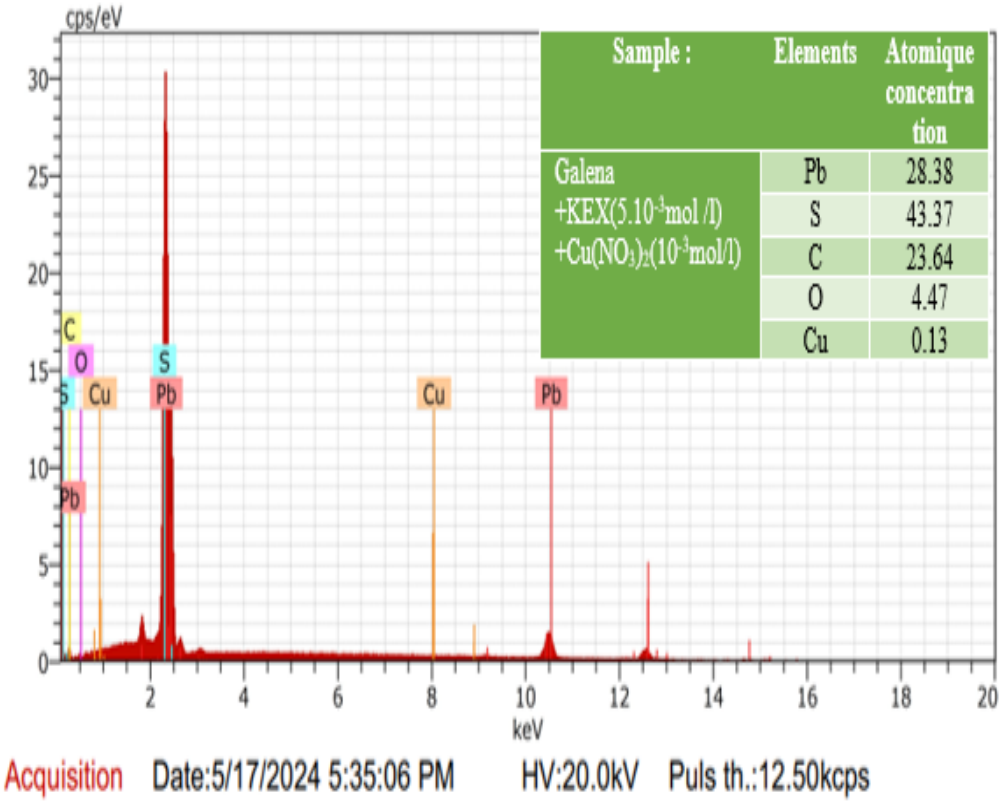

Figure III.15: EDS spectrograms of sample 6,(Galena activated by $Cu(NO_3)_2(10^{-3}mol/L)$ surfaces after KEX ($5.10^{-3}mol/l$)

The quantitative EDS analysis for the galena sample treated with copper nitrate(10^{-3}mol/L) , EDTA (0.1mo/L)) , and KEX(5.10^{-3}mol/l), Figure III.16, provides a crucial insight into the system's chemistry. The spectrogram reveals a significant increase in the carbon concentration to 27.29%, up from the 23.64% observed in the sample without EDTA. Since carbon is the primary indicator of adsorbed xanthate, this data demonstrates that the addition of EDTA has, in fact, led to a greater amount of collector on the mineral surface. This suggests that EDTA's dominant role was not to strip the activator ions, but rather to clean the galena surface by removing pre-existing oxidation layers that were inhibiting the activation process. By exposing a more reactive mineral surface, the copper ions from the nitrate solution were able to activate the galena more effectively, which in turn promoted a higher degree of xanthate adsorption, highlighting a synergistic effect even with a less optimal activator. This aligns with the "surface cleaning" mechanism proposed by Baker et al. for the action of (46), where oxidation products are removed from the surface.

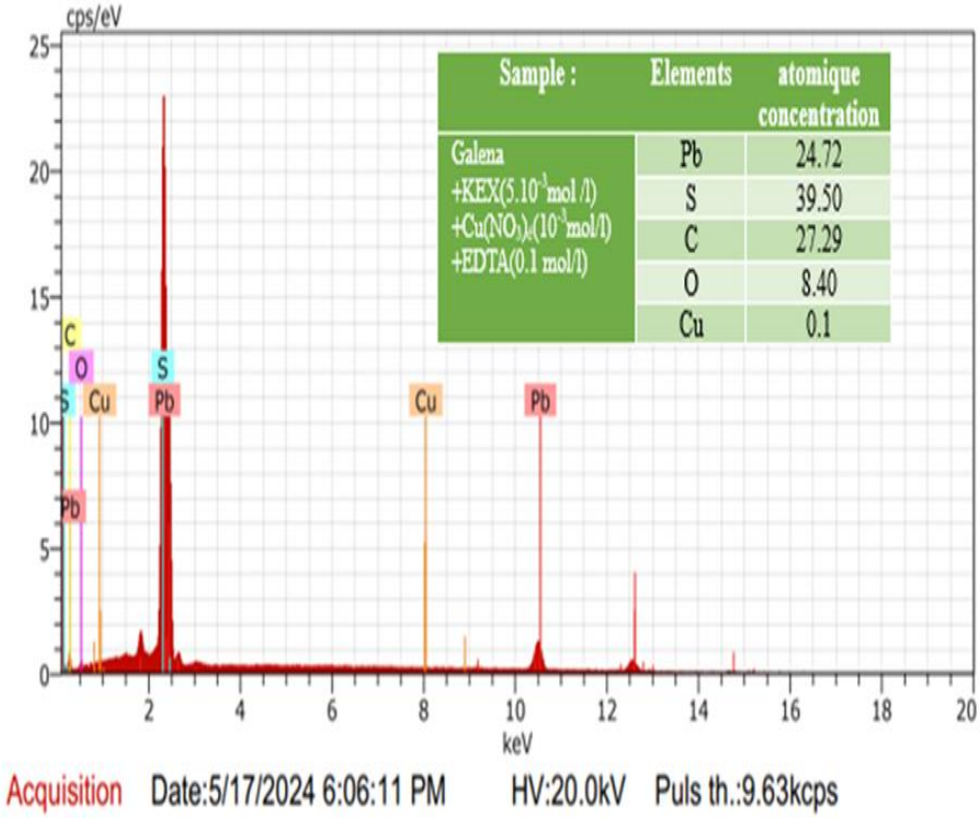

Figure III.16: EDS spectrogram ofsample10: (galena activated by $Cu(NO_3)_2$ (10^{-3}mol/l) surface after KEX (5.10^{-3}mol/l) and treatment in presence of EDTA(0.1mol/l)).

III.5. Conclusion

This chapter systematically investigated the fundamental hypothesis that pretreatment with the chelating agent EDTA can synergistically enhance the adsorption of low-concentration xanthate onto Galena by copper. By conducting a comparative analysis of both Copper Sulfate and Copper Nitrate pretreatments within a sequential treatment framework, the results provided consistent and conclusive confirmation of this hypothesis.

Spectroscopic analyses using XRD and FTIR techniques definitively confirmed a clear hierarchy of EDTA pretreatment efficacy. The greatest improvement in collector adsorption was achieved through the sequential application of Copper Sulfate pretreatment followed by EDTA compared to Copper Nitrate. This optimized protocol led to profound morphological changes, with SEM indicating widespread aggregation of hydrophobic molecules, which was quantitatively confirmed by EDS through the highest surface concentrations of Carbon resulting from the adsorbed Xanthate. Multi-technological surface characterization revealed these results, showing a high-density, highly uniform Copper Xanthate surface layer under these conditions (low Xanthate concentration). The results support the hypothesis that EDTA acts as

a highly effective surface "cleaning" agent, removing inhibiting oxidation products (such as Lead oxides and Sulfates) that could impede activation. By exposing a purer and more reactive Galena surface, subsequent Copper activation becomes more homogeneous and complete, increasing the number of sites available for strong Xanthate chemisorption despite low concentrations. This synergistic effect was observed for both Copper Sulfate and the inherently less effective Copper Nitrate activator, reinforcing the primary role of EDTA as surface preparation.

...In conclusion, this chapter provides an evidence-based framework for improving the surface chemical properties of Galena in the flotation process. This confirms that the sequential cleaning and activation strategy is significantly more effective than activation alone, and reaffirms the superiority of Copper Sulfate as the preferred activator. These results contribute important fundamental insights into the interactions of metals with reagents and provide a proven, practical pathway for enhancing the efficiency and robustness of Galena flotation processes.

GENERAL CONCLUSION

This doctoral thesis set out to address a persistent and fundamental challenge in sulfide mineral processing: the depression of galena flotation due to surface oxidation. By systematically investigating a novel, sequential conditioning strategy, this research has successfully validated the central hypothesis that a targeted chemical cleaning of the mineral surface prior to activation can synergistically enhance collector adsorption. The comprehensive, multi-technique surface analyses presented herein provide a cohesive body of evidence that not only supports this hypothesis but also redefines the optimal protocol for galena surface preparation.

The key contributions of this work can be distilled into three primary conclusions.

First, this research has unequivocally demonstrated the superiority of a sequential treatment paradigm over conventional, single-step activation. The introduction of Ethylenediaminetetraacetic acid (EDTA) as a pre-treatment agent was shown to be highly effective in removing inhibitory oxidation products. This "cleaning" mechanism exposes a more pristine and electrochemically active sulfide surface, thereby creating a superior substrate for subsequent chemical modification.

Second, a clear hierarchy of activator efficacy has been established. The direct comparison between copper sulfate ($CuSO_4$) and copper nitrate ($Cu(NO_3)_2$) confirmed that copper sulfate is an inherently more potent activator for galena under the studied conditions.

Third, and most significantly, the synergy between surface activation and cleaning has been quantitatively and qualitatively proven. The optimal protocol—sequential ctivation with $CuSO_4$ followed by a EDTAtreatment—yielded the most robust and extensive xanthate adsorption layer. This was confirmed through a convergence of evidence: SEM analysis revealed pronounced hydrophobic agglomeration, EDS quantified the highest surface concentrations of both copper and Carbon (from the Xanthate), and FTIR spectroscopy provided definitive molecular evidence of the most intense Copper-Xanthate formation.

In conclusion, this thesis provides not only a fundamentally improved conditioning protocol for enhancing Galena flotation but also contributes to a deeper understanding of the complex interfacial chemistry at play. By treating surface passivation as a barrier to be systematically removed rather than simply overcome, this work offers a validated pathway toward improving the efficiency, selectivity, and robustness of industrial lead flotation circuits.

The findings of this thesis serve as a robust foundation for several promising avenues of future inquiry, bridging the gap between fundamental surface science and applied mineral engineering. Industrial Validation and Process Optimization: The immediate and most critical next step is the validation of the optimized EDTA-$CuSO_4$ protocol at the pilot and industrial scales. Future

studies should focus on applying this strategy to real ore feeds, which feature complex mineralogies and variable water chemistry. Such investigations would be crucial for assessing the protocol's robustness, determining optimal reagent dosages under dynamic conditions, and conducting a thorough techno-economic analysis to quantify the potential gains in lead recovery versus the additional reagent costs.

Elucidating the Counter-Anion Mechanism at a Molecular Level: While this work demonstrated that sulfate is a superior counter-anion to nitrate, the fundamental reason why remains a compelling area for research. Future studies employing more advanced surface-sensitive techniques, such as X-ray Photoelectron Spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), could be used to probe the molecular-level differences. Such research could elucidate whether the sulfate ion participates directly in the surface complex, alters the speciation of aqueous copper, or modifies the surface charge in a way that promotes a more favorable activation.

Application to Complex and Polymetallic Sulfide Ores: The "cleaning-activation" principle is likely not limited to galena. Many complex sulfide ores (e.g., Cu-Pb-Zn systems) suffer from issues of surface oxidation and inadvertent activation, leading to poor selectivity. A significant research opportunity exists to apply this sequential EDTA treatment strategy to these more complex systems. The goal would be to determine if this approach can be tailored to selectively clean and activate target minerals while simultaneously passivating gangue sulfides, thereby improving overall separation efficiency.

Development and Integration of "Green" Chelating Agents: In alignment with the increasing global demand for sustainable mining practices, future research should explore environmentally benign alternatives to EDTA. Investigating the efficacy of biodegradable chelating agents (e.g., glutamic acid diacetic acid - GLDA, or iminodisuccinic acid - IDS) within the sequential conditioning framework could lead to the development of a process that is not only more efficient but also has a significantly reduced environmental footprint. This research would be at the forefront of "green flotation" chemistry.

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Copper nitrate for galena activation: A surface chemistry study of xanthate adsorption

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ABSTRACT

The efficient recovery of lead by selective flotation of galena (PbS) is crucial, yet often hindered by its insufficient inherent hydrophobicity, necessitating surface activation. While copper sulfate ($CuSO_4$) is a conventional activator, the potential and mechanistic details of alternative copper salts, particularly copper nitrate ($Cu(NO_3)_2$), remain largely unexplored for galena activation. This study, for the first time, systematically investigates copper nitrate ($Cu(NO_3)_2$) as an activator for galena, focusing on its impact on surface chemistry and subsequent potassium ethyl xanthate (KEX) adsorption. Copper sulfate ($CuSO_4$) was employed as a well-established benchmark to evaluate the relative activation power of $Cu(NO_3)_2$. A suite of analytical techniques, including X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and Energy-Dispersive X-ray Spectroscopy (EDS), was utilized to characterize the induced surface modifications.

Results demonstrate that $Cu(NO_3)_2$ facilitates KEX adsorption, leading to the formation of copper-xanthate complexes. This was supported by characteristic XRD peaks (e.g., at $2\theta = 24.37°$, $18.40°$) and FTIR absorption bands (e.g., at 1197 cm^{-1}). SEM imaging revealed moderate surface roughening, and EDS analysis confirmed copper deposition at an atomic concentration of 0.11 %. In comparison, the benchmark $CuSO_4$ activation resulted in more extensive copper-xanthate formation, indicated by significantly more intense XRD and FTIR signals (e.g., $2\theta = 19.63°$, $28.35°$), more pronounced morphological changes, a higher copper deposition of 0.39 %, and a corresponding sulfur enrichment to 50.70 % S.

These findings establish $Cu(NO_3)_2$ as a viable, albeit less potent activator than $CuSO_4$ under the studied conditions (0.11 % vs. 0.39 % Cu deposition). This research provides the first detailed surface-chemical evidence of this activation, quantifying elemental changes and highlighting the differential impact of the counterion. This work contributes foundational knowledge for optimizing flotation schemes to improve the efficiency and sustainability of lead ore processing.

1. Introduction

The global demand for lead and other base metals has driven the need for efficient and sustainable mineral processing techniques [1–3]. Galena (PbS) is the primary ore of lead and is often associated with other sulfide minerals such as sphalerite (ZnS) and pyrite (FeS_2) [3,4]. The selective flotation of galena from these minerals is essential for the recovery of lead and the production of high-quality concentrates [3,5–7]. However, the inherent hydrophobicity of galena is often insufficient for effective flotation [4,5], necessitating the use of activators to modify its surface properties and enhance the adsorption of collectors [1,6,8,9].

Copper activation is a well-established method for improving the flotation of galena [10,11]. The addition of copper ions, typically in the form of copper sulfate ($CuSO_4$), promotes the formation of copper sulfide species on the galena surface, which in turn facilitates the adsorption of xanthate collectors [12,13]. This process enhances the hydrophobicity of the mineral surface, leading to improved flotation performance [1,10]. Despite the widespread use of $CuSO_4$, the underlying mechanisms of copper activation and its impact on xanthate adsorption are still not fully understood [10,14]. Furthermore, the influence of different copper salts on the activation process and flotation efficiency remains largely unexplored [14].

Moreover, the mineral processing industry is increasingly under pressure to adopt more environmentally sustainable practices [2]. While

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highly toxic reagents like cyanides (used as depressants) draw significant criticism [2,6,8], the extensive use of metal salts, including activators like copper sulfate, also contributes to the overall chemical load in process water and tailings. There is a continuous drive for alternative reagents and processes that are not only effective but also more ecologically benign and economically viable [6,8]. This includes optimizing reagent consumption and exploring activators that may offer improved performance or a reduced environmental footprint.

Driven by the continuous demand for enhanced efficiency, cost-effectiveness, and environmental sustainability in mineral beneficiation, this study explores copper nitrate ($Cu(NO_3)_2$) as a novel activator in galena flotation. Specifically, the primary objective is to provide a systematic evaluation of the activation capabilities of $Cu(NO_3)_2$, focusing on its effectiveness in enhancing the adsorption of potassium ethyl xanthate (KEX) on galena (PbS) surfaces. Given the importance of activators for collector adsorption in mineral flotation, such an investigation is essential for identifying alternative activators that can improve the flotation performance of galena, optimizing flotation efficiency while maintaining environmental and economic viability.

Despite extensive research on copper sulfate ($CuSO_4$) as an activator for sulfide minerals, the activation performance of copper nitrate ($Cu(NO_3)_2$) has remained largely unexplored. To our knowledge, the only study that has addressed $Cu(NO_3)_2$ in the context of mineral activation was conducted by Nedjar and Barkat [15], which focused on its use as an activator for sphalerite (ZnS) flotation. No studies have systematically investigated the activation of galena (PbS) by $Cu(NO_3)_2$, leaving a critical gap in the understanding of its surface interactions, activation mechanisms, and flotation efficiency. This study is the first to directly address this gap, providing a comprehensive evaluation of $Cu(NO_3)_2$ as an activator for galena.

To achieve this objective, a suite of advanced surface characterization techniques will be employed. X-ray diffraction (XRD) confirmed the structural integrity of galena post-activation, while Fourier-transform infrared spectroscopy (FTIR) identified chemisorbed xanthate species (e.g., Pb–X and Cu–X complexes) on the mineral surface. Scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS) provided spatial and elemental evidence of $Cu(NO_3)_2$-induced surface modification, corroborating enhanced xanthate adsorption. These analytical methods align with established protocols for studying sulfide mineral activation (e.g., Nedjar and Barkat, 2013), ensuring accurate and reproducible results.

Moreover, to establish the practical relevance of $Cu(NO_3)_2$, its activation efficiency will be benchmarked against that of copper(II) sulfate ($CuSO_4$), a widely recognized activator in galena flotation [16]. Through this direct comparative analysis, the study seeks to determine whether $Cu(NO_3)_2$ offers a more effective and sustainable alternative to $CuSO_4$. By providing a detailed, evidence-based assessment of the activation potential of $Cu(NO_3)_2$, this research addresses the ongoing demand from the mineral processing community for improved and alternative flotation reagents.

2. Materials and methods

2.1. Samples, reagents, and sample preparation

The galena (PbS) samples used in this study were obtained from the Shaibet El Hamra mine in Algeria. The raw ore was manually separated, then crushed and ground in an agate mortar. For adsorption tests, a galena fraction of $-208 + 108$ μm (i.e., particles passing a 208 μm sieve and retained on a 108 μm sieve) was utilized. For scanning electron microscopy (SEM) examination, a ground product sieved to $-74 + 38$ μm was used. For Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Diffraction (XRD) analyses, a portion of the -108 μm powder (i.e., particles passing a 108 μm sieve) was further ground to a particle size of approximately less than 2 μm.

Potassium ethyl xanthate (KEX, purity 96 %), copper (II) sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$, purity 98.5 %), and copper (II) nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$, analytical grade) were procured from Sigma-Aldrich Co. (St. Louis, MO, USA). Sodium hydroxide (NaOH, analytical grade), also from Sigma-Aldrich Co., was used for pH adjustment. All solutions were prepared using distilled water.

2.2. Methods

2.2.1. Scanning electron microscopy with energy dispersive spectrometer (SEM-EDS) analysis

The surface morphology and elemental composition of galena were analyzed before and after reagent treatments using a Bruker Nano GmbH scanning electron microscope (SEM) equipped with an Xflash Detector 610 M energy-dispersive X-ray spectrometer (EDS). The EDS analysis area corresponded to the SEM observation region, typically ranging between 1 and 100 μm^2. The accuracy of the EDS spectral analysis was approximately 1 %. The SEM was operated at an accelerating voltage of 20 kV to determine the atomic concentrations of elements such as lead, sulfur, copper, carbon, and oxygen on the sample surfaces.

2.2.2. Fourier Transform Infrared Spectroscopy (FTIR) analysis

FTIR spectra were collected using a PerkinElmer Spectrum Two spectrometer (PerkinElmer Inc., Waltham, MA, USA) with a resolution of 8 cm^{-1}. The analysis was performed in transmission mode across the wavenumber range of 400–4000 cm^{-1}. For every sample, 120 scans were accumulated. Prior to analysis, approximately 100 μg of the powder sample was mixed with 23 ± 2 mg of KBr, and compressed using a cold isostatic press (CIP) at 150 MPa to form a pellet with a thickness of 200–250 μm. The IR spectra display transmittance (T) as a function of the incident wavenumbers.

2.2.3. X-ray diffraction (XRD)

X-ray powder diffraction (XRD) analysis was employed to qualitatively identify the crystalline mineral phases present in the samples. XRD patterns were obtained using a Rigaku MiniFlex 600 benchtop diffractometer (Rigaku Corporation, Tokyo, Japan) equipped with a CuKα radiation source ($\lambda = 1.542$ Å). Data were collected at a scan rate of 0.03°/s over a 2θ range of 5°–90°. Phase identification was performed by comparing experimental diffraction patterns with reference data from the JCPDS (International Center for Diffraction Data) database.

2.3. Adsorption and activation procedure

The experimental conditions for KEX adsorption and copper activation (pH, reagent concentrations, contact times) were selected based on a review of established literature for galena flotation, aiming to ensure relevant conditions for comparing the effects of $CuSO_4$ and $Cu(NO_3)_2$ on surface chemistry rather than performing a comprehensive optimization study. The rationale for each specific parameter is detailed below.

pH **Conditions:** The pH of the galena suspension was adjusted to and maintained between 9.0 and 10.0 using NaOH (10^{-1} mol/L). This moderately alkaline range is consistent with optimal conditions reported for galena flotation, particularly when using xanthate collectors and copper activators. Studies such as Özün & Ergen [17] found the highest galena recoveries at pH 9–9.5, correlating this with favorable surface chemistry for xanthate chemisorption. Similarly, Nedjar & Barkat [18–20] consistently employed pH values around 9–9.5 for their studies on copper activation and xanthate adsorption on galena, noting that basic pH is generally favorable. Popov & Vucinic [16] also found optimal flotation with KEX between pH 8 and 10 after copper activation.

KEX Concentration: Potassium ethyl xanthate (KEX) was used at a concentration of 5×10^{-2} mol/L. While specific collector dosages vary, this concentration ensures sufficient collector availability for surface coverage and is within the range of concentrations explored in fundamental adsorption studies, allowing for clear detection of surface species. For comparison, Nedjar & Barkat [18,19] used xanthate

concentrations in the order of 10^{-3} M for their surface characterization work.

Activator Dosage: For activated samples, copper sulfate ($CuSO_4$) or copper nitrate ($Cu(NO_3)_2$) was used at a concentration of 10^{-3} mol/L. This dosage is consistent with concentrations reported in literature for effective copper activation of sulfide minerals (e.g., Nedjar & Barkat, [18,19], used 10^{-4} M $CuSO_4$; Popov & Vucinic, [16], used $3x10^{-5}$ M $CuSO_4$ for flotation tests, with higher concentrations for zeta potential). The 10^{-3} M concentration was chosen to ensure significant activation for clear comparative analysis of the surface modifications. An equivalent molar concentration of Cu^{2+} ions was used for both $CuSO_4$ and $Cu(NO_3)_2$ to allow for a direct comparison of the counterion effects.

Contact Time: A contact time of 10 min was employed for the activation step (when activators were used) and subsequently for the KEX adsorption step. This duration was selected to allow sufficient time for the respective surface reactions to proceed towards equilibrium, as indicated by studies monitoring rest potential stabilization or observing adsorption kinetics (e.g., Nedjar & Barkat, [18–20], reported activation times around 8–30 min based on rest potential; Özün & Ergen, [21], used 5–10 min for xanthate conditioning).

2.3.1. Experimental protocol for sample preparation

Three types of samples were prepared for surface characterization. For each preparation, 3 g of galena powder was added to 30 ml of distilled water. The suspension was then subjected to the following treatments, with adequate agitation during each reagent addition and conditioning period:

Sample 1 (KEX alone): The pH of the galena suspension was adjusted to 9.0–10.0 using NaOH (10^{-1} mol/L). KEX solution was then added to achieve a final concentration of 5 x 10^{-2} mol/L, and the suspension was conditioned for 10 min.

Sample 2 ($CuSO_4$ activated + KEX): The pH of the galena suspension was adjusted to 9.0–10.0. $CuSO_4$ solution was added to achieve a final concentration of 10^{-3} mol/L, and the suspension was conditioned for 10 min (activation step). Subsequently, KEX solution was added to a final concentration of 5 x 10^{-2} mol/L, and the suspension was conditioned for an additional 10 min.

Sample 3 ($Cu(NO_3)_2$ activated + KEX): The pH of the galena suspension was adjusted to 9.0–10.0. $Cu(NO_3)_2$ solution was added to achieve a final concentration of 10^{-3} mol/L, and the suspension was conditioned for 10 min (activation step). Subsequently, KEX solution was added to a final concentration of 5 x 10^{-2} mol/L, and the suspension was conditioned for an additional 10 min.

After the final treatment step, each sample mixture was allowed to rest for 5 min. The solids were then separated by repeated rinsing with distilled water and filtration to remove unadsorbed reagents prior to surface characterization analyses.

3. Results and discussion

This section presents and discusses the experimental findings from our investigation into the comparative effects of copper sulfate (CuSO4) and copper nitrate (Cu(NO3)2) as activators for galena. In line with our study's primary aim to elucidate the surface modifications and their impact on xanthate adsorption, we first detail the baseline characterization of the pristine galena mineral and the potassium ethyl xanthate (KEX) collector. Subsequently, we present the results obtained from X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and Energy Dispersive X-ray Spectroscopy (EDS) analyses. These analyses systematically examine the galena surface chemistry and morphology after interaction with KEX alone, and then after activation with CuSO4 or Cu(NO3)2 prior to KEX treatment. The ensuing discussion interprets these findings in the context of existing literature, focusing on the mechanisms of copper activation, xanthate adsorption, and the differential impacts of the two copper salts, thereby providing insights relevant to optimizing galena flotation processes.

3.1. Galena characterization

The XRD analysis of the galena, Fig. 1, revealed distinct diffraction peaks at 2θ angles of 26.07°, 30.2°, 43.23°, 51.18°, 53.64°, and 62.79°, corresponding to d-values of 3.41 Å, 2.95 Å, 2.09 Å, 1.78 Å, 1.70 Å, and 1.47 Å, respectively. These peaks are consistent with the reference JCPDS file No. 96-901-3401 for galena (PbS), confirming the presence of galena as the primary phase in the sample. The most intense peak at 2θ = 30.2° (d = 2.95 Å) indicates the preferred orientation of the galena crystals, which is typical for this mineral. The relative peak intensities suggest a well-crystallized structure; the peak at 2θ = 26.07° (d = 3.41 Å), also exhibiting significant intensity (92.6 %), further supports the dominance of galena in the sample.

These findings are consistent with the XRD patterns of galena reported across multiple studies. For instance, the characteristic diffraction peaks of galena were similarly observed by Basilios et al. [22]. Similarly, Nedjar and Barkat [12] and Leppinen JO et al. [1] also observed the main characteristic peaks of galena in their XRD analyses, confirming its crystalline nature. Although the specific peak intensities in our study differ slightly from some of these studies, such variations can be attributed to differences in the origin and processing of the samples, as well as the experimental conditions used for XRD analysis [12,22]. The high intensity of the peak at 2θ = 30.2° in our study is also in agreement with the findings of Nedjar et al. [23], who reported this peak as the most intense in their XRD analysis of galena. This consistency across various studies confirms the reliability of our XRD analysis in identifying galena as the primary mineral phase.

The SEM images, Fig. 2, of galena at magnifications of 1000× (a), and 4000 × (b) reveal the granular and crystalline nature of the galena. The images show well-defined crystal faces and a relatively uniform particle size distribution, which is characteristic of galena. These observations are consistent with the morphological features of galena described in various studies. For instance, Nedjar et al. [23] observed similar granular morphology with well-defined crystal faces in their SEM analyses. Additionally, the findings align with Leppinen JO et al. [1], who found that galena samples exhibited well-defined cubic crystal morphology, which they attributed to the cubic crystal structure of PbS. The consistency in morphological features across these studies underscores the typical characteristics of galena.

The EDS analysis, Fig. 3, confirmed the elemental composition of the

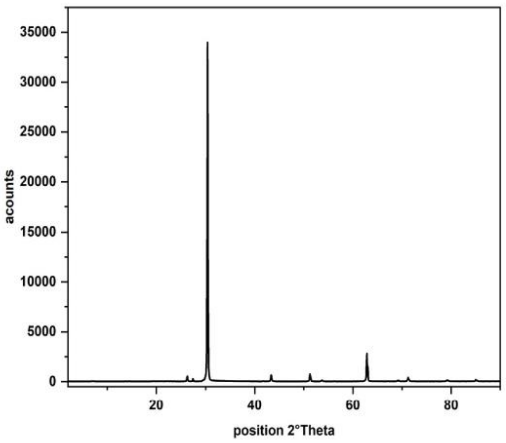


Fig. 1. X-ray diffraction pattern of galena.

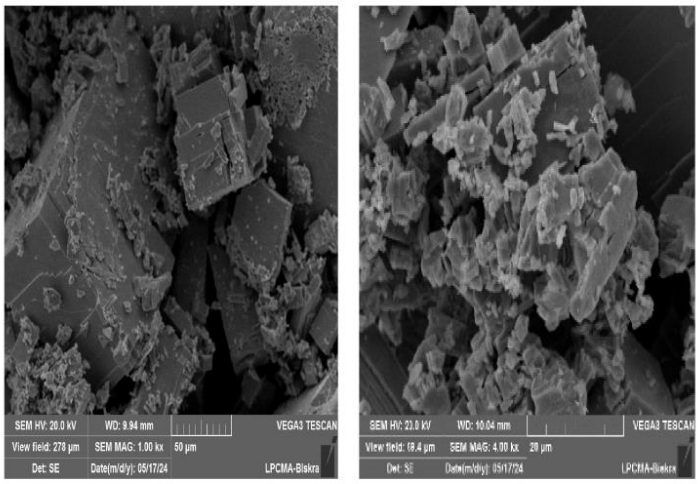


Fig. 2. SEM images of galena showing magnification of 1000 × (a), and 4000 × (b).

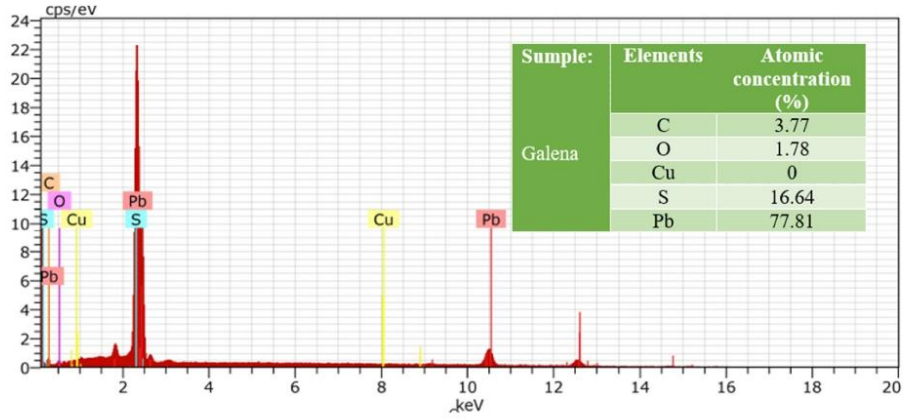


Fig. 3. EDS spectrogram of galena.

sample, with lead (Pb) and sulfur (S) being the predominant elements, accounting for 77.81 % and 16.64 % by weight, respectively. Trace amounts of oxygen (O) and carbon (C) were also detected, likely due to surface oxidation or contamination during sample preparation. The absence of copper (Cu) in the EDS analysis suggests that the galena sample is relatively pure, with no significant copper-bearing phases. This is consistent with the findings of Basilios et al. [22] and Özün et al. [24], who also reported the absence of copper in their galena samples. The presence of trace amounts of oxygen and carbon in our EDS analysis is likely due to surface oxidation, which is a common phenomenon in galena samples exposed to air [25], [26].

The Fourier Transform Infrared Spectroscopy (FTIR) spectrum of galena, Fig. 4, exhibits a characteristic absorption band at approximately 1415 cm^{-1}, which is attributed to the stretching vibrations of Pb–S bonds. This confirms the presence of lead sulfide in the sample. Minor peaks at higher wavenumbers (e.g., around 1385 cm^{-1} and 1622 cm^{-1}) may be associated with surface hydroxyl groups or adsorbed water molecules, suggesting a relatively clean galena surface with minimal organic or inorganic contamination. These findings are in line with the FTIR spectra reported by Xie et al. [27] and Vucinic et al. [28], where similar absorption bands were observed and attributed to Pb–S vibrations and surface species. The presence of minor peaks related to surface species in our FTIR spectrum is a common observation in mineral analysis and is consistent with similar findings in the literature, where such peaks are often attributed to surface oxidation or adsorbed water [28,29]. While some studies like Leppinen et al. [1] do not focus on the FTIR analysis of pure galena, they present FTIR spectra of galena after interaction with other reagents and also detect peaks corresponding to Pb–S vibrations.

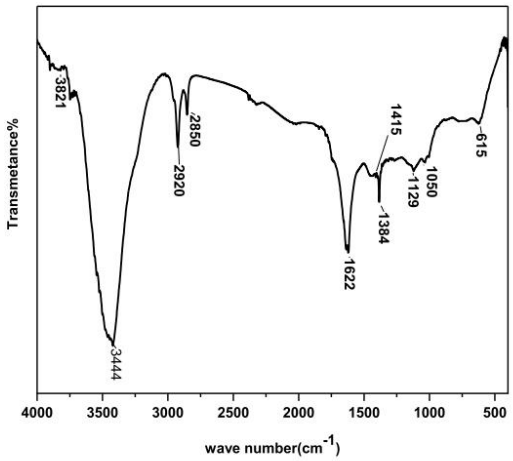


Fig. 4. Ftir spectrum of galena.

3.2. Potassium ethyl xanthate (KEX) characterization

The XRD analysis of potassium ethyl xanthate (KEX), Fig. 5, revealed several diffraction peaks at 2θ angles of 7.90°, 8.25°, 24.44°, 26.28°, 29.19°, and 33.13°, corresponding to d-values of 11.17 Å, 10.70 Å, 3.637 Å, 3.38 Å, 3.065 Å, and 2.70 Å, respectively. These peaks are consistent with the reference JCPDS file No. 00-009-0700 for KEX, confirming the identity of the compound.

The most intense peak at 2θ = 7.908° (d = 11.17 Å) indicates a highly ordered crystalline structure, which is typical for KEX. The relative intensities of the peaks suggest a well-defined crystalline phase, with the peak at 26.28° (d = 3.38 Å) also showing significant intensity (78 %).

The observed diffraction patterns align with the expected crystalline nature of xanthates used in flotation processes, as discussed in multiple studies. Although none of the reviewed studies specifically address the XRD analysis of pure KEX, the crystalline nature of xanthates is well-acknowledged [1,30]. Nedjar et al. [31] note that xanthates are commonly used as thiol collectors in flotation, underscoring their well-defined structure.

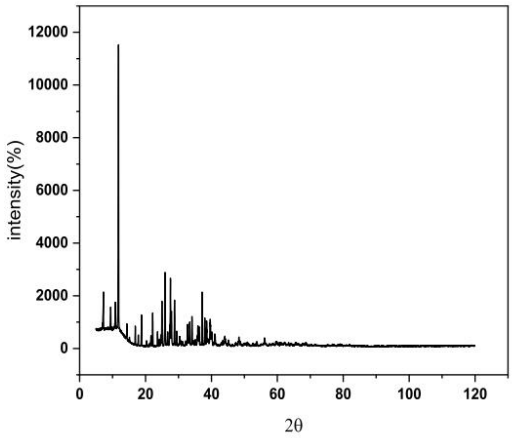


Fig. 5. X-ray diffraction pattern of KEX.

The SEM images of KEX, Fig. 6, at magnifications of 1000 × and 4000 × reveal a flaky and layered morphology, which is consistent with the crystalline nature of the compound. The images show a relatively uniform particle size distribution, with some agglomeration observed at higher magnifications. This morphology is typical for KEX, which is known to form layered structures due to its molecular arrangement. Similar morphological features have been described for xanthates in other studies. For instance Refs. [30,32], mention the layered structures of xanthates in their studies. The observed morphology aligns with the descriptions of KEX's physical appearance in the literature. Prestidge et al. [33] describe the purification and characterization of KEX, providing a basis for understanding the physical properties of the compound. Furthermore, the flaky and layered morphology observed in our study is consistent with the general behavior of xanthates, as described by Nedjar et al. [31], who noted that the morphology of the products is influenced by the structure of the xanthate molecules.

The FTIR spectrum of KEX, Fig. 7, exhibits characteristic absorption bands associated with the functional groups of the compound. The strong absorption band at approximately 1050 cm^{-1} corresponds to the C–O stretching vibrations of the xanthate group. Additionally, the spectrum shows absorption bands at 2850 cm^{-1} and 2920 cm^{-1}, which are attributed to the C–H stretching vibrations of the ethyl group. These findings confirm the molecular structure of KEX and its suitability for use in the adsorption experiments. The presence of the ethyl group vibrations is consistent with the known structure of potassium ethyl xanthate. The FTIR results are in agreement with the findings reported in several studies, such as [30,34], who identified similar absorption bands for xanthate compounds. The identification of these characteristic bands confirms the successful synthesis of KEX and its suitability for use in the subsequent adsorption experiments. Additionally, the comprehensive review of xanthate adsorption mechanisms by Rao et al. [35] provides additional context for interpreting the FTIR spectrum of KEX, supporting the identification of the characteristic absorption bands. The FTIR spectrum of KEX is also consistent with the findings reported by Nedjar and Barkat [12], where the characteristic peaks of xanthates were identified and used to analyze their adsorption on mineral surfaces.

3.3. Adsorption and surface modifications induced by copper activation

3.3.1. XRD analysis

The XRD patterns of galena samples treated with KEX (5.10^{-2} mol/L) and activated with either $CuSO_4$ (10^{-3} mol/L) or $Cu(NO_3)_2$(10^{-3} mol/L) revealed significant differences in the extent of surface interactions and complex formations. For galena treated with KEX (5 x 10^{-2} mol/L) alone, as shown in Fig. 8, the characteristic PbS peaks (JCPDS No. 96-901-3401) dominated. Minor, low-intensity peaks at 2θ values of 27.569°, 27.304°, and 22.78°, attributed to the formation of lead-xanthate complexes, were also observed and found to be consistent with phases indexed under JCPDS file No. 96-901-1805. However, these peaks were faint (<5 % intensity), indicating a limited interaction between KEX and the galena surface in the absence of copper activation. This observation is consistent with studies where minimal xanthate adsorption was noted on galena without activation [23,34,36,37]. The limited formation of lead-xanthate complexes in the absence of copper ions can be attributed to the relatively low solubility of PbS, which restricts the availability of Pb^{2+} ions for reacting with xanthate [13]. This aligns with findings suggesting that lead xanthate formation is limited without activators [38].

In contrast, samples activated with $CuSO_4$ (Sample 2) exhibited, in addition to the main galena peaks (JCPDS No. 96-901-3401), additional peaks at 2θ values of 19.63°, 28.35°, and 18.31° (Fig. 9). These peaks correspond to copper-xanthate complexes and are consistent with phases indexed under JCPDS file No. 96-711-7190. The intensities of these copper-xanthate peaks were significantly higher than those of lead-

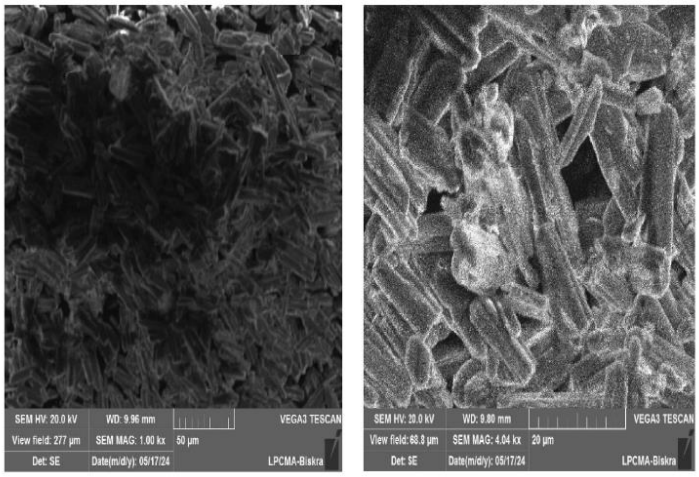


Fig. 6. SEM images of KEX showing magnification of 1000 × (a), and 4000 × (b).

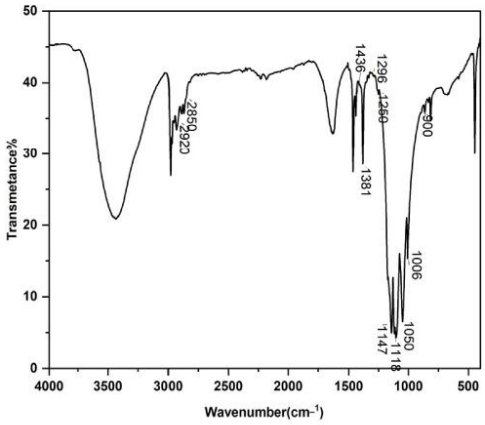


Fig. 7. Ftir spectrum of KEX

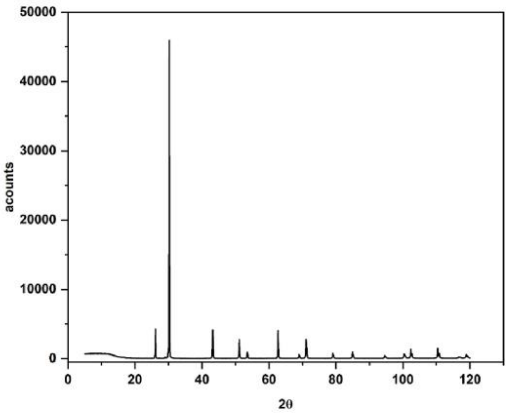


Fig. 8. X-ray diffraction pattern of galena sample treated with KEX (5.10^{-2} mol/L).

xanthate in Sample 1, suggesting that $CuSO_4$ effectively modifies the galena surface, facilitating robust copper-xanthate complex formation. This finding is well-supported by research demonstrating that copper activation enhances the formation of metal-xanthate complexes on sulfide mineral surfaces [11,24,28,39]. The presence of distinct copper-xanthate peaks in our study supports the notion that copper activation plays a crucial role in promoting xanthate adsorption [40,41]. The effectiveness of $CuSO_4$ in promoting complex formation is further supported by studies indicating that copper ions enhance xanthate adsorption on mineral surfaces [35,42].

Samples activated with $Cu(NO_3)_2$ (10^{-3} mol/L) (Sample 3) also displayed, alongside the main galena peaks (JCPDS No. 96-901-3401), peaks indicative of copper-xanthate complexes at 2θ values of 24.37°, 24.38°, and 18.40° (Fig. 10). These peaks, consistent with phases indexed under JCPDS file No. 96-711-7190, exhibited lower intensities compared to those from $CuSO_4$ activation, reflecting less extensive surface modifications.

This difference in peak intensities between the $CuSO_4$- and Cu $(NO_3)_2$-activated samples could be related to the different counterions (SO_4^{2-} vs. NO_3^-) in the activating agents, similar to observations made in studies involving different ionic species in flotation systems [25,38,40,43]. The lower intensity of copper-xanthate peaks in the case of Cu $(NO_3)_2$ activation suggests that the nitrate counterion may not promote complex formation as effectively as sulfate ions [1,44]. This observation is consistent with research indicating that different copper salts result in varying degrees of surface activation and subsequent xanthate adsorption [37,42,45].

3.3.2. FTIR analysis

Fourier Transform Infrared (FTIR) spectroscopy was utilized to

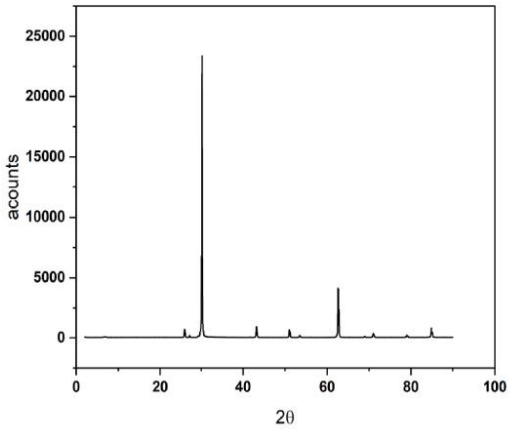


Fig. 9. X-ray diffraction pattern of galena sample activated with $CuSO_4$(10^{-3} mol/L) and treated with KEX (5.10^{-2} mol/L).

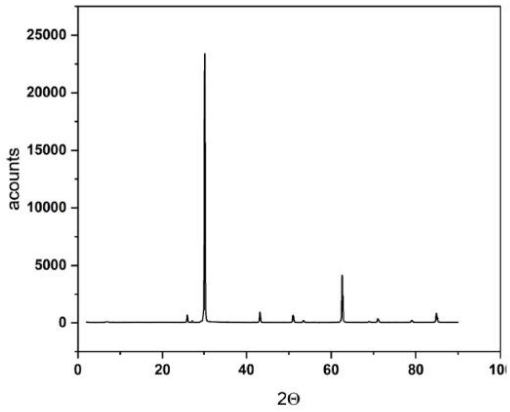


Fig. 10. X-ray diffraction pattern of galena sample activated with $Cu(NO_3)_2$ (10^{-3} mol/L) and treated with KEX (5.10^{-2} mol/L).

further investigate the adsorption mechanisms and the influence of different copper activation treatments on the galena surface. The FTIR spectra of untreated galena, KEX ($5x10^{-2}$ mol/L)-treated/unactivated galena (Sample 1), $CuSO_4$ (10^{-3} mol/L)-activated galena subsequently treated with KEX (Sample 2), and $Cu(NO_3)_2$ (10^{-3} mol/L)-activated galena subsequently treated with KEX (Sample 3) are comparatively analyzed.

The spectrum for **untreated galena** displays a characteristic broad absorption band centered around 3444 cm^{-1}. This feature is attributed to O–H stretching vibrations arising from surface hydroxyl groups or adsorbed water molecules, a common occurrence on mineral surfaces [46,47]. A distinct peak at 1622 cm^{-1} corresponds to the O–H bending vibration of adsorbed water, often associated with physisorbed water or water within the crystal lattice [19]. The band appearing at 1415 cm^{-1}, previously suggested as Pb–S stretching, is more accurately assigned to the stretching vibrations of lead carbonate (cerussite-like) species. Cerussite is a known oxidation product of galena, and its characteristic absorptions are found in the 1407-1435 cm^{-1} range [47,48]. It is important to emphasize that Pb–S stretching vibrations for galena are typically observed in the Far-IR region, below 400 cm^{-1}, due to the heavier atomic masses involved [47]. A weaker feature around 1385 cm^{-1} may also be related to carbonate species, either as a component of the broader lead carbonate absorption or from minor atmospheric CO_2 interaction [48].

For the galena sample treated with **KEX ($5x10^{-2}$ mol/L) alone (Sample 1)**, without prior copper activation, very weak new absorption features are discernible in the 1200-1220 cm^{-1} region. These bands are attributable to C–O stretching vibrations of adsorbed xanthate species [49,50]. The extremely low intensity of these signals indicates minimal interaction and adsorption of KEX onto the galena surface in the absence of an activator. This observation is consistent with findings suggesting limited xanthate adsorption on unactivated galena surfaces [48].

Upon activation with **$CuSO_4$ (10^{-3} mol/L) followed by KEX treatment (Sample 2)**, a significant transformation in the FTIR spectrum is evident. A strong and well-defined absorption band appears at approximately 1197 cm^{-1}, often accompanied by a smaller shoulder or distinct peak near 1190 cm^{-1}. These prominent peaks arise from C–O bond vibrations and are characteristic of the formation of copper-xanthate complexes on the galena surface [18,34,45]. The intensity of these bands, markedly greater than those in Sample 1, confirms a substantial increase in xanthate adsorption facilitated by copper ions. The broad O–H stretching band around 3463 cm^{-1} persists, indicating the continued presence of surface water or hydroxyl groups.

Finally, for the sample activated with $Cu(NO_3)_2$ (10^{-3} mol/L) and subsequently treated with KEX (Sample 3), peaks are again observed at approximately 1197 cm^{-1} and 1190 cm^{-1}. These positions are similar to those identified in the $CuSO_4$-activated sample, confirming the formation of copper-xanthate species. However, the intensity of these bands in the Sample 3 spectrum is notably less than that observed for Sample 2. This suggests that while $Cu(NO_3)_2$ also facilitates xanthate adsorption, the extent of copper-xanthate formation or the stability/orientation of the surface complex may be less pronounced compared to activation with $CuSO_4$ under these experimental conditions. The O–H stretching vibration is observed around 3469 cm^{-1}.

In summary, the FTIR spectra provide direct spectroscopic evidence for the enhancing effect of copper activation on xanthate adsorption onto galena. While untreated galena shows negligible evidence of xanthate adsorption, and KEX treatment alone results in minimal interaction, both $CuSO_4$ and $Cu(NO_3)_2$ activation clearly promote the formation of surface copper-xanthate complexes. The data suggest that $CuSO_4$ activation leads to a more substantial presence of these copper-xanthate species compared to $Cu(NO_3)_2$ activation under the investigated conditions. This spectroscopic evidence directly supports and complements conclusions drawn from XRD, SEM, and EDS analyses regarding the surface chemistry transformations during these flotation-related processes.

3.3.3. SEM and EDS analysis

SEM images of galena treated solely with KEX (5.10^{-2} mol/L) at pH 9–10, Fig. 12, revealed minimal alterations to the surface morphology. At 1000 × magnification, Fig. 12a, the surface appeared relatively smooth with only a few scattered particles. While slight roughness was observed at higher magnifications (4000 ×) in Fig. 12b, the overall surface remained largely intact. These observations suggest a limited interaction between KEX and the galena surface under these conditions, which is consistent with the findings of Arnaud et al. [51], who reported a relatively unaltered surface morphology for galena treated with ethyl xanthate in the absence of an activator. They attributed this to the weak interaction between xanthate and the galena surface in alkaline conditions.

EDS analysis of the KEX-treated galena (Fig. 13) confirmed the presence of carbon and oxygen, consistent with xanthate adsorption and minor surface species, alongside lead and sulfur from the native galena composition. This finding aligns with the work of Basilio et al. [22], who

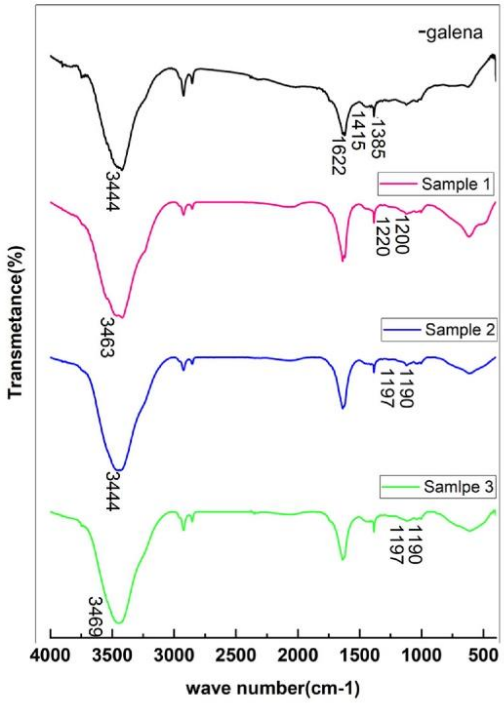


Fig. 11. FTIR spectra of galena's surfaces before and after reagents treatment. *Note: Samlpe 1:galena treated by KEX* (5.10^{-2} mol/L)*; sample 2 galena activated by* $CuSO_4(10^{-3}$ *mol/l) and treated with KEX* (5.10^{-2} mol/L)*;sample 3 galena activated by* $Cu(NO_3)_2(10^{-3}$ *mol/L) and treated by KEX* (5.10^{-2} mol/L).

observed negligible xanthate adsorption on sphalerite in the absence of copper ions. The limited interaction between KEX and galena at pH 9–10 without an activator can be attributed to insufficient adsorption of the collector, emphasizing the necessity of heavy metal ions for effective xanthate adsorption on sulfide minerals.

In stark contrast to the unactivated samples, SEM images of galena activated with $CuSO_4(10^{-3}$ mol/L), Fig. 14, revealed significant surface modifications. The activated surfaces exhibited pronounced roughness and dense particle aggregation, indicative of strong surface interactions and robust copper-xanthate complex formation. These morphological changes align with previous studies that have linked increased surface roughness and particle aggregation to enhanced reagent adsorption [11,23,24,28,39].

EDS analysis of these samples confirmed a higher copper atomic concentration (0.39 %) and an increase in sulfur content, Fig. 15, further supporting the formation of sulfur-rich (50.70 %), copper-xanthate complexes [1,37,42,52].

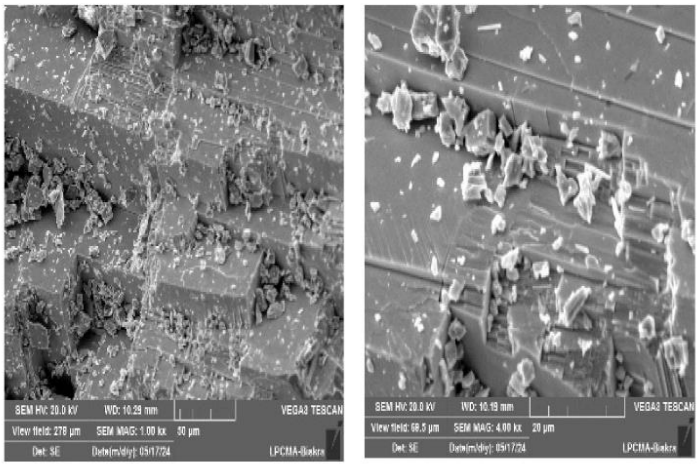
Galena samples activated with $Cu(NO_3)_2(10^{-3}$ mol/L) showed moderate surface roughness and less particle aggregation in SEM images compared to $CuSO_4$ activated samples, Fig. 16.

EDS analysis revealed a lower copper atomic concentration (0.11 %) on the $Cu(NO_3)_2(10^{-3}$ mol/L)activated samples, Fig. 17, indicating less effective activation.

These findings are consistent with previous research demonstrating that different activators can have varying degrees of effectiveness in modifying mineral surfaces [33,34,38,43,53,54]. The reduced effectiveness of $Cu(NO_3)_2$ might be attributed to the different chemical behavior of the nitrate counterion compared to sulfate, potentially leading to less extensive surface modifications [41,42].

3.3.4. *Proposed adsorption mechanism*

Based on the comprehensive surface characterization results obtained from XRD, FTIR, SEM, and EDS analyses, a proposed mechanism for the adsorption of potassium ethyl xanthate (KEX) onto the galena (PbS) surface in the presence of copper activators is illustrated schematically in Fig. 18. This process, supported by established literature on copper activation of galena [16,18], can be described in two primary stages.



(a) (b)

Fig. 12. SEM images of galena surfaces after KEX(5.10^{-2} mol/L) treatment showing magnification of 1000 × (a), and 4000 × (b).

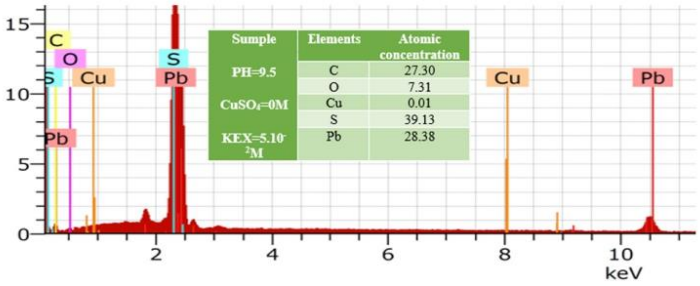


Fig. 13. EDS spectrogram of the Galena surface after KEX (5.10^{-2} mol/l) treatment.

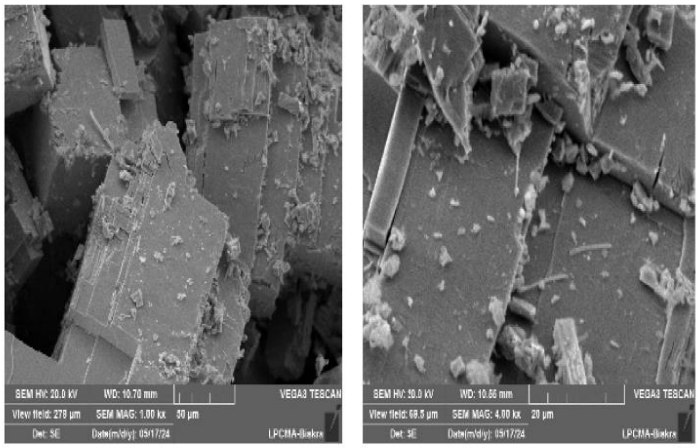


Fig. 14. SEM images of galena activated by $CuSO_4$ (10^{-3} mol/L) surface after KEX (5.10^{-2} mol/L) treatment showing magnification of 1000 × (a), and 4000 × (b).

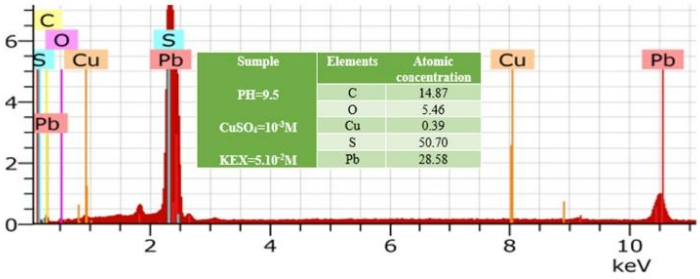


Fig. 15. EDS spectrogram of galena activated by $CuSO_4$ (10^{-3} mol/L) surface after KEX (5.10^{-2} mol/L) treatment.

A. Copper Activation of the Galena Surface

Initially, the galena surface is predominantly composed of lead (Pb^{2+}) and sulfide (S^{2-}) sites (Fig. 18A, left). Upon introduction of copper ions (Cu^{2+}) into the solution (e.g., from the dissolution of $CuSO_4$ or $Cu(NO_3)_2$), these Cu^{2+} ions interact with the galena surface. A key activation mechanism involves an ion-exchange process where Cu^{2+} ions replace Pb^{2+} ions at the mineral surface, or through the formation of copper sulfide (CuS-like) species [16,18]. This results in the formation of a copper-rich layer, effectively creating copper sulfide-like sites (e.g., CuS or Cu_2S) on the galena, as depicted in Fig. 18A (right). This "copper-activated galena" surface is more amenable to subsequent collector adsorption compared to the original PbS surface [16]. Its formation is confirmed by the presence of copper in EDS analysis (Figs. 15 and 17)

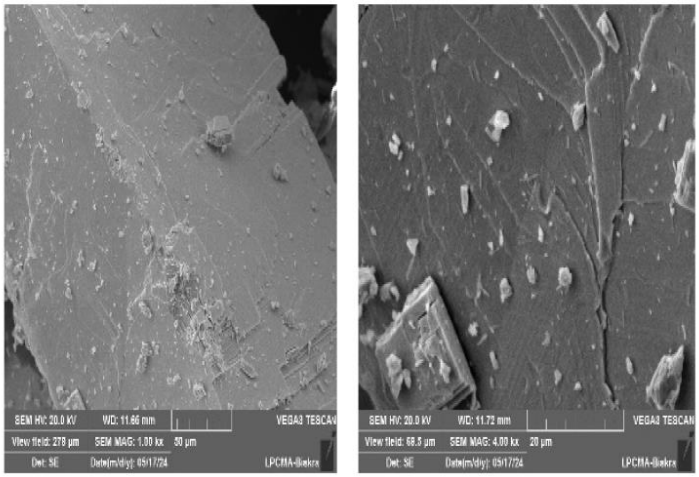


Fig. 16. SEM images of galena activated by $Cu(NO_3)_2$ (10^{-3} mol/L) surface after KEX(5.10^{-2} mol/L) treatment showing magnification of 1000 × (a), and 4000 × (b).

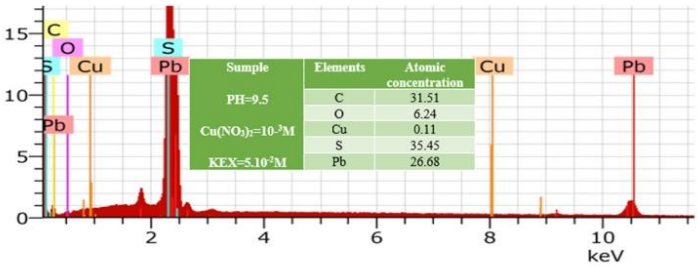


Fig. 17. EDS spectrogram of galena activated by $Cu(NO_3)_2$ (10^{-3} mol/L)surface after KEX (5.10^{-2} mol/L)treatment.

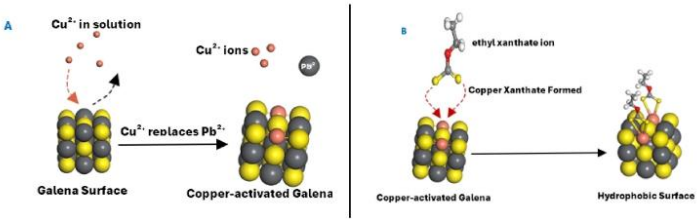


Fig. 18. Schematic illustration of the proposed adsorption mechanism of KEX on copper-activated galena.

and by the identification of copper-xanthate species via XRD (Figs. 9 and 10) and FTIR (Fig. 11, Samples 2 and 3). Displaced Pb^{2+} ions are released into the aqueous phase.

B Adsorption of Ethyl Xanthate onto the Activated Surface

Following copper activation, the ethyl xanthate ions (EX^-, $CH_3CH_2OCS_2^-$, from KEX dissociation) present in the solution interact with the newly formed copper sites on the galena surface (Fig. 18A, right, and 18B, left). The polar head group of the xanthate ion (specifically the sulfur atoms in the $-OCS_2^-$ group) chemisorbs onto these copper sites, leading to the formation of copper ethyl xanthate complexes (e.g., Cu(EX) or $Cu(EX)_2$) [16,18]. This adsorption is strongly supported by the XRD peaks corresponding to copper-xanthate phases (Figs. 9 and 10) and the characteristic C–O stretching vibrations of adsorbed xanthate observed in the FTIR spectra of activated samples (Fig. 11, Samples 2 and 3). As shown in Fig. 18B (right), the adsorption of multiple xanthate molecules, with their non-polar ethyl groups (CH_3CH_2-) oriented

outwards from the mineral surface, imparts hydrophobicity to the galena particles. The morphological changes observed by SEM, such as increased surface roughness and particle aggregation on activated surfaces (Figs. 14 and 16), are consistent with extensive collector adsorption and surface species formation. This increased hydrophobicity is essential for the attachment of the mineral particles to air bubbles during the froth flotation process, facilitating their recovery.

4. Conclusion

This study addressed a critical gap in galena flotation by systematically evaluating copper nitrate ($Cu(NO_3)_2$) as a novel activator, benchmarked against the conventional copper sulfate ($CuSO_4$). The investigation focused on the comparative effects of these activators on the surface chemistry of galena and their efficacy in enhancing potassium ethyl xanthate (KEX) adsorption, aiming to determine if $Cu(NO_3)_2$ offers a viable alternative. Through comprehensive analysis using X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and Energy-Dispersive X-ray Spectroscopy (EDS), distinct differences in their activation mechanisms and outcomes were elucidated.

The findings clearly establish that while both activators promote KEX adsorption, $CuSO_4$ activation leads to a more substantial enhancement of xanthate interaction with the galena surface. This is evidenced by the more extensive formation of copper-xanthate complexes observed through stronger XRD and FTIR signals, more pronounced surface roughening and particle aggregation seen in SEM images, and a significantly higher deposition of copper (0.39 %) as determined by EDS. In contrast, $Cu(NO_3)_2$ also facilitated KEX adsorption, but its impact on surface modification and copper-xanthate formation was consistently less pronounced (0.11 % Cu via EDS) under the investigated conditions. These differences are likely attributable to the distinct roles of the sulfate versus nitrate counterions in the activation mechanism and subsequent complex formation.

The insights gained from this research have significant application prospects. Firstly, they provide practical guidance for mineral processing operations: while $Cu(NO_3)_2$ is confirmed as a viable activator, $CuSO_4$ remains more effective under conditions similar to those tested, potentially leading to improved lead recovery and optimized reagent usage. This systematic evaluation helps in informed decision-making. Secondly, this work contributes to a deeper fundamental understanding of counterion effects in mineral activation, which is crucial for predicting the behavior of various activators and can inform the rational design of more selective or environmentally benign reagent schemes. A detailed comparison with prior studies, presented in Table 1, further highlights the specific advancements and novelty contributed by this investigation. Thirdly, the detailed surface characterization provides a valuable benchmark for future research, which could explore the optimization of $Cu(NO_3)_2$ (e.g., concentration, pH, synergistic effects) or investigate a broader range of alternative activators and counterions, aiming to enhance both efficiency and sustainability in sulfide mineral flotation.

Ultimately, by providing a detailed, evidence-based assessment of the activation potential of $Cu(NO_3)_2$ relative to $CuSO_4$, this study underscores the critical role of activator selection in galena flotation and contributes to the ongoing efforts to improve the efficiency and sustainability of lead ore processing.

CRediT authorship contribution statement

Koriche Ibtissem: Writing – review & editing, Writing – original draft, Visualization, Validation, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Nedjar Zohir:** Writing – review & editing, Supervision, Conceptualization.

Table 1
Contextual comparison of the current investigation with previous studies on copper activation of galena and xanthate adsorption.

Authors, [ref]	Activator Used	Target Mineral (s)	Effectiveness/Key Surface Species Formed (with Xanthate)	Experimental Methods (brief)	Key Findings Relevant to Activated Galena-Xanthate System	Notes/Remarks
Koriche, I. & Nedjar, Z. (2025). (Current Study)	$Cu(NO_3)_2$ (primary); $CuSO_4$ (benchmark)	Galena (PbS)	$Cu(NO_3)_2$: Copper-xanthate complexes (less intense than $CuSO_4$). $CuSO_4$: More extensive copper-xanthate complex formation.	XRD, FTIR, SEM-EDS	$Cu(NO_3)_2$ activates galena for KEX adsorption via a similar mechanism to $CuSO_4$, but is less effective. Both lead to copper-xanthate surface species. Counter-ion (NO_3^- vs. SO_4^{2-}) influences activation extent.	First systematic study directly comparing $Cu(NO_3)_2$ and $CuSO_4$ as activators for KEX adsorption on galena.
Popov & Vučinić [16],	$CuSO_4$	Galena (PbS)	$Pb(EX)_2$ and Cu(I)EX identified. $CuSO_4$ enhances KEX flotation.	Flotation, Zeta-potential, ATR-IR.	$CuSO_4$ activates galena for KEX flotation. Co-existence of Pb and Cu xanthate species on the surface. Adsorption mechanism is pH-dependent.	Excellent benchmark for $CuSO_4$ activation mechanism and resulting surface species on galena with ethyl xanthate.
Nedjar & Barkat [12],	$CuSO_4$	Galena (PbS)	Colloidal Pb-IAX, dixanthogen, Cu(I) isoamyl xanthate.	Electrochemical potential, FTIR, SEM.	$CuSO_4$ activates galena for KIAX adsorption. Detection of Cu(I) isoamyl xanthate and dixanthogen on the surface, alongside Pb-IAX, depending on Cu addition levels.	Focuses on isoamyl xanthate (KIAX). Provides SEM evidence and confirms formation of various xanthate-derived species after copper activation.
Nedjar & Barkat [18],	$CuSO_4$	Galena (PbS)	$Pb(IPX)_2$, $(IPX)_2$, and Cu-IPX identified. CuS formation on the surface.	Rest potential, FTIR, SEM.	$CuSO_4$ activates galena for potassium isopropyl xanthate (PIPX) adsorption. CuS formation is implicated. Surface species include lead, copper xanthates, and dixanthogen.	Uses isopropyl xanthate (PIPX). Reinforces the general mechanism of copper activation leading to mixed metal-xanthate and dixanthogen species.
Grano et al., [46]	$CuSO_4$ (in context of MTC formation from oxidized galena)	Galena (PbS)	MTC, lead xanthate, copper xanthate. Sulphite interferes with these processes.	UV spectroscopy, XPS, Flotation, Dissolution studies.	Copper ions (implicitly including activators like $CuSO_4$) react with xanthate on oxidized galena to form MTC, alongside metal xanthates. Highlights the role of surface oxidation and pre-existing Cu^{2+}.	Main focus is sulphite effects, but discusses Cu^{2+} interaction with xanthate on oxidized galena. Relevant for understanding complex surface chemistry when activators are present or Cu^{2+} is released from the mineral.

Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this work the author(s) used AI Google Studio in order to improve readability and language. After using this tool/service, the author(s) reviewed and edited the content as needed and take full responsibility for the content of the publication.

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Declarations of competing interest

None.

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