



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 ($\text{Cu}(\text{NO}_3)_2$), remain largely unexplored for galena activation. This study, for the first time, systematically investigates copper nitrate ($\text{Cu}(\text{NO}_3)_2$) 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 $\text{Cu}(\text{NO}_3)_2$. 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 $\text{Cu}(\text{NO}_3)_2$ facilitates KEX adsorption, leading to the formation of copper-xanthate complexes. This was supported by characteristic XRD peaks (e.g., at $2\theta = 24.37^\circ, 18.40^\circ$) 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., $2\theta = 19.63^\circ, 28.35^\circ$), more pronounced morphological changes, a higher copper deposition of 0.39 %, and a corresponding sulfur enrichment to 50.70 % S.

These findings establish $\text{Cu}(\text{NO}_3)_2$ 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 ($\text{Cu}(\text{NO}_3)_2$) as a novel activator in galena flotation. Specifically, the primary objective is to provide a systematic evaluation of the activation capabilities of $\text{Cu}(\text{NO}_3)_2$, 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 ($\text{Cu}(\text{NO}_3)_2$) has remained largely unexplored. To our knowledge, the only study that has addressed $\text{Cu}(\text{NO}_3)_2$ 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 $\text{Cu}(\text{NO}_3)_2$, 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 $\text{Cu}(\text{NO}_3)_2$ 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 $\text{Cu}(\text{NO}_3)_2$ -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 $\text{Cu}(\text{NO}_3)_2$, 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 $\text{Cu}(\text{NO}_3)_2$ offers a more effective and sustainable alternative to CuSO_4 . By providing a detailed, evidence-based assessment of the activation potential of $\text{Cu}(\text{NO}_3)_2$, 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 $-208 + 108 \mu\text{m}$ (i.e., particles passing a $208 \mu\text{m}$ sieve and retained on a $108 \mu\text{m}$ sieve) was utilized. For scanning electron microscopy (SEM) examination, a ground product sieved to $-74 + 38 \mu\text{m}$ was used. For Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Diffraction (XRD) analyses, a portion of the $-108 \mu\text{m}$ powder (i.e., particles passing a $108 \mu\text{m}$ sieve) was further ground to a particle size of approximately less than $2 \mu\text{m}$.

Potassium ethyl xanthate (KEX, purity 96 %), copper (II) sulfate

pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, purity 98.5 %), and copper (II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 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 $100 \mu\text{m}^2$. 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 $400\text{--}4000 \text{ cm}^{-1}$. For every sample, 120 scans were accumulated. Prior to analysis, approximately $100 \mu\text{g}$ of the powder sample was mixed with $23 \pm 2 \text{ mg}$ of KBr, and compressed using a cold isostatic press (CIP) at 150 MPa to form a pellet with a thickness of $200\text{--}250 \mu\text{m}$. 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 $\text{CuK}\alpha$ radiation source ($\lambda = 1.542 \text{ \AA}$). Data were collected at a scan rate of $0.03^\circ/\text{s}$ over a 2θ range of $5^\circ\text{--}90^\circ$. 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 $\text{Cu}(\text{NO}_3)_2$ 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 $5 \times 10^{-2} \text{ mol/L}$. 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 ($\text{Cu}(\text{NO}_3)_2$) 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 3×10^{-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 $\text{Cu}(\text{NO}_3)_2$ 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 5×10^{-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 5×10^{-2} mol/L, and the suspension was conditioned for an additional 10 min.

Sample 3 ($\text{Cu}(\text{NO}_3)_2$ activated + KEX): The pH of the galena suspension was adjusted to 9.0–10.0. $\text{Cu}(\text{NO}_3)_2$ 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 5×10^{-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 (CuSO_4) and copper nitrate ($\text{Cu}(\text{NO}_3)_2$) 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 $\text{Cu}(\text{NO}_3)_2$ 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.

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 $2\theta = 30.2^\circ$ ($d = 2.95$ 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 $2\theta = 26.07^\circ$ ($d = 3.41$ 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 $2\theta = 30.2^\circ$ 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 $1000\times$ (a), and $4000\times$ (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

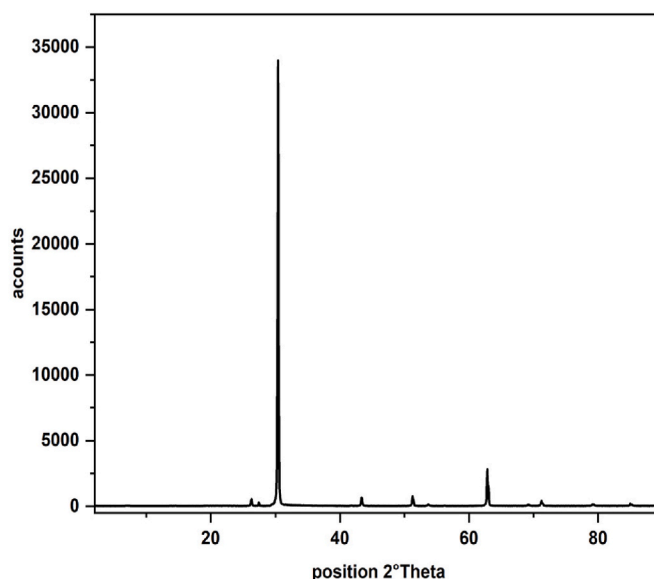


Fig. 1. X-ray diffraction pattern of galena.

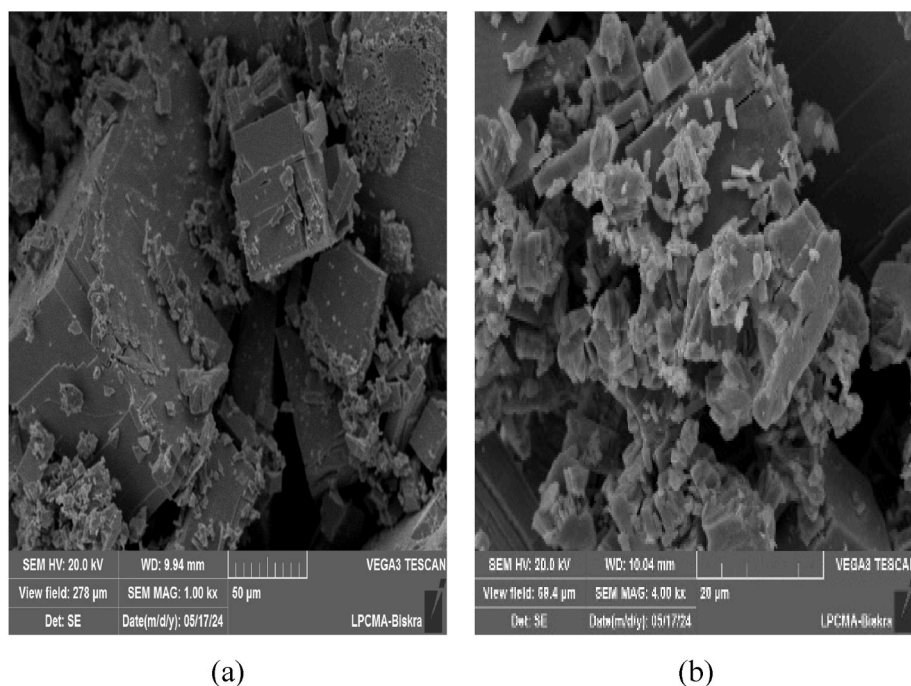


Fig. 2. SEM images of galena showing magnification of 1000 × (a), and 4000 × (b).

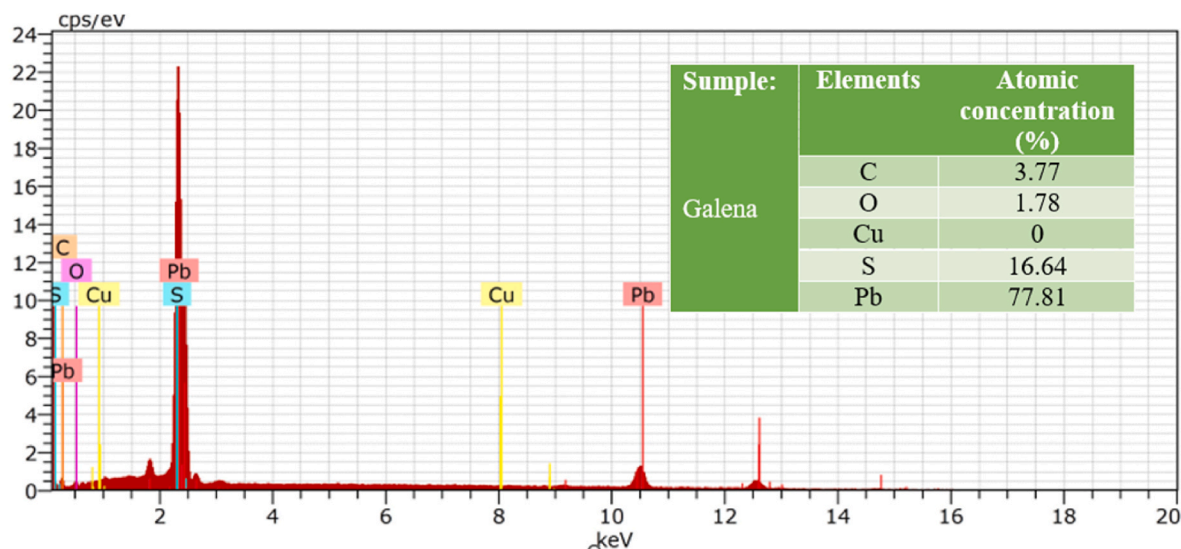


Fig. 3. EDS spectrogram of galena.

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.

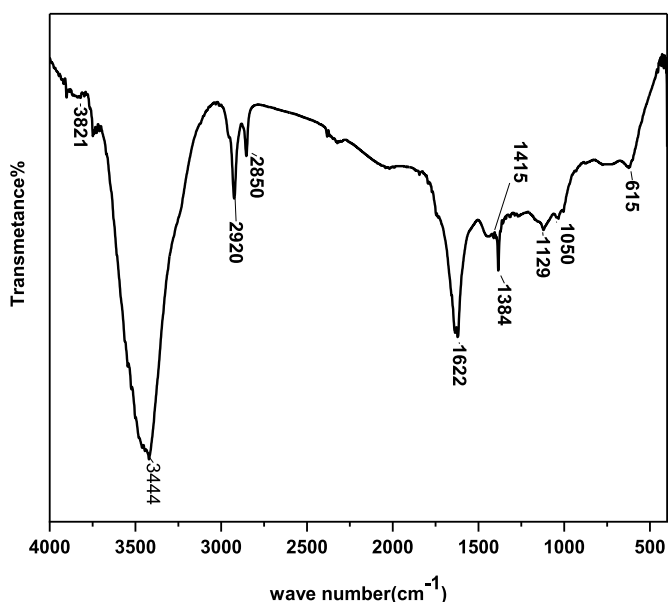


Fig. 4. Ftir spectrum of galena.

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 $11.17 \text{ \AA}$, $10.70 \text{ \AA}$, $3.637 \text{ \AA}$, $3.38 \text{ \AA}$, $3.065 \text{ \AA}$, and $2.70 \text{ \AA}$, 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 $2\theta = 7.908^\circ$ ($d = 11.17 \text{ \AA}$) 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° ($d = 3.38 \text{ \AA}$) 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

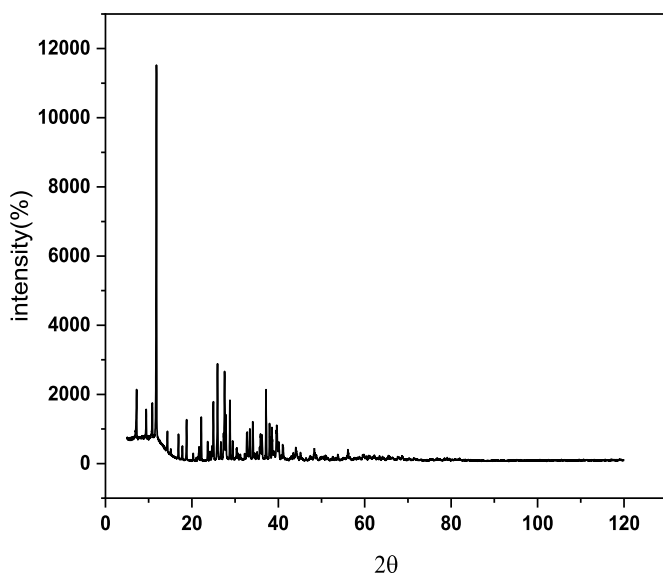


Fig. 5. X-ray diffraction pattern of KEX.

commonly used as thiol collectors in flotation, underscoring their well-defined structure.

The SEM images of KEX, Fig. 6, at magnifications of $1000\times$ and $4000\times$ 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 $\text{Cu}(\text{NO}_3)_2$ (10^{-3} mol/L) revealed significant differences in the extent of surface interactions and complex formations. For galena treated with KEX ($5 \times 10^{-2} \text{ mol/L}$) 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-

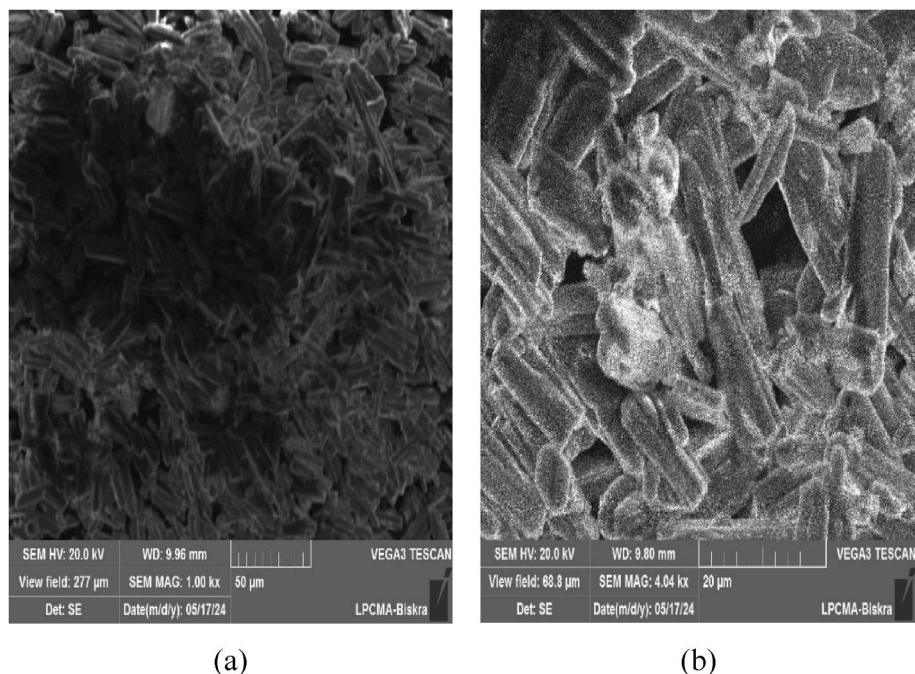


Fig. 6. SEM images of KEX showing magnification of 1000 × (a), and 4000 × (b).

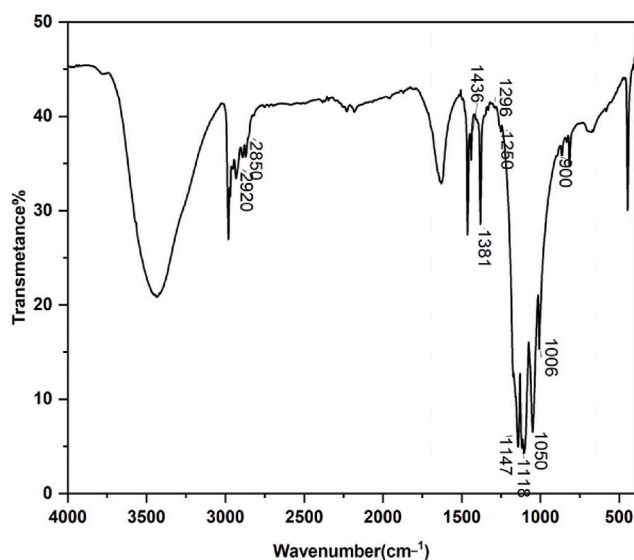


Fig. 7. Ftir spectrum of KEX

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 $\text{Cu}(\text{NO}_3)_2$ (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

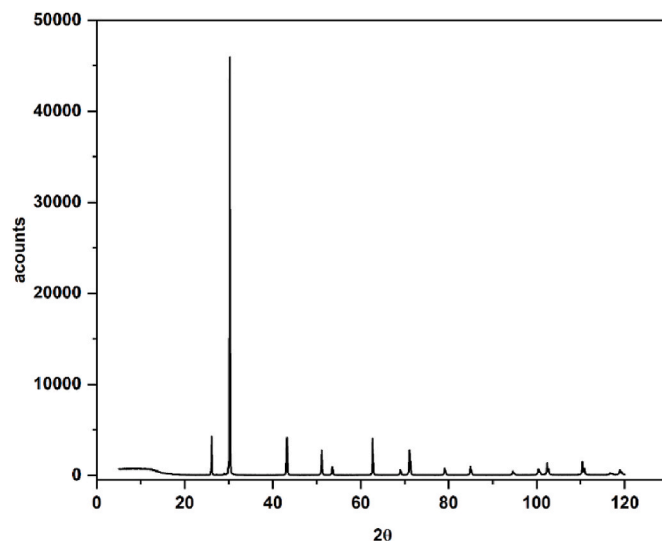


Fig. 8. X-ray diffraction pattern of galena sample treated with KEX (5.10^{-2} mol/L).

compared to those from CuSO_4 activation, reflecting less extensive surface modifications.

This difference in peak intensities between the CuSO_4 - and $\text{Cu}(\text{NO}_3)_2$ -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 $\text{Cu}(\text{NO}_3)_2$ 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

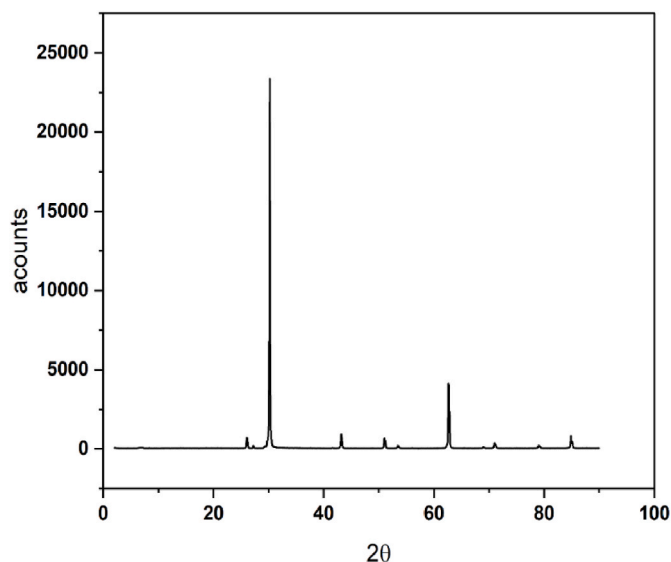


Fig. 9. X-ray diffraction pattern of galena sample activated with CuSO_4 (10^{-3} mol/L) and treated with KEX (5.10^{-2} mol/L).

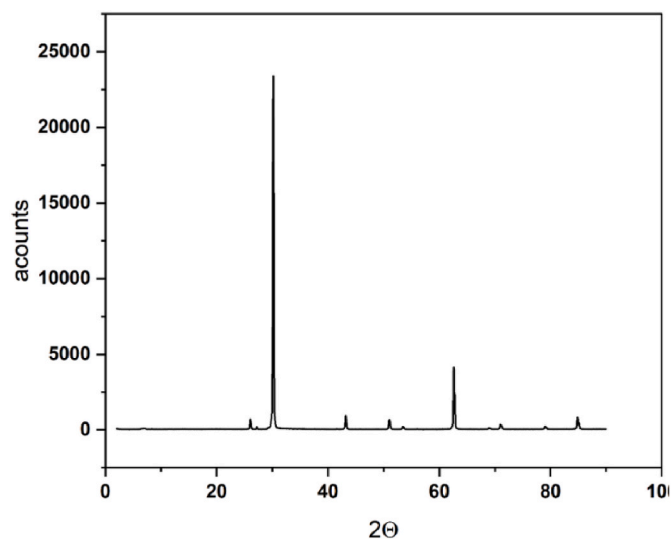


Fig. 10. X-ray diffraction pattern of galena sample activated with $\text{Cu}(\text{NO}_3)_2$ (10^{-3} mol/L) and treated with KEX (5.10^{-2} mol/L).

further investigate the adsorption mechanisms and the influence of different copper activation treatments on the galena surface. The FTIR spectra of untreated galena, KEX (5×10^{-2} mol/L)-treated/unactivated galena (Sample 1), CuSO_4 (10^{-3} mol/L)-activated galena subsequently treated with KEX (Sample 2), and $\text{Cu}(\text{NO}_3)_2$ (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 $1407\text{--}1435 \text{ cm}^{-1}$ 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 (5×10^{-2} mol/L) alone (Sample 1), without prior copper activation, very weak new absorption features are discernible in the $1200\text{--}1220 \text{ cm}^{-1}$ 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 $\text{Cu}(\text{NO}_3)_2$ (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 $\text{Cu}(\text{NO}_3)_2$ 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 $\text{Cu}(\text{NO}_3)_2$ 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 $\text{Cu}(\text{NO}_3)_2$ 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 $1000\times$ magnification, Fig. 12a, the surface appeared relatively smooth with only a few scattered particles. While slight roughness was observed at higher magnifications ($4000\times$) 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

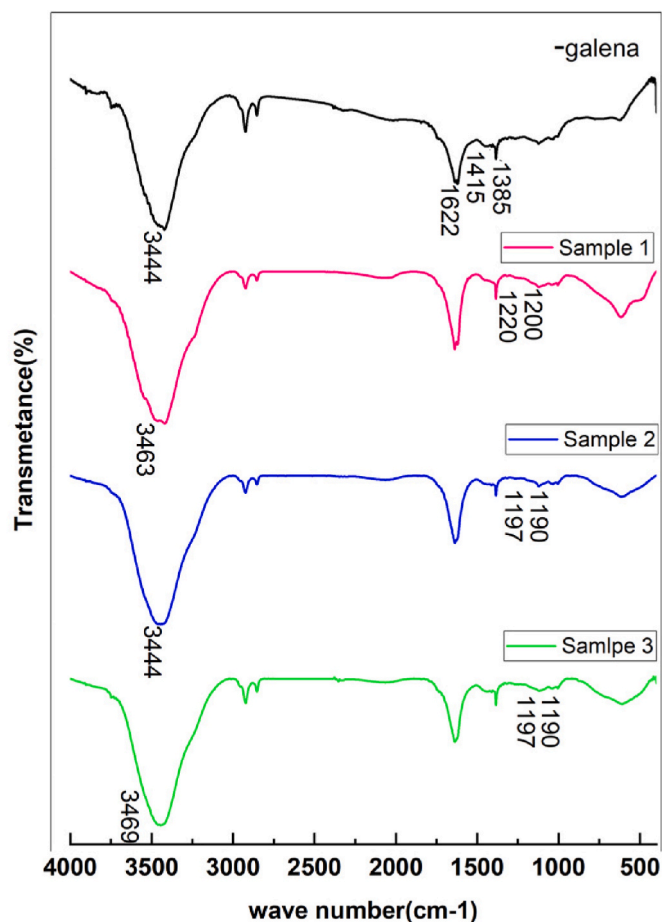


Fig. 11. FTIR spectra of galena's surfaces before and after reagents treatment. Note: Sample 1: galena treated by KEX (5.10^{-2} mol/L); sample 2 galena activated by $\text{CuSO}_4(10^{-3}$ mol/L) and treated with KEX (5.10^{-2} mol/L); sample 3 galena activated by $\text{Cu}(\text{NO}_3)_2(10^{-3}$ 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 $\text{CuSO}_4(10^{-3}$ 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 $\text{Cu}(\text{NO}_3)_2(10^{-3}$ 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 $\text{Cu}(\text{NO}_3)_2(10^{-3}$ 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 $\text{Cu}(\text{NO}_3)_2$ 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.

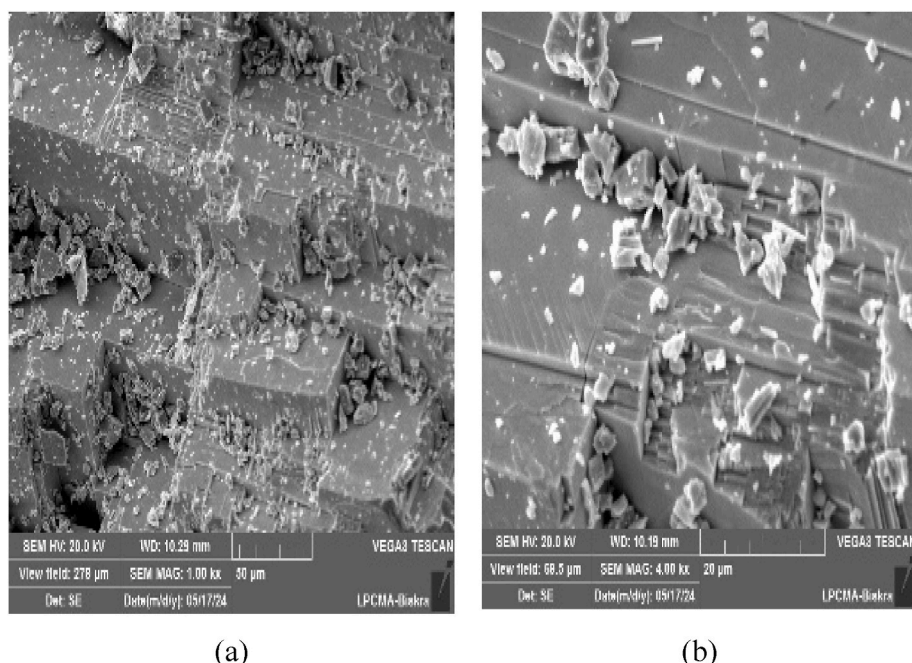


Fig. 12. SEM images of galena surfaces after KEX (5.10^{-2} mol/L) treatment showing magnification of $1000\times$ (a), and $4000\times$ (b).

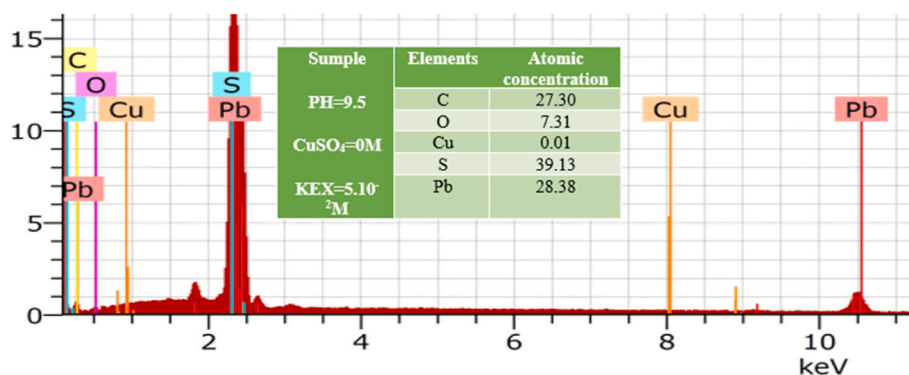
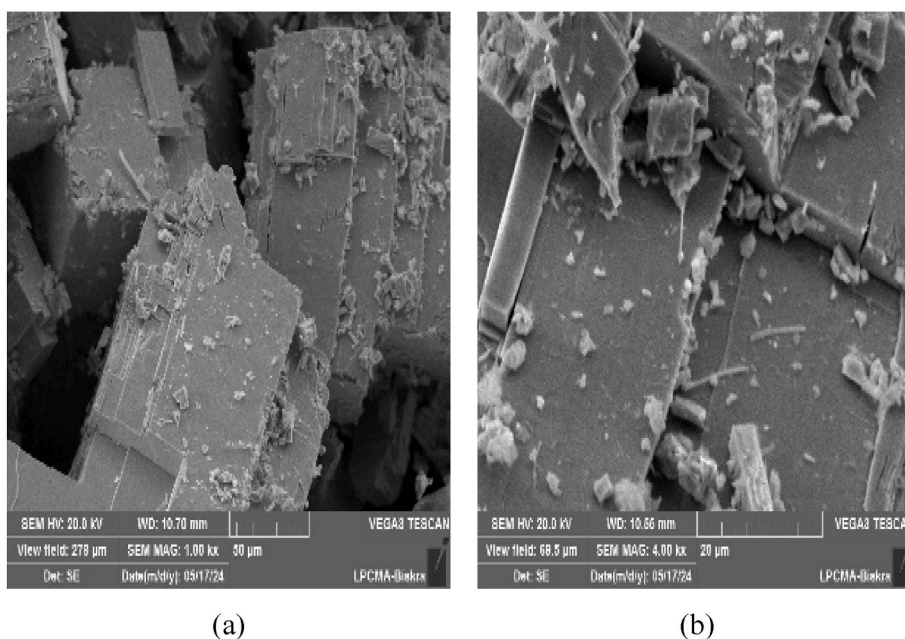


Fig. 13. EDS spectrum of the Galena surface after KEX (5.10^{-2} mol/l) treatment.



(a)

(b)

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 $1000 \times$ (a), and $4000 \times$ (b).

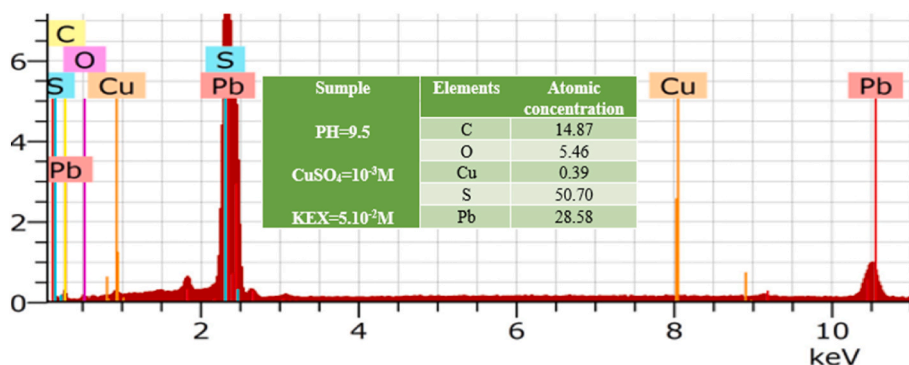


Fig. 15. EDS spectrum of galena activated by CuSO_4 (10^{-3} mol/L) surface after KEX (5.10^{-2} mol/L) treatment.

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 $\text{Cu}(\text{NO}_3)_2$), 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)

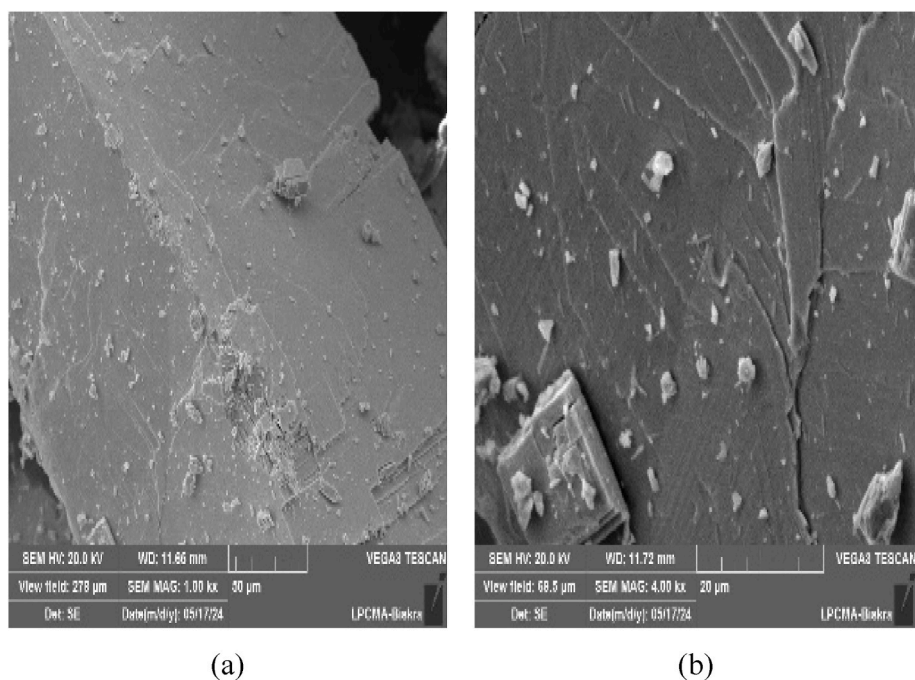


Fig. 16. SEM images of galena activated by $\text{Cu}(\text{NO}_3)_2$ (10^{-3} mol/L) surface after KEX (5.10^{-2} mol/L) treatment showing magnification of $1000 \times$ (a), and $4000 \times$ (b).

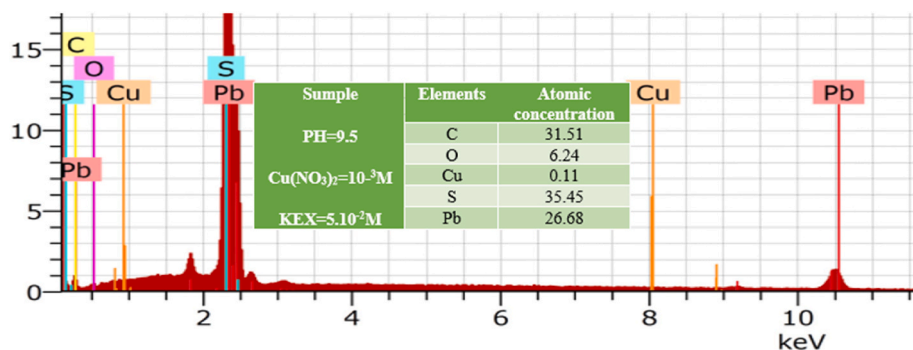


Fig. 17. EDS spectrogram of galena activated by $\text{Cu}(\text{NO}_3)_2$ (10^{-3} mol/L) surface after KEX (5.10^{-2} mol/L) treatment.

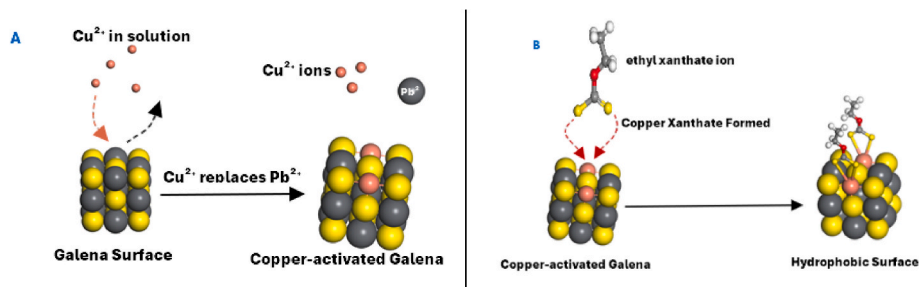


Fig. 18. Schematic illustration of the proposed adsorption mechanism of KEX on copper-activated galena.

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^- , $\text{CH}_3\text{CH}_2\text{OCS}_2^-$, 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 $-\text{OCS}_2^-$ group) chemisorbs onto these copper sites, leading to the formation of copper ethyl xanthate complexes (e. g., $\text{Cu}(\text{EX})$ or $\text{Cu}(\text{EX})_2$) [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 ($\text{Cu}(\text{NO}_3)_2$) 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 $\text{Cu}(\text{NO}_3)_2$ 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, $\text{Cu}(\text{NO}_3)_2$ 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 $\text{Cu}(\text{NO}_3)_2$ 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 $\text{Cu}(\text{NO}_3)_2$ (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 $\text{Cu}(\text{NO}_3)_2$ 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)	$\text{Cu}(\text{NO}_3)_2$ (primary); CuSO_4 (benchmark)	Galena (PbS)	$\text{Cu}(\text{NO}_3)_2$: Copper-xanthate complexes (less intense than CuSO_4). CuSO_4 : More extensive copper-xanthate complex formation.	XRD, FTIR, SEM-EDS	$\text{Cu}(\text{NO}_3)_2$ 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 $\text{Cu}(\text{NO}_3)_2$ and CuSO_4 as activators for KEX adsorption on galena.
Popov & Vučinić [16],	CuSO_4	Galena (PbS)	$\text{Pb}(\text{EX})_2$ and $\text{Cu}(\text{I})\text{EX}$ 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, $\text{Cu}(\text{I})$ isoamyl xanthate.	Electrochemical potential, FTIR, SEM.	CuSO_4 activates galena for KIAX adsorption. Detection of $\text{Cu}(\text{I})$ 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)	$\text{Pb}(\text{IPX})_2$, $(\text{IPX})_2$, 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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