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# Probing pyrite–carbofuran interactions with $\zeta$ potential and IR spectroscopic measurements

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#### 1. Introduction

Pyrite, FeS<sub>2</sub> is ubiquitous in sulfate reducing environments; it plays a key role in many natural processes; i.e. acid mine drainage, redox cycling of metals at oxic–anoxic boundaries and degradation of pollutants [1–3]. Disulfide groups on the pyrite surface ( $S_2^{2-}$ ) have been the proposed electron donor in the oxidation by different oxidants [4]. Pyrite is also gained attention as a material for solar cells due to its environmental compatibility and very high light absorption coefficient [5]. Pyrite is an intrinsic semi-conductor that exhibits both p and n-type conductivity [4,6]. When compared to hydrous metal oxides relatively few studies have been carried out to probe surface properties of pyrite–water interface [1].

Presently we aimed at determining the chemistry of pyritewater interface using electrokinetic mobility of particles and FTIR spectroscopy. The ionization of the surface groups and/or the sorption of ions lead to the separation of electrical charge at the solid/water interface which can be described by an electrical double layer models such as the Gouy Chapman or Stern layer model [7,8]. In an electric field, the particle and its inner layer ions move through the solution as a unit, whereas the ions in the outer diffuse

#### ABSTRACT

The  $\zeta$  potential of pyrite and pyrite–carbofuran suspensions was examined as a function of pH by electrokinetic mobility measurements. The pH<sub>IEP</sub> of pyrite was approximated to 1.70 when inert conditions were maintained. The pH<sub>IEP</sub> shifted from ~1.70 to ~3 and the  $\zeta$  potential had increased indicating intimate interactions of carbofuran with the pyrite surface. The IR spectral variations in the lattice vibration region, i.e. 700–1100 cm<sup>-1</sup> offered confirmatory evidence for the chemisorption of carbofuran. Carbofuran degraded upon prolonged contact with the pyrite.

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layer outside the shear plane remain associated with the bulk solution. Often the outside of the Stern layer is taken as the shear plane, and the potential at this plane is designated as zeta potential. The notion of slipping plane is generally accepted in spite of the fact that there is no unambiguous way of locating it. It is also accepted that  $\zeta$  potential is fully defined by the nature of the surface, its charge, the electrolyte concentration in the solution, and the nature of the electrolyte and of the solvent. It can be said that for any interface with all these parameters fixed,  $\zeta$  potential is a welldefined property [7]. Particular attention was made to examine the effect of carbofuran adsorption on the  $\zeta$  potential. For a long time, measurements of the electrokinetic mobility have been used in the calculation of electrostatic interaction forces in colloids [1,7]. These measurements are also increasingly successful in characterization of solid surfaces [7,8]. When combined with spectroscopic data, the  $\zeta$  potential values can be used to characterize the behavior of adsorbing species (presently carbofuran) in the vicinity of the interfacial region. In this research, the selection of carbofuran was made due to its widespread use of agriculture in crop protection. Carbofuran is susceptible to leaching than volatilization which result its ubiguitous presence in surface and subsurface waters [9]. Previously, we observed a rapid adsorption of carbofuran on pyrite when pH < 4.5. Upon prolonged equilibration, carbofuran showed a slow dissociation [9]. Rapid proton titration data were utilized to estimate pH<sub>zpc</sub> of pyrite around 1.77 [10,11]. When pH<2, it is noted for goethite that small errors in the determination of proton concentrations are shown to strongly affect the shape

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of the charging curves [11]. Forenasiero et al. [11], Dekkers and Schoonen [12], Bebie et al. [13] and Widler and Seward [14] showed that for pyrite the pHIEP values obtained by electrokinetic mobility measurements always converged to  $\sim$ 3. Further, when subjected to different experimental conditions, a moving pHIEP values were observed [11]. The pHIEP around 7 was ascribed to rapid conversion of Fe<sup>2+</sup> into iron oxy-hydroxide. When compared to metal oxides, metal sulfides exhibit iso-electric points that are largely independent of the nature of cation/s in the lattice [13]. The objective of this study is to calculate the  $\zeta$  potential values of pyrite and pyrite + carbofuran suspensions as a function of pH and ionic strength. The  $\zeta$  potential values were derived by electrokinetic mobility measurements according to Smoluchowski model [7,15], and they were used to estimate the location of the slipping plane. Transmission IR spectroscopic data were used as a complimentary source to characterize the carbofuran and pyrite interactions.

### 2. Materials and methods

The pyrite samples used were handpicked from a vein graphite deposit in Sri Lanka. Water was de-ionized from Advantec (Japan). Carbofuran (99.8%) from Sigma–Aldrich (USA) was used as received. The chemical structure and other pertinent data are given below:





All chemicals were obtained from Fluka (Switzerland) or Sigma–Aldrich (USA). Pyrite reacts slowly with NO<sub>3</sub><sup>-</sup> at extremely acidic conditions. The Fe<sup>2+</sup> forms weak complexes with Cl<sup>-</sup> [16]. The adjustments of background ionic strength were made with 5 M NaClO<sub>4</sub>. Prior to use, all glass and other laboratory ware were soaked overnight in  ${\sim}1\,\text{M}$  HClO\_4 followed by  ${\sim}1\,\text{M}$  NaOH and washed with distilled water. According to XRD and FTIR analyses, we confirmed the presence of pyrite phase. About 10-15 g pyrite was crushed and sieved to  $1-4\,\mu$ m. The powdered material was cleaned with  $\sim$ 2 M HCl for 36 h and solid-solution separation was made by centrifugation. The solid suspension thus obtained was rinsed well with distilled water till the pH was around 2 (the pH of the 1:1 pyrite: distilled water mixtures were around 2). The whole process was carried out under continuous N<sub>2</sub> purging. The cleaning process had dissolved oxides and other impurities present in the raw sample or oxides formed during the grinding. Pyrite is susceptible for rapid oxidation when exposed to atmosphere. Therefore the dried sample was stored in a vacuum-desiccator.

Rapid pH titrations were performed to determine  $\zeta$  potential of pyrite on 100 mL suspensions. Suspensions of 0.01–0.20 g L<sup>-1</sup> solid were equilibrated in a water-jacketed reactor at 0.001, 0.005, or 0.01 M NaClO<sub>4</sub>. Due to the data scatter, the electrokinetic mobility measurements in 0.1 M NaClO<sub>4</sub> were not considered. When pH < 2.5, it was not possible to maintain the ionic strength of the suspension exactly at 0.001 M due to the addition of 0.982 M HClO<sub>4</sub> in large proportions. The well mixed sample was transferred to the cell for the measurement of electrokinetic mobility. The reactor was connected to the micro-electrophoresis cell via a peristaltic pump. The reactor lid had the facility to insert pH, temperature and conductivity probes for monitoring relevant parameters. Separate batch solutions were prepared for the determination of electrokientic mobility at each pH value. The batch reactor was always placed inside a glove box to minimize O<sub>2</sub> concentration. Special precautions were taken to ensure gas tight conditions of the micro-electrophoresis cell. Particular attention was made when measuring pH values less than 2.5. The pH sensing electrode and a double junction reference electrode were used to monitor pH. The outer compartment of the double junction electrode was filled with NaClO<sub>4</sub> solution of matching ionic strength to minimize diffusion. These measurements were used to calculate  $\zeta$  potential using Helmholtz–Smolukhowski equation [15].  $U_0 = (\varepsilon_0 \varepsilon_r / \eta) \zeta$  where  $\eta$  is the viscosity of solvent,  $U_0$  the electrophoretic mobility of suspensions,  $\varepsilon_0$  and  $\varepsilon_r$  are the dielectric constants of the liquid and the vacuum. The increase in the ionic strength decreases the absolute value of  $\zeta$  potentials in the suspensions. All electrokinetic mobility measurements of carbofuran-pyrite suspensions were performed in  $\sim$ 0.005 M NaClO<sub>4</sub>. The 500  $\mu$ M carbofuran stock solution was used to spike the pyrite-water suspension to reach final concentration 20 or 200 µM. The solubility of carbofuran in water is low. Therefore stock solutions were prepared by dissolving known quantity of carbofuran in small amounts of HPLC grade methanol prior to dilution with distilled water. For each pH separate batch solution was prepared.

The electrokinetic mobility of particles upon these treatments were measured at 298 K using a Zeta Meter 4.0+ equipped with a microprocessor unit. A small volume cell (2 mL) flow cell with Mo anode and Pt cathode were used in all measurements. The mobility was measured three times of which average was used to calculate the  $\zeta$  potential. The error bars in Figs. 1 and 2 (see Section 3) denote the maximum deviation of the three electrokinetic



**Fig. 1.** Variation of  $\zeta$  potential of pyrite as a function of solution pH for NaClO<sub>4</sub> solutions of 0.001 M, 0.005 M and 0.01 M. The samples were prepared under N<sub>2</sub> atmosphere. The electrokinetic mobility values in the vicinity of pH<sub>zpc</sub> (~1.77) varied widely. The maximum deviations of the  $\zeta$  potential values were ±10.2 mV. All measurements were completed with 20 min. Pyrite ~0.2 g L<sup>-1</sup> and T 298 K.



**Fig. 2.** Variation of compact layer thickness ( $\delta$ ) as a function of pH. The surface potential was calculated from proton adsorption data in ~0.005 M NaClO<sub>4</sub>. Refer to the text for the details of calculation.

mobilities. Overall accuracy of the  $\zeta$  potential calculations of samples was found to be better than 10%.

Infra red (IR) analyses were carried out using a Fourier Transform Infra Red Spectrometer at  $4 \text{ cm}^{-1}$  spectral resolutions (Nicolet 6700). The pyrite or carbofuran treated pyrite samples were received from the experiments were mixed with KBr at 1:6 (w/w) ratio, crushed in an agate mortar and pestle to achieve particle size less than 0.01 mm. The KBr was fused at 800 °C and cooled to room temperature prior to use. In order to check the interference of methanol for IR spectral data of pyrite, a separate experiment was conducted by interacting pyrite with methanol for the same equilibration period and concluded the absence of any discernible changes in spectral data with respect to bare pyrite after methanol treatment. The homogeneous samples were transferred to the sample holder to collect IR spectra at mid IR region (400–4000 cm<sup>-1</sup>) under transmission mode.

# 3. Results and discussion

The experimental data obtained from electrokinetic mobility measurements of colloid particles are used for the characterization of interfacial interactions of particles with the surrounding medium. As discussed elsewhere [7], it should be noted that considerable difficulties arise when the electrokinetic mobility values are transformed into  $\zeta$  potentials. Indeed, this step requires certain theoretical idealizations such as: (a) spherical particles, and (b) homogeneity of electric charge distribution throughout the solid surface. It is clear that none of these requirements is strictly applicable to "real world" fine pyrite suspensions (or any other colloids). As discussed below, the  $\zeta$  potential of pyrite is a function of potential determining ions, in the present case, i.e. H<sup>+</sup>, OH<sup>-</sup>, S<sup>2-</sup> and Fe<sup>2+</sup> [10]. In this case, the release of Fe<sup>2+</sup> into the solution is ascribed to a surface complexation of H<sup>+</sup> onto pyrite sites according to following reaction scheme [17]:

$$\equiv FeS_2 + H^+ \rightarrow \equiv FeS_2H^+ \rightarrow \equiv Fe^{2+}HS_2 \rightarrow Fe^{2+} + \equiv HS_2$$

It has also been reported that the effectiveness of OH<sup>-</sup> as a bridging ligand to transfer electrons as:

$$\equiv$$
 FeS<sub>2</sub> + OH<sup>-</sup>  $\rightarrow \equiv$  S<sub>2</sub>FeOH<sup>-</sup>  $\rightarrow \equiv$  FeOHS<sub>2</sub><sup>-</sup>

The surface bound OH<sup>-</sup> ions migrated to  $\equiv$ S<sub>2</sub><sup>2-</sup> sites releasing S<sub>2</sub><sup>2-</sup>. Subsequently S<sup>2-</sup> is converted into SO<sub>4</sub><sup>2-</sup> or S<sub>2</sub>O<sub>3</sub><sup>2-</sup> [17,18]. Therefore, any specifically adsorbed species on the surface will also affect the  $\zeta$  potential (or surface charge).

Fig. 1 shows  $\zeta$  potential as a function of pH for three NaClO<sub>4</sub> concentrations. The apparent iso-electric point is observed around pH 1.40-1.70. However, caution has to be exercised when calculating ionic strength of solutions with pH < 2. Under these conditions, the background ionic strength always converges to a value around  $\sim$ 0.05 M. Therefore even if there were specific adsorption of Na<sup>+</sup> or ClO<sub>4</sub><sup>-</sup> ions, under these conditions it would not have been possible to discern this which results that the precise determination of cross over point in titrations in suspensions at such low pH is difficult [19]. The curves shown in Fig. 1 tend to merge at acidic pH. Butler [20] showed an empirical correlation of iso-electric points of metal oxides with bulk electro-negativity of compounds. However, metal sulfides showed peculiar behavior with the bulk electro-negativity. Metal sulfides have a much smaller range of electro-negativities than found for oxides, which is due to the small contribution of the sulfur atom ( $\chi = 6.22$ ) compared to oxygen ( $\chi = 7.54$ ). Hence, the implication is that all metal sulfides the pH<sub>IEP</sub> is predicted to lie below pH 3.5. Based on potentiometric titrations [10], the pH<sub>zpc</sub> of pyrite suspension was approximated around 1.77 which is comparable with pH<sub>IEP</sub>. Further, pyrite suspensions always known to show an iso-electric point below pH 3 when anaerobic experimental conditions are maintained. The estimated pHIEP is in good agreement with the published data when inert atmospheric conditions were maintained in the measurements [10-14].

Presently the Poisson–Boltzmann equation (known as Gouy–Chapman model of electric double layer) was used to calculate the zeta potential. Details of these calculations are given in Ref. no. [21] and only a brief account is given below. The surface potential ( $\Psi_0$ ) was determined by the proton adsorption data. Previously for pyrite surface, two sites, namely >FeSS<sup>-1/3</sup> and >SSFe<sup>5/3</sup> had been used for proton adsorption modeling by multi-site approach [10]. Presently in the calculation of  $\Psi_0$ , these sites were lumped together into one hypothetical charge entity (of charge equal to  $\sigma_0 = \sigma_{>FeSS} + \sigma_{>SS}$ ). From the Gouy Chapman theory for flat double layers the charge–potential relationship is derived from the following model:

$$\sigma_0 = 2\kappa\epsilon_0\epsilon_b \frac{k_BT}{e} \sinh\left(\frac{e\psi_0}{2k_BT}\right) \tag{1}$$

where  $\epsilon_0$  is the permittivity of free space (8.854 × 10<sup>-12</sup> CV<sup>-1</sup> m<sup>-1</sup>),  $\epsilon_b$  is the dielectric constant of bulk phase,  $\psi_0$  is the surface potential, and  $\kappa$  is the Debye parameter (the inversion of double layer thickness) defined as:

$$\kappa = \sqrt{\frac{2e^2 \sum n_i z_i^2}{\epsilon_0 \epsilon_b k_B T}}$$
(2)

where  $n_i$  is the number of ions per m<sup>3</sup> and  $z_i$  is the valence of the ion. Using  $\sigma_0$  measured by potentiometric titrations of the pyrite suspensions, and solving Eq. (1) for  $\psi_0$ , the potential at a given distance *x* is calculated using

$$\zeta \equiv \psi_D(x) = 2\frac{k_B T}{e} \ln \frac{g+1+(g-1)\exp(-\kappa\delta)}{g+1+(g-1)\exp(-\kappa\delta)}$$
(3)

where  $g = \exp(e\psi_0/2k_BT)$ .

The  $\zeta$  potential values were calculated from electrokientic mobility measurements and  $\psi_0$  potential was calculated from proton adsorption. Subsequently using Eqs. (1)–(3), the  $\delta$  values (equaled to the distance of slipping plane from the surface) were calculated and the results are given in Fig. 2. As shown in the data, the  $\delta$  dependent on pH observing an optimal value when pH  $\sim$  2. The thickness of the compact layer (hereafter designated as  $\delta$ )



**Fig. 3.** Variation of  $\zeta$  potential of pyrite as a function of pH in ~0.005 M NaClO<sub>4</sub> in the presence of carbofuran (~20 and 200  $\mu$ M). All measurements were completed within 20 min. Pyrite ~0.2 g L<sup>-1</sup> and *T* 298 K.

of the pyrite–water interface was calculated from the  $\zeta$  potential and surface charge density by Eqs. (2)–(4). As shown in Fig. 2 the  $\delta$ values showed a gradual decrease with the pH. When pH ~2, the  $\delta$  value was around 20 Å. The calculated average diameter of carbofuran was estimated by semi-empirical calculations (under AM1 level) to be 10 Å. As shown in Fig. 2 in the presence of carbofuran the compact layer thickness has somewhat broadened. This conditions favored intimate interaction of carbofuran within the compact region of the double layer.

Fig. 3 shows the variation of  $\zeta$  potential of pyrite suspensions as a function of pH at different carbofuran loadings. The  $\zeta$  potential of pyrite measured without carbofuran at the same experimental conditions is also shown as a reference. Relative changes in the  $\zeta$  potential with respect to the reference data showed indirect evidence about carbofuran interactions with surface sites. In the presence of carbofuran, the values of  $\zeta$  potential moved towards positive direction. Variation of the  $\zeta$  potential is marked with the increase of the carbofuran loading. However below 30 µM carbofuran, variations of  $\zeta$  potential were not that marked. The pHIEP shifts from 2.4 to 4.5 with respect to the loading of carbofuran in the range  ${\sim}20{-}200\,\mu\text{M}.$  This provided confirmatory evidence for intimate interactions between carbofuran and pyrite. Eventually, these interactions enhanced upon the auto-oxidation of carbofuran. Previously, it is shown that the specific adsorption of cations onto mineral oxides has shifted the pHzpc downwards and the pHIEP upwards; in the presence of chemisorbed adsorbed anions the situation is reversed [22]. It is also known that large organic molecules can specifically be adsorbed on a solid surface when the energy of hydration of the adsorbate is low [23]. However, it cannot be elucidated from the nature of the present data whether, first the undissociated molecules are adsorbed and then dissociated or the molecules already dissociated in the solution phase had adsorbed. At excess concentrations of carbofuran (e.g.  $\sim$ 200  $\mu$ M), the  $\zeta$  potential vs. pH curve convex up showing isoelectric points around pH 4 and 6. Similar observations were made in the case of xanthate adsorption on pyrite [22]; the presence of second iso electric point at pH 7 was ascribed to the formation of ferric hydroxide layer. Further these observations suggest that



**Fig. 4.** Infra red spectra of (A) pyrite, (B) carbofuran and (C) pyrite–carbofuran systems. All measurements were obtained under transmission mode of the FITR spectrometer. Details of the band assignments are given in Tables S-1 and S-2.

pyrite surface underwent oxidation possibly during the sample preparation. Presently, if such arguments are valid, the double iso-electric points should be observed in all cases irrespective of the carbofuran loading. Therefore, the presence of double  $pH_{IEP}$  can be ascribed to surface interactions of carbofuran at high loadings.

Fourier Transform Infrared spectroscopy was utilized to examine the interactions of carbofuran with the pyrite surface. For a comparison, IR spectra of pure carbofuran and pyrite samples obtained in the range  $400-4000 \text{ cm}^{-1}$  are also shown in Fig. 4(A-C). A detailed assignment of band positions of pure carbofuran is shown in Table S-1 (support documentation). Presently, only the important features relevant for this study are discussed briefly. As shown in Fig. 4(B) for pure carbofuran, the bands occurred at 1231 and 1260 cm<sup>-1</sup> assigned due to stretching of C–O–C where one carbon atom is bonded to aromatic ring while the other is attached to an aliphatic structure (refer to the structure of carbofuran). The bands at 1334 and 3362 cm<sup>-1</sup>, respectively, resulted by the presence of C-N and N-H groups. Presence of -CH<sub>2</sub> and -CH<sub>3</sub> moieties in carbofuran is confirmed by IR bands shown in the range 2880–3000 cm<sup>-1</sup>. In the region of high frequencies (3500–3800 cm<sup>-1</sup>), the observed absorption bands, i.e. wideband at 3389 cm<sup>-1</sup>, characterize the vibrations of surface hydroxyl groups, which is regarded as local vibrations of the admixtures adsorbed on the surface. As shown in Fig. 4(A), pyrite contains a characteristic discrete IR spectrum in the 700–1220 cm<sup>-1</sup>, often referred as lattice vibrations region, which contains vital information on adsorptive interactions of molecules. Basically, IR bands in this region either disappear or shift upon adsorption of foreign molecules. This frequency-change range which characterizes vibrations of metal-oxygen bonds is determined by changes in the order of these bonds. Hence, the number of maxima which appear in the region of M=O vibrations and the positions of the maxima characterize energetic non-homogeneity of metal-oxygen groups [24]. In par with these arguments, the bands in the region  $1200-882\,\text{cm}^{-1}$  are considered as characteristic of pyrite. Remarkably IR bands of pyrite at 1141, 1073, 1000, 882 and 1219 cm<sup>-1</sup> are discrete and sharp (Fig. 4(A)). This means that at least five different energy states are present on pyrite surface. However, in most of the studies of pyrite, such distinct bands were not readily observed or often obscured [24]. For example, as shown in Rath et al. [25] the band at  $1073 \text{ cm}^{-1}$  appeared as a shoulder at  $1083 \text{ cm}^{-1}$ . Presence of IR bands in the region 600–800 cm<sup>-1</sup> is indicative of the initiation of surface oxidation of pyrite. The IR spectrum of pyrite after interactions with carbofuran is shown in Fig. 4(C). In general the characteristic bands of pyrite disappeared, shifted or reduced intensities indicating a direct interaction of carbofuran with the surface. When compared to pure carbofuran following changes were noted in the spectrum of carbofuran–pyrite. The bands at 2973 and 2943 cm<sup>-1</sup> (in the case of pure carbofuran) due to C–H stretching of the –CH<sub>2</sub> and –CH<sub>3</sub> groups are split into a doublet and appears at 2960 and 2923 cm<sup>-1</sup> respectively. The bands correspond to N–H and C–N vibrations were disappeared completely and the intensity of the band corresponds to C=O decreased significantly, which may result possible bonding with the surface.



Complete disappearance of the band at 1334 cm<sup>-1</sup> indicates possible breakdown of the C-N bond yielding surface complex shown. The degradation kinetics of carbofuran in the presence of pyrite is currently under study.

# 4. Conclusions

Variations of  $\zeta$  potential and IR spectroscopic data with respect to bare pyrite point to direct interactions of carbofuran with surface sites. These sites seem to catalyze carbofuran degradation upon prolonged equilibration. Mass spectroscopic identification of carbofuran degradation products in pyrite mediated systems is in progress with an aim of fabricating H<sub>2</sub>O<sub>2</sub> absent Fenton system for pollution control.

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# Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.colsurfa.2011.12.054.

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