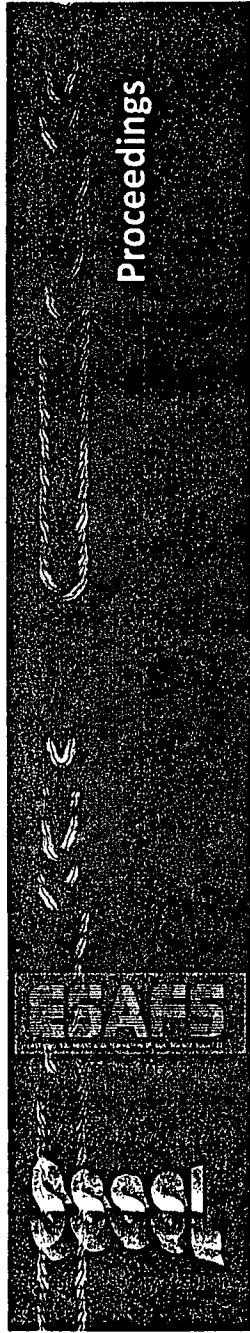


Dr. Naddeeshan

ENVIRONMENTAL ENGINEERING /
Electrochemistry research group

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PROCEEDINGS OF
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THE EAST AND SOUTHEAST ASIA FEDERATION OF
SOIL SCIENCE SOCIETIES

Soil, A Precious Natural Resource:
Agricultural Ecosystems, Environmental Health &
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THE ZETA POTENTIAL AND IR SPECTROSCOPIC MEASUREMENTS OF
PYRITE-CARBOFURAN INTERACTIONSN. Walelawala¹, R. Weerasooriya^{1,2*}, N. Nanayakkara¹, L. Jayarathne¹,
S.P. Indrarathna³ and A. Bandara¹¹ Dept of Chemistry, Faculty of Science, University of Peradeniya, Peradeniya, Sri Lanka² Institute of Fundamental Studies, Hantana, Kandy, Sri Lanka³ Dept of Soil Science, Faculty of Agriculture, University of Peradeniya, Peradeniya, Sri Lanka

* Corresponding Author. rohan@uwu.ac.lk

Introduction

Pyrite, FeS₂ is ubiquitous in sulfate reducing environments, and it plays a key role in many natural processes such as acid mine drainage, redox cycling of metals at oxic - anoxic boundaries and degradation of pollutants. Disulfide groups on the pyrite surface (S₂²⁻) are proposed electron donor in the oxidation by different oxidants. Pyrite is also of interest as a material for solar cells due to its environmental compatibility and very high light absorption coefficient. In this research we aimed at determining the chemistry of pyrite - water interface using ζ potential or electro kinetic measurements and FTIR spectroscopy. Particular attention was paid to examine the effects of carbofuran adsorption on the behavior of electro kinetic potential data. When combined with spectroscopic data, the ζ potential data can be used to characterize the behavior of adsorbing species in the near vicinity of the interfacial region.

Keywords: Pyrite, ζ potential, IR spectroscopy, Carbofuran

Materials and Methods

The pyrite samples used were handpicked from a vein graphite deposit in Bogala, Sri Lanka. Three samples were collected from the graphite vein of about 2 m³ to prepare a composite sample. The solid suspension was rinsed well with distilled water till the pH was around 2. Rapid electro kinetic titrations were performed to determine ζ potential of pyrite on 100 ml suspensions in a water-jacketed reactor at 0.001 and 0.01M NaClO₄. These measurements were used to calculate ζ potential using Helmholtz-Smoluchowski equation (Smoluchowski, 1921). In order to measure the ζ potential of carbofuran-pyrite suspensions, the batch reactor was spiked with desired concentration of carbofuran within 20 - 200 μ M. Infra red (IR) analyses were carried out using a Fourier Transform Infra Red Spectrometer at 4 cm⁻¹ spectral resolutions (Nicolet 6700).

Results and Discussion

Based on ζ potential measurements the iso-electric point is observed around pH 1.40-1.70. This is in agreement with the p*H*_{zpc} of 1.77 for pyrite (Weerasooriya, 2005). As shown in Figure 1 in the presence of carbofuran the values of ζ potential moved towards less negative direction which indicates direct surface interactions. At excess concentrations of ~200 μ M carbofuran, the ζ potential vs. pH curve convexed up yielding iso-electric points around pH 4 and 6. It has been suggested that the formation of oxidation phases such as iron oxy-hydroxides are accounted for double iso-electric points (Appelo and Postma, 2009).

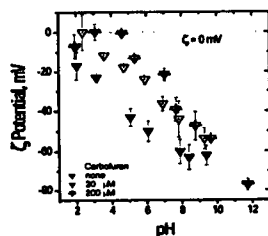
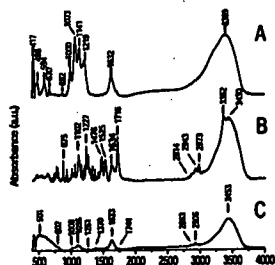
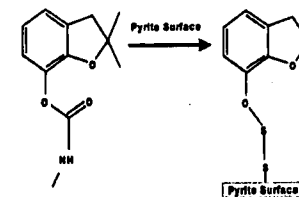
Fig. 1. Variation of ζ potential of pyrite in the presence of carbofuran concentration

Fig. 2. Infra red spectra of A) pyrite (A), carbofuran (B) and pyrite-carbofuran system (C)

If such arguments are valid, then the double iso-electric points should be observed in all instances irrespective of carbofuran loading and an inert atmosphere has been maintained ensuring minimum contact with the ambient conditions. Therefore, it is believed that the formation of the possible ferric hydroxide phase to be identified) yet is promoted in the presence of high doses of carbofuran. Fourier Transform Infrared Spectroscopy was utilized to examine the interactions of carbofuran with the pyrite surface [Figs. 2 (A-B)]. In the region of high frequencies from 3500 to 3800 cm⁻¹, the observed absorption bands, i.e. wideband at 3389 cm⁻¹, characterize the vibrations of surface hydroxyl groups. As shown in Fig. 2. (A), pyrite contains a characteristic discrete IR spectrum in the 700 - 1220 cm⁻¹ range, often referred as lattice vibrations region. 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. In par with these arguments, the bands in the region of 1200 - 882 cm⁻¹ are considered as characteristic of pyrite. Remarkably IR bands of pyrite at 1141, 1073, 1000, 882 and 1219 cm⁻¹ are discrete and sharp. The IR spectrum of pyrite after interactions with carbofuran is shown in Fig. 2 (C). 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⁻¹ indicates possible breakdown of the C-N bond yielding surface complex shown.



Conclusions

Variations of ζ potential and IR spectroscopic data with respect to bare pyrite point to direct interactions of carbofuran with heterogeneous surface sites. These sites seem to catalyze carbofuran degradation, when in contact with the pyrite for a long period.

Acknowledgement

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