

Kinetics Modelling of Partial Degradation of Carbofuran by Pyrite

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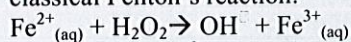
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Introduction

Fenton Process is initiated by the formation of hydroxyl radical in accordance with the classical Fenton's reaction:



If the product Fe^{3+} is reduced, the Fe^{2+} is regenerated for the next Fenton cycle; hence, Fe^{3+} acts as an auto-catalyst. This reaction is also known to occur when Fe^{2+} is present in solid phase (Cohn *et al.*, 2006; Kwan and Voelker, 2003; Watts *et al.*, 2003). The slow conversion of $\text{H}_2\text{O}_2 \rightarrow \text{OH}^{\cdot}$ when magnetite, iron hydroxides, or pyrite are present is ascribed to a Fenton like mechanism (Cohn *et al.*, 2006).

In nature pyrite is the most abundant of metal sulfides. In Sri Lanka pyrite is an unwanted substrate in graphite industry. It is intimately associated with graphite by degrading the quality of the nation's graphite resource and it is confirmed that pyrite can be used as a starting material for purification of the water polluted with organic pollutants in both the presence and absence of light (Weerasooriya *et al.*, 2006). When properly fabricated, pyrite based OH^{\cdot} generation technology will hold a great promise in water treatment industry due to its simplicity, cost-effectiveness, and environmentally friendliness.

Carbofuran (2,2-dimethyl-2,3-dihydro-1-benzofuran-7-yl methylcarbamate) is a broad spectrum carbamate pesticide. Because of high water solubility of carbofuran (320 mg/liter at 25 °C) the risk of ingestion in to the human body is high Kidd and James (1991). Carbofuran, was selected for the present study with the aim of investigating its degradation in pyrite mediated aqueous environments under anaerobic conditions due to its wide use as an insecticide and nematicide in agricultural applications and high toxicity (Bachman *et al.*, 1999).

Methodology

Zeta potential values of pyrite were measured using a ZETA-METER SYSTEM 4.0 in various pH values in the presence of carbofuran. Infra red (IR) analyses were carried out using a Fourier Transform Infra Red Spectrometer at 4 cm^{-1} spectral resolutions (Nicolet 67000). To elucidate degradation products of carbofuran, the pyrite mediated systems were monitored with RP-HPLC (Reversed phase High-Performance Liquid *Chromatography*) and gas chromatography-mass spectroscopic (GC-MS) methods.

Results and discussion

Surface charge, hence the zeta potential of pyrite is a function of potential determining ions, in the present case, i.e. H^+ , OH^- , S^{2-} and Fe^{2+} (Weerasooriya and Tobschall, 2005). Any specifically adsorbed species on the surface will also affect the zeta potential (or surface charge). Figure 01 shows zeta potential as a function of pH for three $NaClO_4$ concentrations. The iso-electric point is observed around pH 1.40-1.70. The curves show a symmetric behavior over the common cross point. That observation is typical for an electrolyte that do not specifically adsorbed. According to the Figure 02, in the presence of carbofuran, the values of zeta potential moved towards a less negative direction. It indicates the direct surface interactions. Upon the carbofuran loading from $\sim 20 - 200 \mu M$, pH_{IEP} was shifted from 2.4 to 4.5. That provides confirmatory evidence of its intimate surface interactions, and these interactions ultimately enhanced upon auto-oxidation of carbofuran by pyrite.

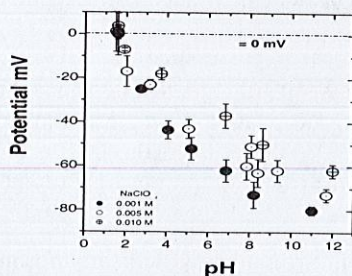


Figure 01: Variation of zeta potential of pyrite as a function of solution pH for $NaClO_4$ solutions of 0.001M, 0.005M and 0.01 M

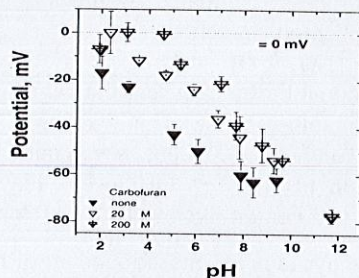


Figure 02: Variation of zeta potential of pyrite as a function of pH in 0.01M $NaClO_4$ in the presence of carbofuran

As shown in the Figure 03 the variations of IR spectrum of pyrite – carbofuran mixture were monitored with respect to time for a period of 0.5 hour. With the time a clear decrease was observed in the intensity of the IR band at $3363 cm^{-1}$ due to $-NH_2$ stretching. According to the IR spectral data of bare pyrite, it does not show any variations in the vicinity of $3363 cm^{-1}$. The band at $3363 cm^{-1}$ appeared as a result of carbofuran and pyrite interactions.

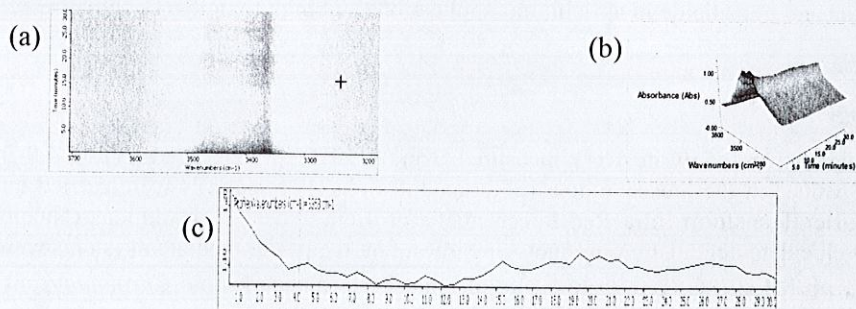


Figure 03: Time resolved IR spectra of pyrite-carbofuran system. The data collection under the transmission mode; time-step 0.5 s. Red circled spectral region monitored for rate determination. (a) Band intensity variation with time. (b) Variation of absorbance with time. (c) Intensity variation of the band at $3364/3 cm^{-1}$ with time.

Initial conditions: $\frac{[\text{carbofuran}]}{[\text{pyrite}]} \sim 5$

A - 2,3-dihydro-3-oxo-2,2-dimethyl
benzofuran-7-ol

B - 2,3-dihydro-2,2-
dimethylbenzofuran-7-yl-formate

C - 2,3-dihydro-3-hydroxyl-2,2-dimethyl
benzofuran-7-ol

D - 2,3-dihydro-2,2 dimethylbenzofuran-
7-yl methylcarbamate

Figure 04: Mass spectroscopic fragmentation patterns of carbofuran and its degradation products.

Conclusions

When the pH \sim 1.7-2.0 the partial degradation of carbofuran occurs with a highest efficiency in the presence of pyrite. Dominant degradation products of the carbofuran degradation process are A, B, C with some unidentified intermediates due to low resolution of the mass spectrometer. In the presence of natural pyrite, nearly 40% of carbofuran degraded within an hour.

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