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The effect of EDTA on the adsorption efficiency of xanthate KEX on pyrite

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ABSTRACT/RESUME

Abstract: *In flotation process of the mineral recovery operation, the adsorption of Xanthate (KEX)(potassium ethyl xanthate) on copper activated pyrite, is affected by oxides,and hydroxides present on the surface of mineral sulfide. In order to increase the adsorption efficiency of Xanthate (KEX) on pyrite, a complexing agent EDTA (ethylene diamine tetra acetic) was used. FTIR, SEM, X-Rays diffraction and EDAX technics were used to investigate the effect of EDTA (10^{-1} M). The experimental work was carried out in a pH value of 5.5, Xanthate (KEX) concentration of 10^{-1} M and the pyrite sample was activated with $CuSO_4$, 10^{-3} M. The tests was realized with EDTA and without EDTA, the comparison between the results indicated that EDTA helped in extracting oxides an hydroxides from the mineral surface hence improving the efficiency of adsorption.*

I. Introduction

Pyrite (iron disulfide, FeS_2) is the dominant gangue mineral in flotation separation of sulfide mineralores [1].

The interaction between xanthates and sulfide mineral surfacesis very important step in the flotation process. This interaction is very complex, because of the different reaction mechanisms and reaction products, depending on the conditions that prevails in the interaction. Many factors affects the system xanthate-sulfide such as pH, oxidation potential, and the different species of solution, in addition to the history of the mineral. The analytical methods in investigating mineral-collector systems are very developed, but many points are still not fully understood. It is generally accepted that most sulfide minerals respond strongly to xanthate in flotation [2, 3].Xanthates collectors are very selective [4] and widely used in flotation of sulfide mineral [5, 6].In the adsorption step of flotation process, xanthate interact with metal ions on mineral surfaces,to increase the hydrophobicity [7].

Finkelstein and Poling, Woods [8, 9], have studied the mechanisms of xanthate adsorption on pyrite; they foundthat dixanthogen (X_2) is the unique product of xanthates, that adsorbs on pyriteand is responsible for pyriteflotation, independent of solution and pyritesurface conditions.

It is difficult to avoid the oxidation of sulfide minerals during processing, due to exposure to oxygen in plant conditions. Every sulfide mineral is influenced at different degrees of oxidation by its chemical composition, crystal structure and most important its electrochemical reactivity [10].

The effect ofsurface oxidation on pyrite flotation is still under debate, it isreportedthat the oxidation of pyrite decreased its floatability [12], howeverXiaopengNiu et al [11], confirmed that the hydrophobicity and floatability of pyrite depends largely on the degree of surface oxidation. Some studies reported that the floatability of sulfide particles is controlled by the level of surface oxidation [13 - 15].

The exposition to air for a long period hinder xanthate adsorption on pyrite surface and reduce the hydrophobicity of pyrite, probably resulting from the formation of hydrophilic iron oxide or hydroxide on the pyrite surface[16].In the presence of a moderate concentration of EDTA, pyrite display good floatability this can be explained by the removal of the hydrophilic metal hydroxide layers by EDTA from these sulfide surfaces [17].Clarke et al [18],found some techniques in cleaning mineral surface from oxidation products, especially metal hydroxides. These techniques are chemical (dissolution by changing the pH, extraction by EDTA), or mechanical (sonification and attrition with quartz).The pH is adjustedto prevent the metal hydroxide formation rather than removing the products previously formedand to improve the mineral recovery.After their study about the oxidation of minerals in the flotationpulps.Rao and Leja[19]found that EDTA extracts metal hydroxides from mineral surfaces.

Shannon and Trahar [20] have shown the ability of ethylene diaminetetra-acetic(EDTA) tosolubilizemetal sulfide oxidation products, without solubilizing the metal sulfide. Kant et al [21].Rumball and Richmond;[22] Greet and Smart[23], confirmed that EDTAsolubilize surface oxidized products,(oxides and hydroxides), and not the metal sulfide.

In the presentwork, the effect of EDTA on the efficiency ofpotassium ethylxanthate KEX, adsorptionontothe copper-activated pyritehas beeninvestigated.The results was verified using FTIR SHIMADZU 8400S (4000-400 cm^{-1}), X-Rays diffraction (D8 BUKER) andSEM, scanning electron micrography (Scanne VEGA3).

II. Materials and methods

A.Materials

Natural sample of pyrite obtained from El ouenza mine Algeria was used in this study. It was crushed in an agatemortar and with mean size of 0,35-0,45 mm was used in the adsorption tests. The analyses of the sample was performed by using the X rays diffraction, ScanningElectron Micrography, and FTIR characterization, the results are shown in figure 1, 2, 3 and table 1.

Table 1. *Elemental composition of pyrite obtained by EDScharacterization.*

Elements	*S*	*Fe*
Wt %	*99.75*	*0.25*

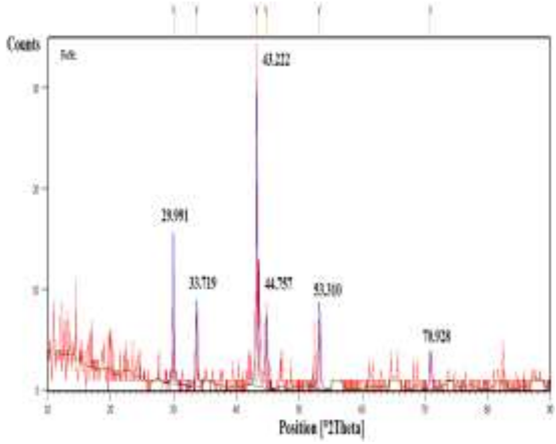

Figure 1. *X-Rays diffraction of pyrite*

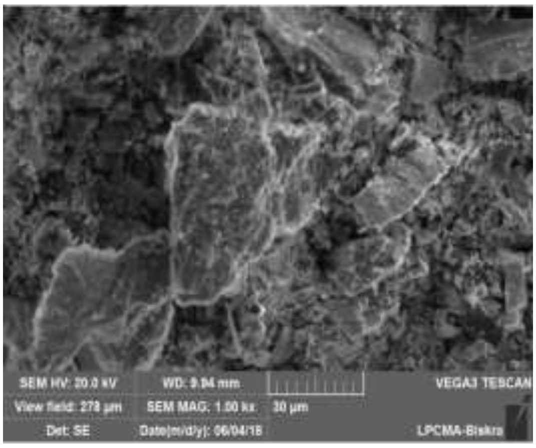

Figure 2. *Scanning Electronmicrography of pyrite surface*

The figure 3shows the FTIR spectrum of pyrite sample, it indicates an absorption band of 515-712 cm^{-1}, that corresponds to the vibration of the connection Fe with Oxygen. Another absorption band at 1431 cm^{-1} corresponds to the vibration of the connection Fe with Carbonates, other absorption band at 1213 cm^{-1} that corresponds to the vibration of the connections Fe-OH, an absorption band at 2560 cm^{-1}characterize OH of hydration water [24].

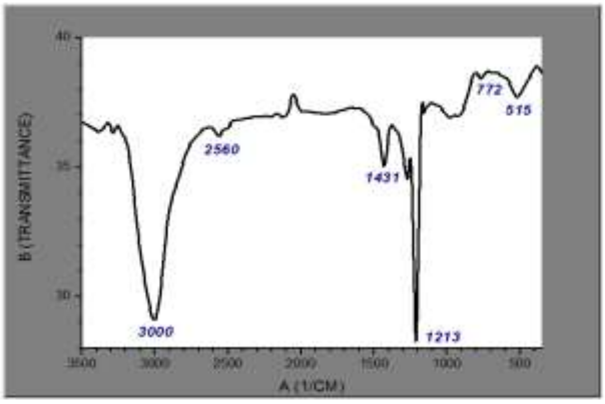

Figure 3. *Pyrite FTIR characterization*

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The potassium ethyl xanthate (KEX) is an organosulfur compound with the chemical formula $CH_3CH_2OCS_2K$. It is a pale yellow powder that is used in the mining industry for the separation of ores.
The (KEX) was firstly examined, the composition is shown in table.2, and the SEM microscopy, X-Rays diffraction and FTIR characterization are in figures 4, 5 and 6.

Table 2. *The composition of xanthate KEX obtained by EDScharacterization.*

Elements	*S*	*C*	*O*
wt %	*46.89*	*40.11*	*13.00*

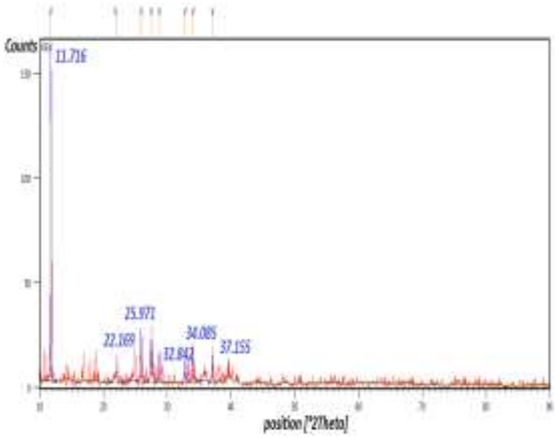


Figure 4. *X-Rays diffraction of Xanthate KEX*

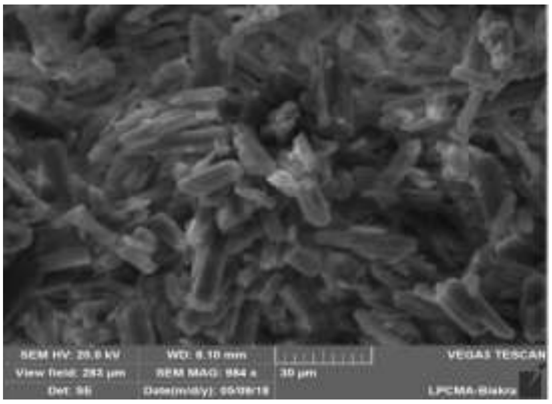


Figure 5. *Scanningelectronmicrography of Xanthate KEX*

In the Figure 4.There is an intensereflexions with 2θ = 11, 81 and 2θ= 37, 96 which corresponds to KEX[25].

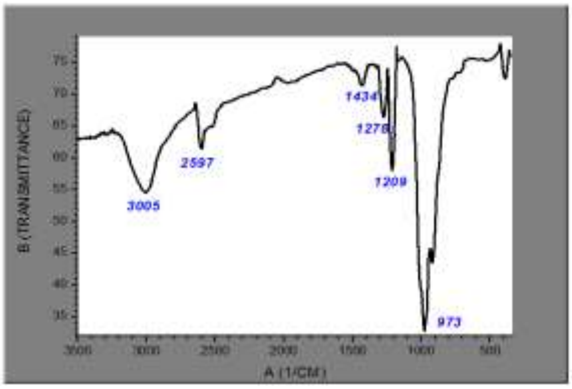


Figure 6. *FTIR characterization of Xanthate KEX*

In the infra-redspectrum (Figure6) appearsanabsorption bands to 1147.44-1120.44-1050.87-1006.66 cm^{-1} and other bands to 1438.64 -1380.78 -1295.93-1250.58 cm^{-1} allotted respectively to the vibrations of connections (C=S) and (O-CS) [26].
The Xanthate (KEX) solution was prepared by dissolving the chemical xanthate (KEX) in pure water,tow solutions was obtained 10^{-1}mol/l, the commercial Xanthate (KEX) purification was carried out by Acetone then it was crystalized. Copper sulfate ($CuSo_4$) of 10^{-3}mol/l was used to activate the mineral surface and introduce the Copper ions in pyrite to create positive charge during the conditioning time.
The EDTA solution was prepared by adding the chemical EDTA to pure water, we obtained 10^{-1}mol/l solution, the EDTA was used to eliminate hydroxides such as $Fe(OH)_2$ and $Cu(OH)_2$.

B. Methods
Mineral suspensions of 3g pyrite in 100 cm^3 of the solution were conditioned at the desired pH for 5 min after each reagent addition in the presence of various activators. One hundred cm^3 of copper sulfate (10^{-4} M) and copper nitrate (10^{-4} M) were used in potassium isobutyl xanthate (KEX 10^{-1} M).
It was conditioned in distilled water for 15 min at pH 5.5 and then electrophoretic mobility was measured.Electrochemical study was conducted using carbon matrix composite (CMC) electrode. Conditioned in copper solution at pH 7.5, pH was regulated with NaOH (10^{-1} M) and HCl (10^{-1}M).
The scanning electron micrograph (SEM) type JSM-6390 is a high-performance device with a resolution of 3.0 nm. The customized GUI interface allows the instrument to be intuitively operated, and Smile Shot™ software ensures optimum operation settings. The JSM-6390 specimen chamber can accommodate a specimen of up to 152 mm in diameter. Standard automated features include auto focus/auto stigmator, autogun (saturation, bias and alignment), and automatic contrast and brightness.

FT-IR measurements were recorded on a SHIMADZU 8400S FTIR spectrometer in the region of 400-4000 Cm^{-1} supplied with OMNIC software. The tablets were prepared by grinding 2mg of the solid sample with 50 mg of KBr. Before every analysis, the background was collected and subtracted from the spectrum of the sample. Two hundred scans at a resolution of 4 Cm^{-1}were recorded for each sample.

III. Results and discussion

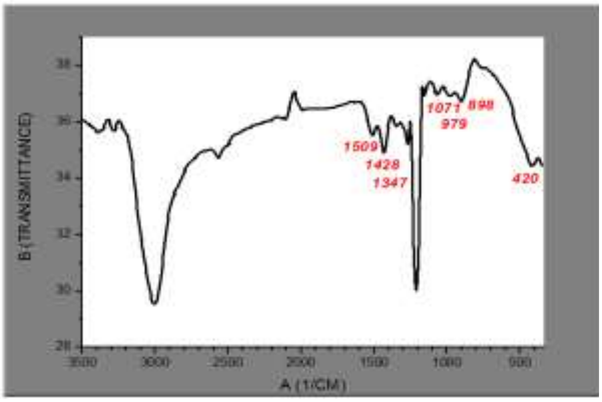
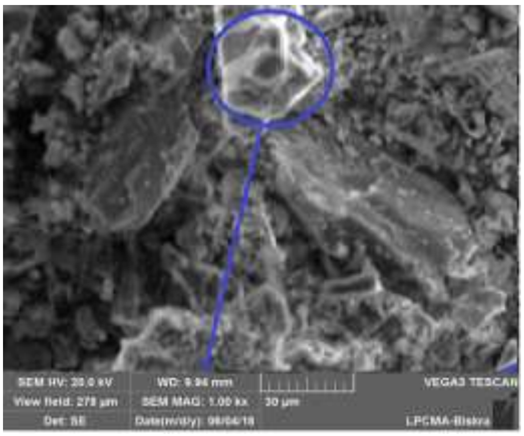


Figure 7. *FTIR spectrum of copper activated pyrite$CuSO_4$ 10^{-3}M treated with KEX 10^{-1}M pH 5.5*

The FTIR spectra of the copper activated pyrite treated with xanthate (KEX) are presented in figures. 7 and 8, the system pyrite-xanthate, reveals that dixanthogen occurs on pyrite with a large IR absorption signal at 1232 cm-' [29], it explains the adsorption of ethyl xanthate on pyrite surface.



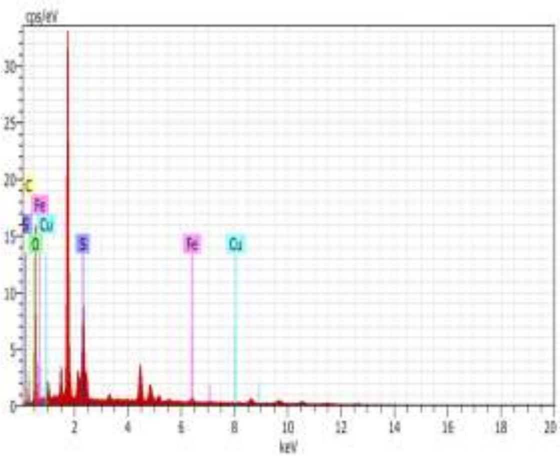


Figure 8. *SEM (X1000) and EDS of copper activated pyrite ($CuSO_4 10^{-3}$M) treated with KEX 10^{-1}M pH 5.5*

Table 3. *EDS analyses of pyrite activated with $CuSO_4$ treated with KEX 10^{-1}M*

Elements	*O*	*C*	*S*	*Fe*	*Cu*
wt%	*13.09*	*9.45*	*24.43*	*52.89*	*0.13*

The SEM pictures show white spots on pyrite that corresponds to the adsorbed xanthate (KEX) on the mineral surface.The existence of oxygen and Carbone in the chemical composition tables of the copper activated pyrite, treated with $CuSO_4$ explains the xanthate adsorption.

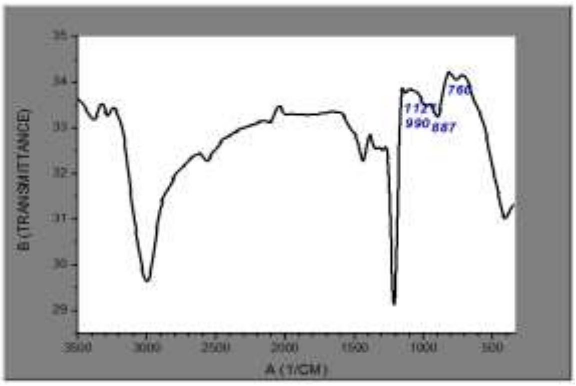


Figure 9. *FTIR spectrum of copper activated pyrite $CuSO_4$ 10^{-3} M treated with xanthate KEX 10^{-1}M in presence of EDTA 10^{-1}M and, pH 5.5*

On the infrared spectrum of copper activated pyrite treated with xanthate (KEX)(10^{-1}M) in presence of EDTA, appears an absorption band of 1230 cm^{-1} that characterizes dixanthogen [30 - 32]. This indicates the adsorption of xanthate (KEX) on pyrite surface.

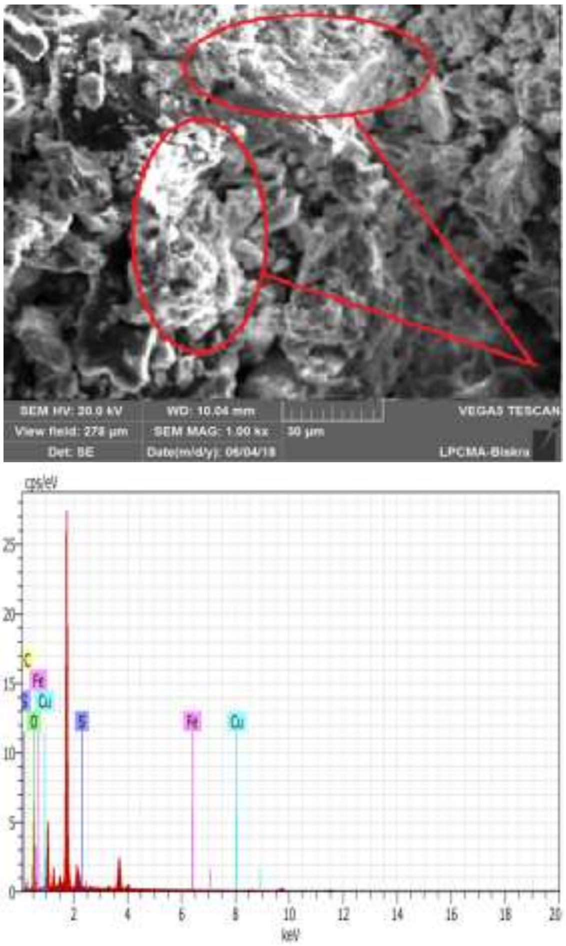


Figure 10. *SEM (X1000) and EDS of copper activated pyrite ($CuSO_4 10^{-3}$M) in presence of EDTA 10^{-1} M treated with KEX 10^{-2}M, pH 5.5*

The white spotes in SEM pictures, of copper activated pyrite treated with xanthate(KEX) in presence of EDTA,indicates the xanthate(KEX) adsorbed on the pyrite surface,

Table 4. *EDS analyses of pyrite activated with $CuSO_4$ in presence of EDTA 10^{-1} M, treated with KEX 10^{-1}M*

Elements	*Fe*	*S*	*O*	*C*	*Cu*
wt%	*54.46*	*19.58*	*18.54*	*7.22*	*0.20*

The absence of nitrogen in the elemental composition showed on thetable of EDS analyses of copper activated pyrite treated with xanthate(KEX) explains that the source of oxygen is xanthate(KEX)adsorbed on pyrite and not EDTA. We notice that the oxygen percentage is high compared to the one in the first experience,whichhas been carried out without EDTA, because the metal sulfide minerals exhibit oxide and hydroxide on their surfacesafter exposure to air or aqueoussolution [33, 34]. The addition of EDTAduring the conditioningtime helped in removing this species (oxides/hydroxides)from the mineral surface and allowed to have a good adsorption of xanthate(KEX) on the clean mineral surface.

IV.Conclusion

The effect of EDTAon the efficiency of xanthate (KEX) adsorption on copper activated pyritewas studiedwith different techniques, and the following conclusions can be draw:

The EDTA extracts the oxides and hydroxidesthat has been formed on the pyrite surface during the exposure to the oxygen of air and aqueous solution. This oxides and hydroxides forms an isolating layer between xanthate molecules and mineral surface.The use of EDTA helps in removing this species and increasing the efficiency of the xanthate (KEX) adsorption on pyrite surface thereby,the recovery of minerals is considerably increased.

Using the SEM technique action of 10^{-1}M potassium ethyl xanthate has been identified (adsorption to specific surface sites and colloidal precipitation from solution).

The FTIR spectra revealed the presence of copper on the surface of pyrite and this is confirmed the adsorption of KEX onto surface (Fe-EX, 1071 Cm-1, $(EX)_2$, 1230 Cm-1).

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