An insight into effect of surface functional groups on reactivity of Sphalerite (110) surface with Xanthate collector: a DFT study

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Abstract

The reactivity of the protonated and hydroxylated sphalerite (1 1 0) surface with xanthate was simulated using the density functional theory (DFT). The difference between the energy of the lowest unoccupied molecular orbital of the sphalerite surface and the energy of the highest occupied molecular orbital of xanthate (ΔE) was used to compare the reaction capability of xanthate with fresh and functionalized surfaces. The Mulliken atomic charge analysis was used to provide an in-depth insight into the effects of $-H^+$ and $-OH^-$ groups on the reactivity of Zn atoms at the sphalerite surface. The ΔE values for different systems showed that the protonated surfaces exposed a higher reactivity with xanthate than the fresh and hydroxylated surfaces. The results of the Mulliken atomic charge analysis demonstrated that after the formation of $-H^+$ and $-OH^-$ contained groups on the sphalerite surface, the surface atoms found a new charge due to the reduction and oxidation mechanism. In addition, the results obtained revealed that the electrophilicity of Zn atoms after the ion adsorption could be considered as a key factor in the reactivity of the sphalerite surface with xanthate. The DFT-based calculations also showed that different alkyl groups of xanthate had no significant influence on the reactivity of their head groups. The findings of this research work provided insights into the reactions of the sphalerite surface with xanthate.

Keywords: *DFT, Surface Species, Xanthate Collector, Surface Reactivity, Mineral Surface.*

1. Introduction

Surface reactivity of minerals plays a key role in the well-known processes like sorption, precipitation, ion exchange, dissolution, and flotation [1]. In flotation systems, natural or induced hydrophobicity of the mineral surfaces are used to achieve selective separation of the valuable minerals from gangues [2]. The difference between the hydrophobicity properties of minerals is helpful for an efficient separation in flotation. For instance, collectors are often added to react with a surface in order to enhance the hydrophobicity of the desired minerals. The surface reactivity of a mineral in a solution is determined by the chemical behavior of its functional groups [1, 3]. The surface ionization and complexation at mineral-aqueous solutions have been investigated for sulfide minerals [1, 3-7]. Sphalerite is the main Zn-bearing sulfide mineral, and xanthates are the most widely used collectors for the recovery of sphalerite from associated sulfide minerals using the flotation method. Due to the presence of other sulfide minerals mainly galena and pyrite in Zn ores, it is important to distinguish the reactivity of different sulfide minerals with different ions and complexes that are present in flotation pulps [8].

It has been demonstrated that in the presence of amyl-xanthate collector, maximum recovery of sphalerite flotation occurs near pH = 3.5, and its floatability is reduced in other pH values [9, 10]. Compared with the other sulfide minerals, sphalerite flotation does not respond well to xanthate. Therefore, the activation of sphalerite with different metal ions has been extensively

studied to increase the reactivity of sphalerite with xanthate [8, 11-16]. The effect of Cu^{2+} activation on the interfacial water structure at the sphalerite surface has been studied using the molecular dynamics simulation, and the results obtained clarify that the activation of sphalerite with copper ions makes the surface more hydrophobic than the fresh sphalerite surface [17].

Quantum mechanical-based computation has also been used to study the Cu^{2+} and Pb^{2+} activation, collector interaction, and electronic structure of the sphalerite mineral surface [18-23]. For instance, DFT-based simulation of diisobutyl dithiophosphinate interactions with fresh and Pb-activated sphalerite has indicated that lead-activation provides attractive sites for the collector attachment on surfaces, while un-activated sphalerite exhibits very low affinity toward the collector [24]. The results obtained from the transition state search study of the migration of Cu absorbed on the S sites of the sphalerite (110) surface have shown that the adsorbed Cu ions on the sphalerite surface can further migrate to the Zn vacancy through a transition state, and coordinate with the S atoms [25]. DFT-based simulation has also been used successfully to study the ethyl xanthate collector interaction with precipitated iron and copper hydroxides [26] and also to study the natural hydrophobicity of sulfide surfaces [27].

Although some research works, as discussed above, have been carried out on the sphalerite-xanthate interaction, the mechanism by which the surface finds the ability of interaction with xanthate has not been well-established. Therefore, it is necessary to understand the role of surface chemical groups on the reactivity of sphalerite surface with xanthate molecules, especially at the molecular level.

In this research work, we employed the density functional theory (DFT)-based calculations to investigate the effect of surface groups on the reactivity of sphalerite surface at the molecular level. The effect of –H^+ and –OH^- complexation at the mineral surface was investigated to explore the mechanisms by which the reactivity of sphalerite surface increased due to the adsorption of the pointed ions. This study provides a new insight into the surface reactivity of sphalerite surface, and explains the effect of subatomic interactions on the reactivity characterization of mineral surfaces, which can be used in similar cases.
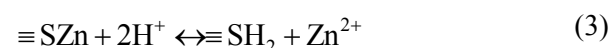
This paper is divided into three parts. At first, we examine the effect of alkyl chain on the reactivity of xanthates. After that, we present our investigations on the effect of –H^+ and –OH^- ions, as surface functional groups, on reactivity changes of the sphalerite surface. The difference between the energy of the lowest unoccupied molecular orbital (LUMO) of the surface $\left(E_{L,S}\right)$ and the energy of the highest occupied molecular orbital (HOMO) of xanthate $\left(E_{H,X}\right)$, as $\Delta E = E_{L,S} - E_{H,X}$, is used to determine the possibility of the interaction between the sphalerite surface and xanthate. The adsorption energies of xanthate on sphalerite surface are calculated to confirm the effect of different ions on xanthate adsorption on different surfaces. In the last part, we focus on the effect of adsorbed –H^+ and –OH^- ions on the charge and electrophilicity of the surface atoms. The results of the Mulliken charge distribution analysis are used to explain the mechanism of reactivity changes of the sphalerite surface due to the –H^+ and –OH^- adsorption.

2. Modeling

The following three reactions occur on the sphalerite surface in contact with water [1, 5, 6]:

$$\equiv ZnS + H^+ \longleftrightarrow \equiv ZnSH^+ \tag{1}$$

$$\equiv SZn + H_2O \longleftrightarrow \equiv SZnOH^- + H^+ \tag{2}$$

$$\equiv SZn + 2H^+ \longleftrightarrow \equiv SH_2 + Zn^{2+} \tag{3}$$

$\equiv ZnS$ and $\equiv SZn$ are the S and Zn atoms of the sphalerite surface, respectively. Depending on the solution pH, the $\equiv ZnSH^+$ or $\equiv SZnOH^-$ species cover the sphalerite surface. Adsorption of H^+ and OH^- at the sphalerite surface sites occurs according to reactions (1) and (2), respectively. Due to the low solubility of sphalerite, reaction (3) has been neglected in the flotation systems [28].

The standard structure of sphalerite with the F-43m space group was used for all calculations. Since sphalerite had a perfect cleavage at (1 1 0) plane [29], all calculations were performed on this plane. Geometry optimizations were performed using the DMol3 package. Local Density Approximation (LDA) with the Perdew and Wang correlation (PWC) was used for exchange correlation energy. DFT semi-core pseudo-potentials (DSPPs) were used for the treatment of the core electron effect, and double numerical plus polarization (DNP) basis set was

used to develop the electronic eigenstates. The model of ZnS (1 1 0) surface with size of $10.8 \times 11.5 \times 13.4 \ \dot{A}$, which was constructed from eight atomic layers of ZnS, was used for the DFT-based calculations. To prevent slab interaction, a 40 $\dot{A}$ of vacuum slab was considered on the top of the surface. Self-consistent with a convergence tolerance of 1.0×10^{-6} was employed, and 2.7×10^{-4} eV, 5.44×10^{-2} eV/$\dot{A}$, and 5×10^{-3} $\dot{A}$ were used as criteria of energy convergence, maximum force, and maximum displacement, respectively. The conductor-like screening model (COSMO) was used to consider the effect of water molecules on the calculations. The modeling procedure of xanthate molecules with different hydrophobic chains were also followed under the same conditions.

After geometry optimizations, the ZnS cell size parameters were a = b = c = $5.42 \ \dot{A}$, which were in appropriate agreement with the experimental results (a = b = c = $5.41 \ \dot{A}$ [30]). After the supper cell construction from the (1 1 0) plane, H$^+$ and OH$^-$ ions were positioned on top of the $\equiv$ZnS and $\equiv$SZn sites on the surface, respectively. After optimization of the structure, the calculated $\Delta E = E_{L,S} - E_{H,X}$ values were used for comparison of the overall surface reactivity with xanthate, where $E_{L,S}$ refers to the energy of LUMO of the surface and $E_{H,X}$ refers to the energy of HOMO of xanthate. Several models were constructed with different numbers of –H$^+$ and –OH$^-$ groups, and the related calculations were performed for each system. Mulliken charge distribution was then used for analyzing the effect of the adsorbed ions on the site reactivity of sphalerite surface with xanthate.

3. Results and discussion
In this section, we describe the simulations results in three sub-sections. Firstly, we present the results of the effect of an alkyl chain on the reactivity of xanthate collectors. In the next part, we interpret the simulation prediction about the effect of adsorbed –H$^+$ and –OH$^-$ groups on the reactivity of the sphalerite surface. Finally, we apply the Mulliken charge analysis results to explain how the surface groups change the surface reactivity.

3.1. Reactivity of different xanthates
The geometric parameters of the xanthate head group with different alkyl chains, as the hydrophobic part, are shown in Table 1.
These parameters were calculated for ethyl, propyl, butyl, and amyl xanthate ions. Figure 1 presents the structural parameters of the head group of the xanthate molecule. What stands out in Table 1 is that the length of the hydrophobic chain has no significant effect on the bond lengths (d_{OC}, d_{CS}, and d_{CS^-}, as described in Figure 1) and also the angle of CS_2^- ($\widehat{SCS^-}$) head group. In addition, the calculated HOMO and LUMO energies for xanthate molecules are not affected by their alkyl chain. Isosurface of HOMO and LUMO orbitals and mapped isosurface of electron density, based on the nucleophilic and electrophilic sites for ethyl and amyl xanthate are shown in Figure 2. As shown in Figure 2.a and Figure 2.c, the nucleophilic sites for both the ethyl and amyl xanthate ions are allocated to the sulfur atoms.
These results show that xanthate with different lengths of hydrophobic chain expose the same reactivity in flotation, and their sulfur atoms, as the active sites, play the main role in any reaction with the mineral surface. In addition, these findings show that in the DFT-based calculations of xanthate interaction with sulfide minerals, the minimum length of alkyl chain can be considered to reduce the size of calculations.

Table 1. Geometric parameters of head group and HOMO and LUMO energies of xanthate ions with different alkyl chains.

	n	$\widehat{SCS^-}$ (Degree)	$d_{OC} \ (\dot{A})$	$d_{CS} \ (\dot{A})$	$d_{CS^-} \ (\dot{A})$	LUMO energy (ev)	HOMO energy (ev)
Ethyl xanthate	2	126.99 (124)[a]	1.362 (1.35)[a]	1.681 (1.67)[a]	1.685 (1.70)[a]	-4.264	-1.439
Propyl xanthate	3	127.02	1.362	1.681	1.684	-4.268	-1.446
Butyl xanthate	4	126.98	1.363	1.681	1.685	-4.269	-1.451
Amyl xanthate	5	127.15	1.364	1.682	1.683	-4.287	-1.465

a. Experimental values from reference [20].

$$C_nH_{2n+1}, \ n = 1 \ \text{to} \ 5 \quad \text{---} \quad O$$
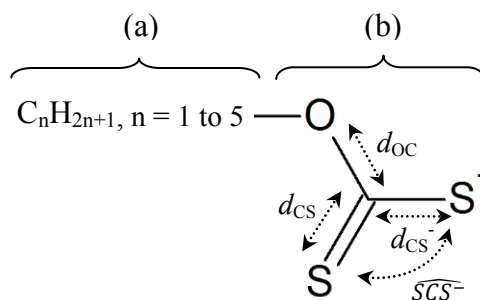
Figure 1. Structure of a xanthate: (a) alkyl chain (C_nH_{2n+1}) and (b) head group (OCS_2)$^-$

(a)

(b)

(c)

(d)
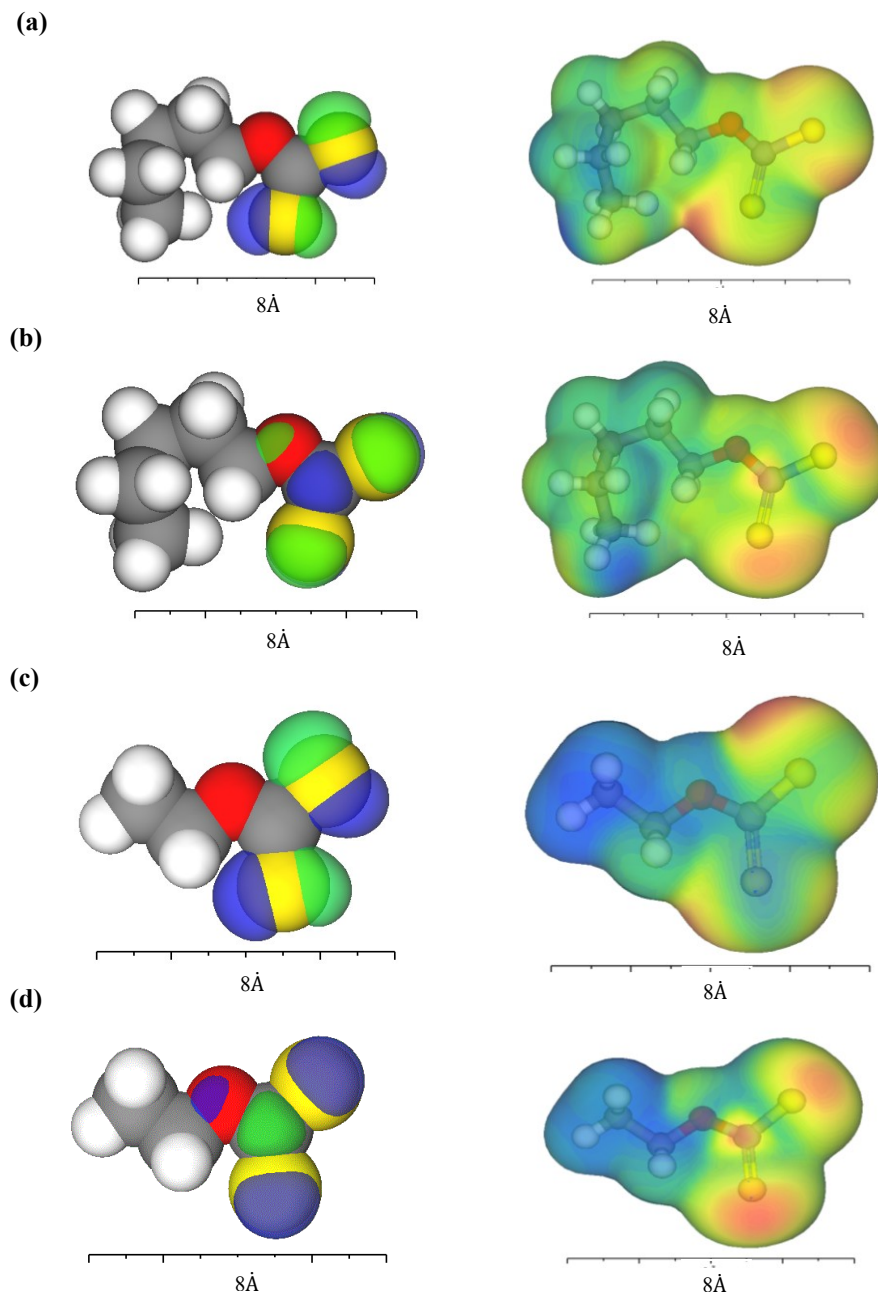
Figure 2. Schematic representations of isosurface of HOMO and LUMO orbitals of amyl xanthate (a and b-left side) and isosurface of HOMO and LUMO orbitals of ethyl xanthate (c and d-left side). Blue and green colors stand for positive and negative signs of molecular orbital wave function, respectively. Schematics at right side of a and c represent nucleophile, and those in right side of b and d show electrophile sites. Red color at head groups shows reactive site positions of xanthate.

3.2. Adsorption of H$^+$ and OH$^-$ ions on sphalerite (1 1 0) surface

Using (1 1 0) plane as the perfect cleavage of sphalerite mineral, the models of sphalerite surface were constructed by positioning the –H$^+$ and –OH$^-$ ions on the ≡ZnS and ≡SZn sites, respectively. To investigate the effect of the adsorbed ions on the reactivity change of the surface, the number of ≡ZnSH$^+$ and ≡SZnOH$^-$ complexes on the surface was increased by bonding the –H$^+$ and –OH$^-$ ions to the ≡ZnS and ≡SZn free sites, respectively. After optimization of the different surface structures, the HOMO and LUMO energies were calculated. The results obtained are shown in Figure 3.

The values for the HOMO and LUMO energies of ethyl xanthate were used for the ΔE calculation. The energies of HOMO and LUMO of sphalerite surface before the adsorption of –H$^+$ and –OH$^-$ ions were -3.96 eV and -3.30 eV, respectively.

From the data in Figure 3, it is obvious that the adsorption of H$^+$ on sphalerite reduces the LUMO energy of the sphalerite surface, so that ΔE reduced as the surface coverage with the ≡ZnSH$^+$ group increased. It points out that the electron transfer from xanthate to the sphalerite surface simply occurs with increase in the surface coverage of the ≡ZnSH$^+$ group, so the sphalerite surface reacts with xanthate. This phenomenon at the molecular level explains the reason of maximum floatability of sphalerite in acidic pH values. In Figure 3, we can see that the adsorption of –OH$^-$ group resulted in the increase in the value of HOMO and LUMO energy of sphalerite (1 1 0). Considering the ΔE calculation, it is expected that these changes cause a reduction in the sphalerite (1 1 0) reactivity with xanthate. The adsorption energies of ethyl xanthate are reported in Table 2.
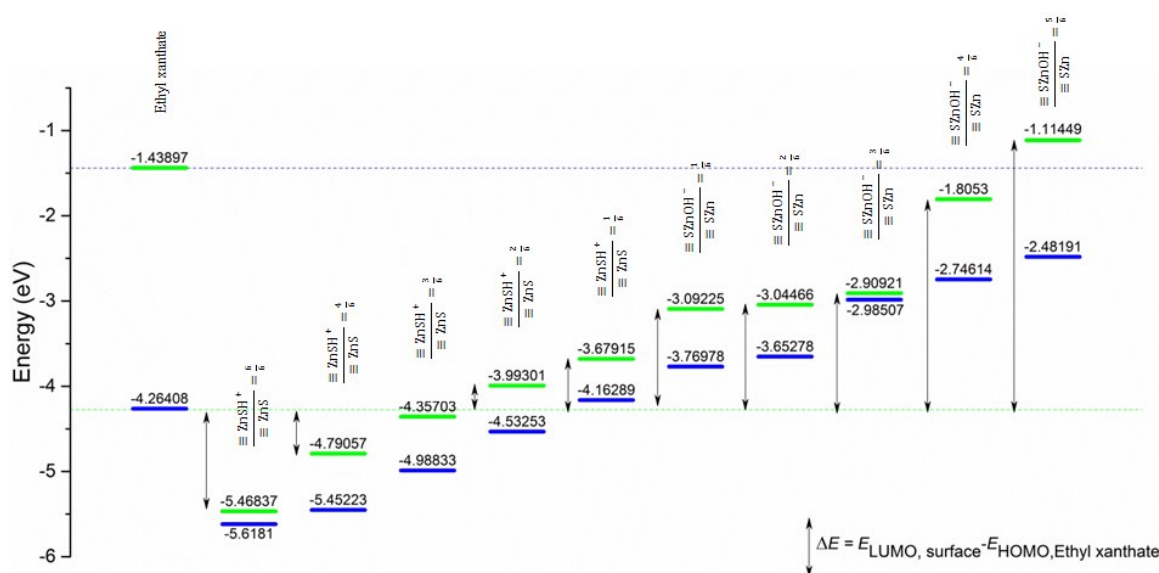

Figure 3. Calculated HOMO and LUMO energies of sphalerite surface in different adsorptions of H$^+$ and OH$^-$ ions. Different values of ΔE show the reactivity changes of surface with ethyl xanthate in different surface coverage of ≡ZnSH$^+$ and ≡SZnOH$^-$ groups.

Table 2. Calculated adsorption energies of ethyl xanthate on sphalerite (1 1 0) surface in different coverage of ≡ZnSH$^+$ and ≡SZnOH$^-$.

$\dfrac{\equiv ZnSH^+}{\equiv ZnS}$	Adsorption energy (kJ mol^{-1})	$\dfrac{\equiv SZnOH^-}{\equiv SZn}$	Adsorption energy (kJ mol^{-1})
$\dfrac{1}{6}$	-418	$\dfrac{1}{6}$	-227
$\dfrac{2}{6}$	-639	$\dfrac{2}{6}$	-77
$\dfrac{3}{6}$	-747	$\dfrac{3}{6}$	-68
$\dfrac{4}{6}$	-775	$\dfrac{4}{6}$	155

The data in this table can be compared with the ΔE value in Figure 3, which indicates that surface coverage of the $\equiv$ZnSH$^+$ and $\equiv$SZnOH$^-$ groups on the mineral surface significantly affects the adsorption energy. The results of adsorption energy calculation indicated that increasing the number of SH$^+$ groups from site 1 to site 4 on the mineral surface resulted in the increase in the absolute values for the interaction energy from -418 to -775 kJ mol^{-1}, and this means that the interaction of xanthate with Zn atoms of the sphalerite surface becomes stronger with increase in the surface coverage of SH$^+$ groups. Conversely, following the addition of –OH$^-$ ions, a significant decrease in the interaction energy was observed. The interaction energy of xanthate with the sphalerite surface was -227 Kj mol^{-1} when a single –OH$^-$ ion was adsorbed on the surface but

this value was +155 Kj mol^{-1} for the sphalerite surface covered with four –OH$^-$ groups. Positive values of interaction energy indicate that there is no effective interaction between xanthate and the –OH$^-$-rich surface. Figure 4 shows the optimized structures of two xanthate-sphalerite(110) systems. From Figure 4.a, it could be seen that xanthate was adsorbed on the protonated surface, while in the hydroxylated surface, as Figure 4.b shows, xanthate ion did not react with the surface atoms.

These results can be compared to the experiments that show that the sphalerite mineral completely floats in acidic pH values in the presence of 2.5×10^{-4} molar of amyl xanthate [9]. The recovery of sphalerite decreased as the pH value for the flotation pulp increased to the basic conditions.
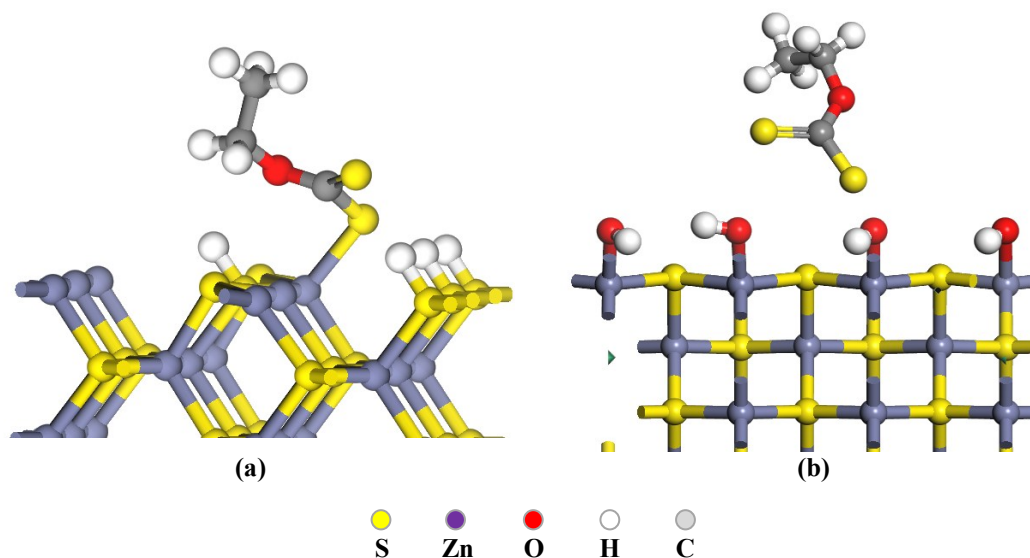

(a)   **(b)**

| ● S | ● Zn | ● O | ○ H | ○ C |

Figure 4. Optimized structures for xanthate-sphalerite (110) systems: a) protonated and b) hydroxylated surfaces.

3.3. Mulliken atomic charge analysis

The Mulliken charge distributions of S and Zn atoms before and after the –H$^+$ and –OH$^-$ ion adsorption on the sphalerite surface are listed in Table 3. Positions of labeled atoms in this table are illustrated in Figure 5.

Comparison of the Mulliken atomic charge before and after ion adsorption helps to track any electron transfer between the atoms. Any change in the charge of the surface atoms indicates the change in their chemical reactivity. From Table 3, it can be seen that the formation of SH$^+$ groups results in the electron transfer from Zn atoms to SH$^+$ groups. The charge of –H$^+$ reduced from +1

to +0.3, and the charge of S atom changed from -0.45 to -0.47. It could obviously be seen that both Zn atoms, adjacent to the SH$^+$ group, lost their electrons, and their charges increased from +0.48 to +0.5. Electron loss of Zn atoms results in the enhancement of their electrophilicity, so Zn sites find a new higher reactivity with the nucleophile head of xanthate. Conversely, the reduction of Zn atoms due to the formation of $\equiv$SZnOH$^-$ group considerably decreases the reactivity of the Zn sites with xanthate. Therefore, the weak reactivity of sphalerite with xanthate in alkaline pH values resulted in the low floatability of sphalerite.

Table 3. Mulliken atomic charges of atoms before and after H⁺ and OH⁻ ion adsorption.

	Marked in Figs. 5 a and b	Mulliken atomic charges	
		Before adsorption	After adsorption
Adsorption of H⁺ , (Figure 5a)	1	+1	+0.3
	2	-0.45	-0.47
	3	+0.48	+0.51
Adsorption of OH⁻, (Figure 5b)	1	+0.189	+0.28
	2	-1.189	-0.77
	3	+0.48	+0.18
	4	-0.45	-0.20
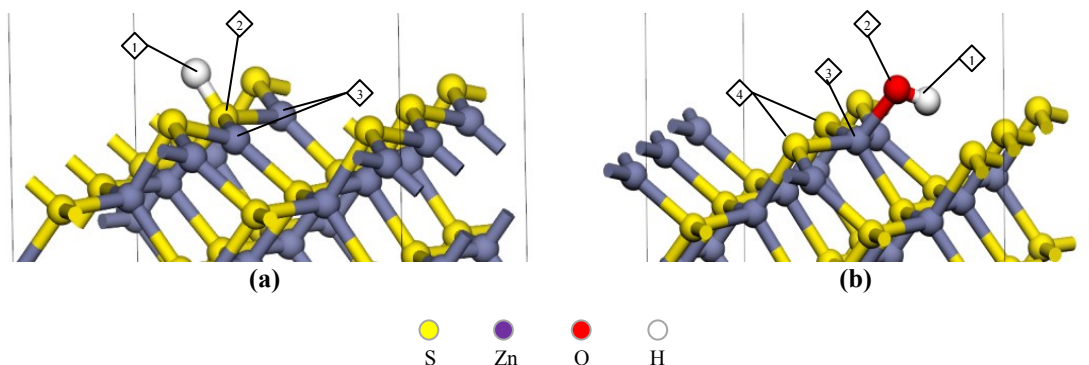
Figure 5. Adsorbed H⁺ (a) and OH⁻ (b) ions on sphalerite (1 1 0) surface; marked atoms were explained in Table 3. Model corners were sketched with straight lines for a better visualization.

4. Conclusions

In this work, quantum mechanical simulations based on DFT were performed to investigate the role of the adsorbed ions on the interaction of the sphalerite (1 1 0) surface with xanthate. Adsorptions of –H+ and –OH- ions, as surface functional groups, were examined. The difference between the LUMO energy of surface and the HOMO energy of xanthate (ΔE) and surface-xanthate interaction energy were used to compare the reactivity of different systems. Analysis of the Mulliken charge distribution was also applied to determine the origin of different reactivities of the surface due to the ion adsorption. Investigation of the reactivity of xanthate head group showed that xanthates with different alkyl chains had the same reactivity properties. Calculation of ΔE and surface-xanthate interaction energy revealed that the reactivity of xanthate with sphalerite surface increased as the surface coverage of $\equiv$ZnSH⁺ increased. Conversely, a significant reduction in the reactivity of the –OH⁻-rich surface with xanthate has been reported. One of the more significant findings that resulted from the Mulliken charge distribution analysis was that the electrophilicity of atoms in the outermost layer of sphalerite was changed due to the adsorption of –H⁺ and –OH⁻ ions. In fact, changes in electrophilicity originated from the electrons transfer due to the reduction and oxidation of atoms caused by the adsorbed ions. In the case of the sphalerite surface, the formation of –SH⁺ group resulted in the oxidation of Zn atoms of the sphalerite surface, which caused a significance enhancement in the electrophilicity of Zn atoms. Conversely, the reduction of Zn atoms due to the adsorption of –OH⁻ ions caused a decrease in the electrophilicity of Zn atoms, and consequently, decreased its reactivity with xanthate. The findings of this research work provided insights for description of the role of the adsorbed ions on the sphalerite surface interaction with xanthate.

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تأثیر گروه‌های عاملی بر واکنش‌پذیری سطح اسفالریت (۱۱۰) با کلکتور گزنتات: مطالعه DFT

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چکیده:

در این پژوهش اثر گروه‌های عاملی H^+- و OH^-- بر واکنش‌پذیری سطح اسفالریت (۱۱۰) با استفاده از نظریه‌ی تابعی چگالی بررسی شده است. اختلاف بین انرژی پایین‌ترین اوربیتال اشغال نشده‌ی سطح و بالاترین اوربیتال اشغال شده‌ی گزنتات، برای مقایسه‌ی واکنش‌پذیری سطوح تمیز و پوشیده شده از گروه‌های عاملی H^+- و OH^-- با اتیل گزنتات استفاده شد. نتایج آنالیز توزیع بار اتمی مولیکن نشان داد بار اتم‌های سطحی به دلیل تشکیل این گروه‌ها روی سطح و در نتیجه‌ی فرایندهای اکسایش-کاهشی تغییر پیدا می‌کند. علاوه بر آن، نتایج به دست آمده نشان داد که الکترون‌دوستی اتم‌های Zn در میزان واکنش‌پذیری سطح اسفالریت با گزنتات نقشی کلیدی ایفا می‌کند. محاسبات نشان داد، طول زنجیره‌ی گروه آلکیل بر واکنش‌پذیری گزنتات‌ها با سطوح تأثیری ندارد. نتایج این پژوهش در درک واکنش‌های سطح اسفالریت با گزنتات نقش مؤثری دارد.

کلمات کلیدی: نظریه‌ی تابعی چگالی (DFT)، گونه‌های سطحی، کلکتور گزنتات، واکنش‌پذیری سطح، سطح کانی.