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Probing reactivity sites on pyrite-oxidative interactions with 4-chlorophenol

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1. Introduction

In environmental applications, pyrite has been identified as a starting material for the degradation of organic pollutants [1–3]. Pyrite is an intrinsic *d*-band semiconductor; it exhibits both *n*and *p*-types of conductivity. The mechanism of bond formation between iron and sulfur atoms in pyrite has already been confirmed [4–7]. Briefly, in the octahedral field of six sulfur atoms, the iron d orbitals split into e_g (d_{x^2} and $d_{x^2-y^2}$) and t_{2g} (d_{xy} , d_{xz} and d_{xz}) states [4]. The six Fe–S σ bonds are formed from the overlap of the empty iron 4s and the occupied sulfur sp^3 orbitals. The uppermost region of the valence band consists of metal non-bonding t_{2g} orbitals that can create a hole in the valence band by changing $Fe^{2+} \rightarrow Fe^{3+}$ without breaking the Fe–S bond. The energy of separation, E_g between the anti-bonding $\sigma^*(e_g^*)$ and non-bonding $\pi(t_{2g})$ orbitals, is ~1 eV [7,8]. The $d_{x^2-y^2}$ orbital of Fe²⁺ is oriented along the direction of Fe–S bonding while t_{2g} orbitals are projected into spaces between Fe–S bonds yielding $\vec{E}_{t_{2g}} < E_{eg}$ [8]. The highest unoccupied molecular orbital (HOMO) states are exclusively composed of the non-bonding t_{2g} like iron d orbitals, whereas the sulfur sp³ orbitals form the first empty states, e.g. lowest unoccupied MO (LUMO). Pyrite exhibits both oxidative and reductive properties; the sulfide on FeS₂ has a lone pair at $\pi^*(HOMO)$ which can be donated to a vacant orbital of an oxidant, or $\sigma^*(LUMO)$ can gain electron from a reductant. Recently, it has been shown

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ABSTRACT

We have examined the oxidative interactions of 4-chrlorophenol (hereafter 4-CP) with pyrite using Diffused Reflectance Fourier Transform Infra Red (DR-FTIR) spectroscopy. In order to enhance the 4-CP adsorption on pyrite, all experiments were conducted in gas phase under ambient atmospheric conditions. When traces of water are present, the pyrite oxidation has occurred both at \equiv Fe(II) and \equiv S₂ sites forming \equiv FeOOH and S₂O₃²⁻ as intermediates. The 4-CP was chemisorbed onto newly developed \equiv FeOOH sites on pyrite with the concomitant release of H₂O. Presence of \equiv FeOOH sites favored the H₂O₂ and OH• radical production. The IR bands observed at 1170, 1203 and 1145 cm⁻¹ evidenced for the presence of HSO₄⁻ and FeSO₄⁰ species in the vicinity.

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that the pyrite has an ability to split water into OH^{\bullet}_{ads} and surface bound H^{+} preferentially at non-stoichiometric Fe(III) surface sites [9]. The hydroxyl radical is a non-specific oxidant that reacts with most recalcitrant organic pollutants in the environment at near diffusion-limited rates.

The specific aim of this work was to examine the reactivity of pyrite and their effects when interacts with a simple organic ligand utilizing DR-FTIR spectroscopy. The 4-CP was selected due to availability of adsorption data in aqueous medium [10]. Further, the 4-CP is listed as a priority pollutant in U.S. EPA, and it exhibits low biodegradability [11,12]. The chlorophenols are introduced into the environment as a result of anthropogenic activities such as water disinfection, waste incineration, and persistent use of pesticides, herbicides and as byproducts in bleaching of paper pulp with chlorine [13]. There are various techniques available to destroy organic pollutants from aquatic systems such as Fenton's [Fe²⁺/H₂O₂] method [14], adsorption [15], and photo-catalytic degradation [16]. Pyrite has been proposed as a potent substrate for the degradation of organic pollutants due to its abundance, environmental friendliness and characteristic bulk and surface properties [8]. Previously several experiments have been reported describing the interactions of iron oxides when exposed to different gases [17,18] but to our knowledge similar investigations with pyrite are scarce. Therefore in this work, the interactive mechanisms of 4-CP and pyrite were resolved by DR FTIR spectroscopy utilizing both experimental and theoretical evidence available. However, during the long-term equilibration time scales, i.e. more than 12 h, 4-CP showed susceptibility for oxidation generating numerous short-lived intermediates which makes it difficult to identify them by DR-FTIR data.

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2. Materials and methods

Unless otherwise mentioned, all chemicals were from Merck (Germany) or BDH (UK). 4-CP was purchased from Fluka (Switzerland), as better than 99% pure, and was used as delivered. Prior to use, the glassware was soaked in \sim 1 M HNO₃ (24 h) followed by \sim 1 M NaOH (24 h), and washed thoroughly with deionized-distilled water. Water was purified with a mixed bed resin to remove any cationic or anionic constituents before distillation. Natural pyrite samples (Wards collection, Peru) were obtained for this study. Pyrite crystals were sorted to remove entities with discoloration or graphite aggregates. The resulting cohort was roughly uniform in color, size, and gross morphology. The small crystals were irregularly shaped, 1-3 mm long, with an average mass of approximately 2 g per crystal. Pyrite crystals were crushed and sieved prior to all experiments. The pyrite particulates were cleaned with ~1.5 M HCl for 36 h and the solid-solution separation was carried out by centrifugation at 14,000 rpm. The pyrite particulates treated in this way were rinsed several times with the distilled water to remove any dissolved impurities under N₂ purging. The dried pyrite sample was stored in a vacuumed desiccator prior to use. The specific surface area of pyrite is $1 \text{ m}^2/\text{g}$; the average particle size around $4 \mu \text{m}$ [19].

According to the previous data [10], the adsorption density of 4-CP by pyrite, Γ_{4-CP} , was 0.11 μ mol m⁻² at pH 4.5 and initial $[4-CP]=4.2 \,\mu$ M. The low 4-CP coverage was due to the presence of excess water. 0.500 g of solid 4-CP material was placed inside a vacuumed container that has a sampling outlet. After 24 h the concentration of the 4-CP inside the container was measured as 11 µM. Based on vapor pressure data, the calculated 4-CP concentration at 300 K was 12.2 µM. The calculations were performed according to the model given by Tabai et al. [20] with the parameters recommended in Ref. [21]. A typical experiment to examine the adsorption of 4-CP on pyrite was designed as follows. Measured volume fractions of saturated 4-CP (2-8 µM) was taken into gas tight syringe and injected into reaction vials sealed with Teflon lined-septa inserted screw caps. All vials were kept at ambient atmospheric conditions. These vials contained a weighted quantity of pyrite (i.e. 0.500 g) and an equal volume of the gas from the head space was taken out prior to 4-CP injection. All samples were prepared in duplicate; control samples without pyrite were also prepared in the same manner. The tubes were equilibrated for 20 min. The 4-CP adsorption density onto pyrite was determined by monitoring the gas phase 4-CP concentration after 20 min. This short-range equilibration time scale was chosen to minimize pyrite induced 4-CP degradation. The analysis of 4-CP was carried out with a gas chromatograph equipped with ECD detector using SE 30 capillary column under split-split less mode. The method detection limit of 4-CP was found to be 1 ng.

As shown earlier [10], the 4-CP in water exhibits a gradual degradation with prolonged interactions with pyrite. Therefore, the 4-CP/pyrite samples were equilibrated for 12 h in gas phase at ambient conditions prior to all spectroscopic measurements. Only the pyrite samples loaded with 4-CP at 8 µM initial concentration were used for the spectroscopic measurements. Infrared (IR) analyses were carried out using a Fourier transform infrared spectrometer at 4 cm⁻¹ spectral resolution (Nicolet 6700, USA) employing a diffused reflectance sample holder. The pyrite or 4-CP treated pyrite samples received from the experiments $(\Gamma_{4-CP} = 0.38 \,\mu\text{mol}\,\text{m}^{-2})$ were mixed with KBr in 6:1 weight ratio, crushed in an agate mortar and pestle to achieve particle size less than 0.01 mm. The KBr was fused at 850 °C and cooled to room temperature prior to use. The homogenized samples were transferred to the sample holder to collect IR spectra at mid IR region ranged 400-4000 cm⁻¹ against pure KBr.



Fig. 1. Variation of Γ_{4-CP} as a function of equilibrium [4-CP]. The equilibrium [4-CP] was determined in gas phase at ambient conditions (P = 102 kPa, T = 300 K). The equilibration time was restricted to 20 min to minimize 4-CP degradation.

3. Results and discussion

3.1. Gas phase 4-CP adsorption by pyrite

Fig. 1 showed the adsorption density of 4-CP, Γ_{4-CP} as a function of equilibrium [4-CP] in gas phase at ambient pressure and temperature conditions. The data were compared against experiments carried out in aqueous phase which showed maximum $\Gamma_{4-\mathrm{CP}}$ values at pH 4.5. In gas phase experiments, the $\Gamma_{4\text{-CP}}$ is always found to be increased by about 2–4 folds with reference to Γ_{4-CP} values in water [10]. The 4-CP adsorption on pyrite showed a linear trend with a partition coefficient, $K_d = 23 \,\mu \text{mol}\,\text{m}^{-3}$ (solid)/ $\mu \text{mol}\,\text{m}^{-3}$ (gas). Zhang et al. [22] examined the physical structure of lipid layers on pyrite by atomic force microscopy, and observed small islands of lipid moieties on selective sites. At excess adsorbate loadings, the growth of the lipid layers was shown only on these islands by bilayer formation. This suggests that pyrite exhibits sites with both hydrophobic and hydrophilic properties which deserve a discussion. The hydrophobic effect is refers to the reject from water of non-polar molecules or moieties and an accompanied characteristically large positive entropy changes for the process of solubility of non-polar molecule or moiety. This effect is driven by the requirement that H₂O molecules wish to maximize H-bonding network structure or as lack of H-bonding between water molecules and a substance and is supported by the presence of the dangling OH bonds [23,24]. As shown in [24], the hydrophobic surfaces can be classified as polar and non-polar. In the case of polar hydrophobic surfaces as pyrite, there is a need to hydrate polar sites. In the case of non-polar hydrophobic surfaces there is no requirement to hydrate the sites at the interface. Indeed the water molecules will seek to be rejected from the interface to assist the process of maximizing their H-bonding possibilities. It was also noted that the hydrophobic materials/water interfaces are most likely negatively charged. It is also shown that the pH_{IFP} of the most hydrophobic interfaces are pH < 3.5 [25,26]. For pyrite, the pH_{IEP} is around 1.4–1.7 [19,27]. This extremely acidic pH suggests that the pyrite interface is neutral whereas bulk is extremely acidic. This suggests that easily polarizable species may preferentially retain on surface sites when compared to small ions [24]. When water is present in excess (i.e. aqueous phase) together with 4-CP this effect would be



Fig. 2. IR spectra of 4-chlorophenol interacted pyrite surface (a) pyrite surface without 4-CP, (b) pyrite surface interacted with 4-CP at Γ_{4-CP} = 23 μ mol m⁻³. The 4-CP interactions were examined at ambient conditions. Equilibration period was 12 h.

masked. The 4-CP adsorption is further reduced due to H-bonding with water. However, in the gas phase these constrains are minimized, therefore the direct bonding of 4-CP with pyrite surface sites is greatly facilitated which results an enhanced adsorption. Therefore, all subsequent measurements were made for the pyrite samples at 8 μ M 4-CP loadings (hereafter Py-4CP) in gas phase. However, pyrite was equilibrated with 4-CP for 12 h to enhance 4-CP degradation. The 12 h equilibration was chosen since the pyrite assisted 4-CP degradation was optimal (in aqueous phase) during this period [10] (Fig. 2).

3.2. IR spectroscopy of 4-CP treated pyrite

The IR spectra of Py-CP are often characterized by band shifts and appearance of new bands with respect to that of bare pyrite (hereafter pyrite). Particular attention is paid to analyze 400–900 cm⁻¹ (Fig. 3), 900–1400 cm⁻¹ (Fig. 4), and 1400–2000 cm⁻¹ (Fig. 5) spectral regions in Fig. 2 to support evidence for oxidation and adsorptive interactions of 4-CP. As shown earlier by in site spec-troscopic methods [28], the oxidation of pyrite by air did not occur randomly across the surface but instead was initiated at specific locations and then spread outward from these points. Therefore, the mechanism of pyrite oxidation is believed to occur utilizing \equiv Fe(II) and \equiv S₂ sites (\equiv denotes the surface). As shown earlier [28,29], pyrite oxidation is thought to occur via multi-steps mechanism/s and currently two model types are suggested, namely "sulfur" oxidation model and "iron" oxidation model. The anti-bonding π^* electron of S₂²⁻ rather than the non-bonding t_{2g} electron of Fe²⁺



Fig. 3. IR spectra of 4-CP interacted pyrite surface (spectral region 400–900 cm⁻¹). The arrows indicate newly appeared bands. The dotted lines indicate shifted bands as referenced to untreated pyrite.



Fig. 4. IR spectra of 4-CP interacted pyrite surface (spectral region $900-1400 \text{ cm}^{-1}$). Spectra of both pyrite and 4-CP interacted pyrite samples were shown. The IR bands were resolved by peak fitting method.

is lost first from "pyrite" molecule [28,30]. According to "ironoxidation" model, the first step of the oxidation process to be electron transfer from \equiv Fe(II). The holes can split water with formation of hydroxyl radicals and high acidity environment in the vicinity of reactive sites as a result of released protons [9,23]. These protons interact with pyrite forming =FeS-S-H. As shown by the IR band at 2500 cm^{-1} , the =FeS₂H sites show enhanced affinity to 4-CP possibly via H-bonding with respect to =S-H stretching vibrations [32] (Fig. 2). However, it is not possible to observe any changes in IR bands for $\equiv OH_{ads}^{\bullet}$ due to high reactivity. As evidenced by the IR band appeared at 821 cm^{-1} (Fig. 3 and reaction (2) in Table 1), the reactive $\equiv OH_{ads}^{\bullet}$ is thought to migrate towards $\equiv Fe(II)$ sites creating =(OH)Fe(III)S₂ species [13–15]. As shown in Table 1 (reactions (3) and (4)), the $\equiv OH_{ads}^{\bullet}$ reacts with another $\equiv OH_{ads}^{\bullet}$ forming highly reactive H_2O_2 , which is reacted further with $\equiv OH_{ads}^{\bullet}$ to produce HO₂• and H₂O. Subsequently, HO₂• attacks on \equiv Fe(II) forming iron(III) oxyhydroxides (reaction (5) in Table 1) as noted by IR bands



Fig. 5. IR spectra of 4-CP interacted pyrite surface (spectral region $1400-2000 \text{ cm}^{-1}$). Spectra of both pyrite and 4-CP interacted pyrite samples were shown. The IR bands were resolved by peak fitting method.

Table 1

Possible reactions on pyrite surface for the oxidation and 4-CP interactions.

	Possible reaction	Specification	IR band/s cm ⁻¹	Ref.
	Fe(II) oxidation on pyrite			
(1)	$FeS_2:[Fe^{III}] + H_2O \rightarrow FeS_2:[Fe^{II}] + OH^{\bullet}_{ads} + H^+$		nd	[29]
(2)	$Fe^{II}S_2 + OH^{\bullet}_{ads} \rightarrow Fe^{III}(OH)S_2$	Fe–O–H str.	821	[28,31,32]
(3)	$OH^{\bullet}_{ads} + OH^{\bullet}_{ads} \rightarrow H_2O_2$		nd	[9,30]
(4)	$OH^{\bullet}_{ads} + H_2O_2 \rightarrow HO_2^{\bullet}_{ads} + H_2O$		nd	[30]
(5)	$Fe^{II}S_2 + HO_2 \bullet_{ads} \rightarrow Fe^{III}(O_2H)S_2$	Fe-O-O- str.	603, 630, 698, 713, 767, 794	[31,40,42]
(6)	$HO_2^{\bullet}_{ads} \leftrightarrow O_2^{\bullet}_{ads} + H^+$		nd	[43]
(7)	$O_2^{\bullet-}_{ads} + OH^{\bullet}_{ads} \rightarrow OH^- + O_2$		nd	
(8)	$Fe^{III}(O_2H)S_2 + OH^- \rightarrow [Fe^{III}(O_2H)(OH)S_2]^-$	[SS] [_]	565, 590	This work
(9)	$HO_2^{\bullet}_{ads} + O_2^{\bullet}_{ads} \rightarrow HO_2^- + O_2$		nd	
(10)	$Fe^{III}(O_2H)S_2 + HO_2^- \rightarrow [Fe^{III}(O_2H)_2S_2]^-$	[SS] [_]	565, 590	This work
(11)	$OH^{\bullet}_{ads} + 4-CP \rightarrow P_i$		nd	
(12)	$Fe^{II}S_2 + O_2 \rightarrow Fe^{III}S_2 + O_2^{\bullet -}_{ads}$		nd	
(13)	$Fe^{III}S_2 + H_2O \rightarrow Fe^{II}S_2 + OH^{\bullet}_{ads} + H^+$		nd	
	S ₂ ²⁻ oxidation on pyrite			
(1)	$Fe-S-S \rightarrow Fe-S-S^+ + e^-$	S–S	426, 441, 449, 457, 463, 470, 489, 503	[31]
(2)	$Fe\text{-}S\text{-}S^+ + 3H_2O \rightarrow Fe\text{-}S\text{-}SO_3 + 6e^- + 6H^+$	S ₂ O ₃	994, 1123	[27,30,43]
(3)	$S_2O_3^{2-} \rightarrow S + SO_3^{2-}$	SO3 ²⁻	916, 1017, 1090, 1036	[27,30,43]
(4)	$S_2O_3^{2-} + H_2O \rightarrow S + HSO_4^{-} + e^- + H^+$	HSO ₄ ⁻	1170, 1203	[31,43]

nd - not detected.

appeared at 630, 603, 698, 713, 767, and 794 cm⁻¹ (Fig. 4) [33–35]. The disappearance of IR bands at 603 and 698 cm⁻¹ (Fig. 2) is due to the chemisorption of 4-CP with \equiv FeO–OH on the pyrite forming 4-chlorophenolate anion with the concomitant release of H₂O. There are two new IR bands appeared at 750 and 887 cm⁻¹ which are assigned to the formation of 4-CP complex with surface \equiv FeO–O⁻ sites on pyrite via inner-sphere mechanism (structure A). In the presence of 4-CP, a new IR band appeared at 1160 cm⁻¹ is assigned to ring C–H in-plane bending vibrations, while the bands at 1291 and 1323 cm⁻¹ are assigned to C–O stretching band of adsorbed 4-CP shifted to high wave number suggesting an additional stretching energy (from 1223 \rightarrow 1291 and 1323 cm⁻¹). Further, the band at 1066 cm⁻¹ is assigned to a chlorine sensitive vibration of 4-CP [36].



The appearance of iron (III) oxyhydroxide on pyrite itself provides strong evidence for the formation of surface mediated H₂O₂ and OH• (reactions (12) and (13) in Table 1). Photo-chemically, the conversion of $Fe(II) \rightarrow Fe(III)$ is occurred through the capturing a photon that promotes an electron from non-bonding Fe(II) d-level to the conduction band producing a hole (h⁺) at sulfurdeficient defect sites [32]. Some oxidants such as NO_3^- , Cl_2 , H_2O_2 , O₂ and Fe³⁺ are also capable of accepting electrons from pyrite thus facilitating a cathodic reaction at =Fe(II) sites [37,38]. In this context, the molecular oxygen acts as a terminal electron acceptor [33,39]. Therefore another reaction mechanism for \equiv Fe(II) oxidation is the donation of an electron to π^* orbital of O₂ forming O₂^{•-} and \equiv Fe(III). The \equiv Fe(III) is reduced to \equiv Fe(II) gaining an electron from H₂O yielding \equiv (OH[•]_{ads})Fe(II)S₂ and surface bound H⁺. Subsequently, the $O_2^{\bullet-}$ reacts with H⁺ resulting HO₂• (Table 1). As shown in [40], essentially the oxidized \equiv Fe(III) sites provided a conduit for electron transfer from \equiv Fe(II) to the terminal electron acceptor O_2 . Moses et al. [40,41] showed that in Fe³⁺ saturated solutions, the Fe³⁺ is the direct oxidant even in the presence of dissolved O₂ and this conclusion has been supported by the theoretical work of Luther [42] who predicted based on HOMO/LUMO arguments that Fe³⁺ would be a much more efficient oxidant of sulfide than molecular oxygen and that the pyrite oxidation would proceed through a $S_2O_3^{2-}$ intermediate.

The formation of sulfur species during oxidation proceeds through several pathways centered on \equiv S₂ sites (Table 1 reactions (1)-(4)). In agreement with previous data [31-33], we report IR spectroscopic evidence for the presence of sulfur species on pyrite surface. The bands appeared at 994 and 1123 cm⁻¹ are assigned to =S-O stretching vibrations of $S_2O_3^{2-}$ [28,32]. The bands at 916, 1017 and 1090 cm^{-1} are associated with SO_3^{2-} symmetric vibrations while a band appeared at 1036 cm⁻¹ assigned to asymmetric stretching vibrations of surface bound SO_3^{2-} [28]. The bands at 1170, 1203 and 1145 cm⁻¹ are evidenced for the presence of bisulfate and iron sulfate species, respectively, on the surface [33]. The H–O–H deformation vibration of hydrated bisulfate is appeared at 1648 cm⁻¹ [43–45] (Fig. 4), the =S–O stretching vibration appeared at 1623 cm⁻¹ [41] and the \equiv S-S-O vibrations appeared at 665 cm⁻¹ (Fig. 3). Therefore, it is concluded that the most dominant sulfur species on the pyrite surface are SO₃²⁻ and HSO₄⁻. The oxidation of the disulfide group begins with the formation of an =S-O bond that transferred OH⁻ from the hydration sphere of Fe³⁺ to the disulfide group [32]. The band at 977 cm^{-1} is assign to the hydrated ferric hydroxide vibrations [31]. The anti-bonding π^* electrons pair of S_2^{2-} is lost forming a σ -type =S-O bond. The OH⁻ transfers are continuing to form $S_2O_3^{2-}$ on the surface [37,46] and the [S–SO₃] completely ionize to $S_2O_3^{2-}$ at low pH thus making the =S-S bond stronger than the =Fe-S bond. However, $S_2O_3^{2-}$ intermediate is difficult to detect in the vicinity of the interfacial region. Based on ATR-FTIR data, Borda et al. [32] have reported that the vibrational modes consistent with SO_4^{2-} and $S_2O_3^{2-}$. The mode at about 1115 cm⁻¹ was proposed to be associated with sulfate in distorted T_d symmetry and that a band at 1010 cm^{-1} was proposed to be associated with a monodendate thiosulfate complex often obscured by the sulfate mode (Fig. 4). It is also proposed that the third species, sulfite or bisulfate could also be present. The sulfur becomes more positive by leaving electrons easily, therefore another water molecule attack to SO_3^{2-} to produce SO_4^{2-} and HSO_4^- at the end [37,47].

Sulfide groups on pyrite surface provide stretching vibrations around $420-510 \text{ cm}^{-1}$ (Fig. 3). The bands at 426, 441, 449, 457, 463, 470, 489 and 503 are assigned to \equiv S-S stretching vibrations at different chemical environments [43,48]. In the presence of 4-CP, the band at 426 cm⁻¹ is shifted to 431 cm⁻¹ indicating a strain conditions due to the formation of H bonds with \equiv S-S-H groups on pyrite. The disappearance of 463 and 470 cm⁻¹ bands and the appearance of an intense band at 458 cm⁻¹ is an indicative of the S-S bond symmetry change (Fig. 3). There is an ability to donate electron pair from π^* orbital (HOMO) of a $[S_A-S_B]^{2-}$ to 4-CP, thus S_B become more positive than S_A by increasing polarity of a molecule that signifies the change of band position. As shown in Fig. 4, the IR band at 489 cm⁻¹ was intense and shifted to 480 cm⁻¹ is also a donation of an electron pair for 4-CP degradation forming innersphere complexes. The formation of $\equiv S_3^-$ on the surface is ascribed for the band at 526 cm⁻¹. In the presence of 4-CP, this band is shifted to 532 cm⁻¹ to accommodate high energy requirements for S–S stretching. As shown in Fig. 2 the bands at 565 and 590 cm⁻¹ are assigned to \equiv SS⁻ stretching vibrations which are shifted to 557 and 584 cm⁻¹, respectively. This is also a good evidence for the formation of an inner-sphere surface complex of 4-CP with pyrite.

4. Conclusions

The DR-FTIR spectroscopic data are used to elucidate different steps of pyrite oxidation in the presence of 4-CP. In the gas phase, enhanced 4-CP adsorption is observed due to a hydrophobic force that drives the organic molecules into pyrite sites for chemical bonding. The generation of reactive OH• radical suggests the potential of pyrite as a starting material in environmental remediation.

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