Inhibition of bioleaching processes by organics from solvent extraction

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Abstract

The influence of the presence of an organic phase composed of 15% LIX 64 as extractant and kerosene as solvent on the ferrous iron biooxidation has been studied. It was found that the specific biooxidation rate decreased as the organic concentration increased form 0 to 60 ppm; further increase in organic concentration up to 800 ppm had no effect on it. The lag time increased with an increase in organic concentration in the whole range. The inhibition effect was more pronounced in shake-flaks than in static conditions, suggesting that the inhibitory effect has a chemico-biological nature instead of a physical one. Pretreatment of the liquor by activated carbon completely removed the inhibitory effect both in synthetic and real liquors.

Keywords: Biooxidation, solvent extraction, Thiobacillus ferrooxidans, bacterial inhibition, LIX 64, kerosene.

1. Introduction

Bioleaching of sulphide minerals is a hydrometallurgical process whereby the leaching of sulphides is catalyzed by microorganisms that get their energy for growth from oxidation of inorganic substances. Of them, *Thiobacillus ferrooxidans* has the ability to oxidize sulphur and sulphur compounds as well as ferrous iron in solution [1].

In recent years, bioleaching has been widely applied at industrial scale due to its features of low cost and non-pollutant process, without strict requirements of raw material composition, and suitable for the treatment of complex and low-grade ores. Currently, more than 15% of the world´s primary copper is produced by bioleaching applied to low-grade secondary copper sulphide ore, by a specific process named BTL (Bacterial Thin Layer) [2]. This process, developed in 1985 by Sociedad Minera Pudahuel (Chile), has been rapidly adopted by the main copper-producing countries (USA, Mexico, Peru, Bolivia and Chile, among others). A considerable increase in copper production by biotechnological methods is expected in the coming years with the application of the IBES process (Indirect Bioleaching with Effects Separation Process) and BRISA process (Biolixiviación Rápida con Separación de Acciones) to flotation concentrates [3, 4].

In both processes, bioleaching is performed in two separate stages: the chemical oxidation of sulphides by ferric iron (chemical stage) and the biological oxidation of the ferrous iron produced (biological stage).

Through bioleaching process, copper is obtained as soluble sulphate and is recovered from the leach solution by solvent extraction and electrowinning (SX-EW). The leach solution is mixed with an organic solvent, the phases are separated, the aqueous phase (aqueous raffinate) is recycled to leaching (as the input liquor to the

bioleaching stage) to reduce acid cost and lower environmental pollution, and copper is recovered from the organic solvent. Figure 1 shows a scheme of the process. The recycled leach liquor will contain different amounts of organic matter depending on the solubility of the solvent used and the mechanical losses due to entrainments, which may affect bacterial activity. Since the microorganisms are strict autotrophs, organic matter is potentially inhibitory to their growth thus slowing the kinetics of copper dissolution and leaching. The dissolved organics adversely affect bacterial activity and, in addition, represent an economic loss. It has been shown that the commercially available organic solvents used primarily for extraction of copper from aqueous leach liquors have a detrimental effect on the chalcopyrite oxidation ability of *Thiobacillus ferrooxidans*, which is the most important microorganism in microbial leaching, and affects the leaching efficiency [5, 6]. When bioleaching is carried out in two separate stages following either the IBES process or the BRISA process, the influence of the organic solvents on the biooxidation of the ferrous iron must be studied in order to determine their influence on the whole bioleaching process. In relation with the ferrous iron oxidation ability of ferrooxidant bacteria, the influence of different solvent extraction reagents on the respiration activity of *Thiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* has been established [7]. As far as the authors know, there is only one paper published concerning the effect of solvent extraction reagents on the ferrous iron oxidation rate [8]. This demonstrated that the ACORGA type reagent M-5640, as well as their components (ACORGA reagent and kerosene) are inhibitors of the bacterial oxidation of iron. The subject of the current paper is the study of how the ferrous iron oxidation rate is affected by dissolved organic compounds used in solvent extraction of copper. The extractant LIX 64 is regarded as one of the most specific extractants for copper recovery from sulphate solutions and it is usually used in a concentration of 15% dissolved in organic solvents such as kerosene. Consequently, this solvent composition was tested for its influence on the bacterial activity. In the present work, the inhibitory effect is determined by measuring the ferrous iron biooxidation.

2. Experimental

The culture used as inoculum was originally isolated from Riotinto mine drainage waters. It consisted mainly of *Thiobacillus ferrooxidans*, *Leptospirillum ferrooxidans* and some heterotrophic bacteria (related mainly to *Acidophilium*). It was routinely maintained on a modified Silverman and Lundgren 9K nutrient medium at pH 1.25 [9].

The culture medium was composed of basal salts of the modified Silverman and Lundgren 9K nutrient medium with 6 g/l of ferrous iron as ferrous sulphate and an organic phase composed 15% of LIX 64 in kerosene. Various concentrations of the organic phase were used.

Ferrous iron biooxidation tests were conducted in 250 ml Erlenmeyer flasks containing 100 ml of solution (80 ml of culture medium and 20 ml of inoculum). The pH was adjusted to 1.25 with sulphuric acid. Static tests were carried out in a thermostated chamber; agitated tests were carried out on an orbital shaker at 180 min^{-1}, thermostated by forced air circulation. The temperature was fixed at 31ºC. At intervals, 1 ml samples were taken and analysed for ferrous iron by automatic titration with standard potassium dichromate.

The activated-carbon treatment was conducted by passing the liquor through a packed-bed column of 2 cm in diameter and 25 cm in height filled with 3-mm particles of activated carbon. The flow rate was 96 ml/h.

3. Results and discussion

The ferrous iron biooxidation is based on the following reaction:

$$4FeSO_4 + O_2 + 2H_2SO_4 \rightarrow 2Fe_2(SO_4)_3 + 2H_2O$$

The kinetic data of this reaction have been evaluated from the Ln $[Fe^{3+}]$ vs time curve in terms of three kinetic parameters:

- Specific biooxidation rate (μ_{Fe}), which is the slope of the straight section of the curve (exponential phase). This is the maximum biooxidation rate and is related to the maximum bacterial growth rate. It has been demonstrated that the specific biooxidation rate is equal to the specific growth rate (μ) if an assumption is made that the number of bacteria per mass of ferric iron produced (yield coefficient) is constant in the whole range of iron concentration [10].
- Lag phase (θ_l), which is the period of time from the inoculation till the beginning of the exponential phase. This indicates the time that a bacterial culture needs to be adapted to a particular medium.
- Generation time (g), which is the time required for a bacterial population to double under given conditions in the exponential phase. Its value is $g = Ln\ (2/\mu)$

3.1. Static ferrous iron biooxidation tests

Kinetic curves for these tests are shown in figures 2, 3, and 4 and figure 5 shows the kinetic parameters determined from them. The results obtained show that the specific biooxidation rate decreased as the organic concentration increased from 0 to 60 ppm; a further increase in the organic concentration up to 800 ppm had no significant effect on μ. The lag phase increased with an increase in organic concentration over the whole range. A supernatant organic phase was observed in tests with organic concentrations in the range from 60 to 800 ppm. Since the specific biooxidation rate did not decrease in that range of concentration, the supernatant organic phase did not act as a barrier for oxygen diffusion.

3.2. Agitated ferrous iron biooxidation tests

Figure 6 shows the kinetic parameters of these tests. As it can be observed, the influence of the organic concentration on kinetic parameters was stronger than in stationary conditions. As the organic concentration increased, the specific biooxidation rate decreased and the lag phase and the generation time increased, these effects being more pronounced than in the corresponding static tests. Besides, it was observed that the organic phase was dispersed or dissolved in the aqueous phase unlike the supernatant organic phase observed in static tests. These results suggests that the inhibitory effect has a chemico-biological nature instead of a physical one (barrier exerted by the organic phase to oxygen diffusion).

3.3. Activated-carbon pretreatment

Figures 7 and 8 show the ferrous iron biooxidation kinetic curves for static tests of a synthetic liquor with 200 ppm of organic phase, and real liquors, (pregnat solution and aqueous raffinate from a bioleaching plant in Cerro Verde, Peru), with the same approximate organic concentration. Kinetic curves after the activated-carbon pretreatment are also shown. Table 1 shows the specific biooxidation rate determined from them. In both cases, the specific biooxidation rate increased after the activated-carbon pretreatment, the values becoming similar to those of an organic-free medium (control). Therefore, the observed inhibitory effect of the organic phase, a mixture of LIX 64 and kerosene, on the ferrous iron biooxidation has been successfully removed by an activated-carbon pretreatment.

One of the main factors affecting the economic efficiency of indirect bioleaching is the rate of ferrous iron biooxidation. As a result, the aqueous recycling liquor (either pregnant solution or aqueous raffinate) should be treated with activated carbon to remove the organic matter (dissolved or entrained) before being returned to leaching.

4. Conclusions

1. The presence of organic matter coming from solvent extraction of copper in the culture medium exerts an inhibitory effect on the oxidative activity of iron-oxidizing bacteria that is revealed by:

a) A decrease in the ferrous iron specific biooxidation rate which is proportional to the organic concentration up to 60 ppm and remains constant at higher concentrations.
b) An increase in the lag phase which is proportional to the organic concentration in the studied range.

2. Shaking enhances the bacterial growth in the absence of organic matter and reduces it in its presence. The results suggest that the inhibition has a chemico-biological nature instead of having a physical one.

3. A pretreatment by activated carbon completely removes the inhibitory effect.

Acknowledgements

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LEGENDS TO ILLUSTRATIONS

Fig. 1. Scheme of copper extraction by Indirect Bioleaching with Effects Separation and SX-EW.

Fig. 2. Influence of organic matter concentration (15% LIX 64 in kerosene) on the ferrous iron biooxidation kinetic.

Fig. 3. Influence of organic matter concentration (15% LIX 64 in kerosene) on the ferrous iron biooxidation kinetic.

Fig. 4. Influence of organic matter concentration (15% LIX 64 in kerosene) on the ferrous iron biooxidation kinetic.

Fig. 5. Influence of organic matter concentration on the kinetic parameters of ferrous iron biooxidation. Static conditions.

Fig. 6. Influence of organic matter concentration on the kinetic parameters of ferrous iron biooxidation. Agitated conditions.

Fig. 7. Influence of the activated-carbon pretreatment on the ferrous iron biooxidation of a synthetic liquor with 200 ppm of organic matter. A: culture medium (control), B: culture medium + 200 ppm of organic matter, C: culture medium + 200 ppm of organic matter after activated-carbon pretreatment.

Fig. 8. Influence of the activated-carbon pretreatment on the ferrous iron biooxidation of a real liquor with 200 ppm of organic matter. A: culture medium (control), B: pregnant solution of the Cerro Verde Plant (200 ppm organic matter), C: aqueous raffinate of the Cerro Verde Plant (200 ppm of organic matter), D: aqueous raffinate after activated-carbon pretreatment.

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Table 1
Specific ferrous iron biooxidation rate of synthetic and real liquors before and after activated-carbon pretreatment.

Test	μ_{Fe} (h^{-1})
Culture medium, (Control , A)	0.0391
Synthetic liquor, 200 ppm organic matter	0.0184
Synthetic liquor after activated-carbon pretreatment	0.0359
Pregnant solution of the bioleaching Cerro Verde plant, 200 ppm organic matter	0.0241
Aqueous raffinate of the bioleaching Cerro Verde plant, 200 ppm organic matter	0.0131
Aqueous raffinate of the bioleaching Cerro Verde plant after activated-carbon pretreatment	0.0379

Figure 1

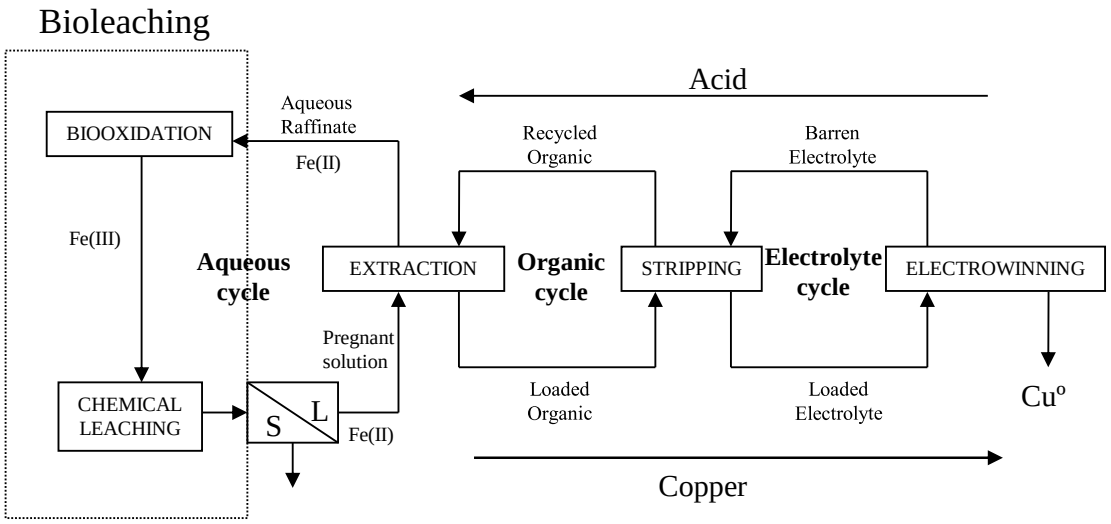


Figure 2

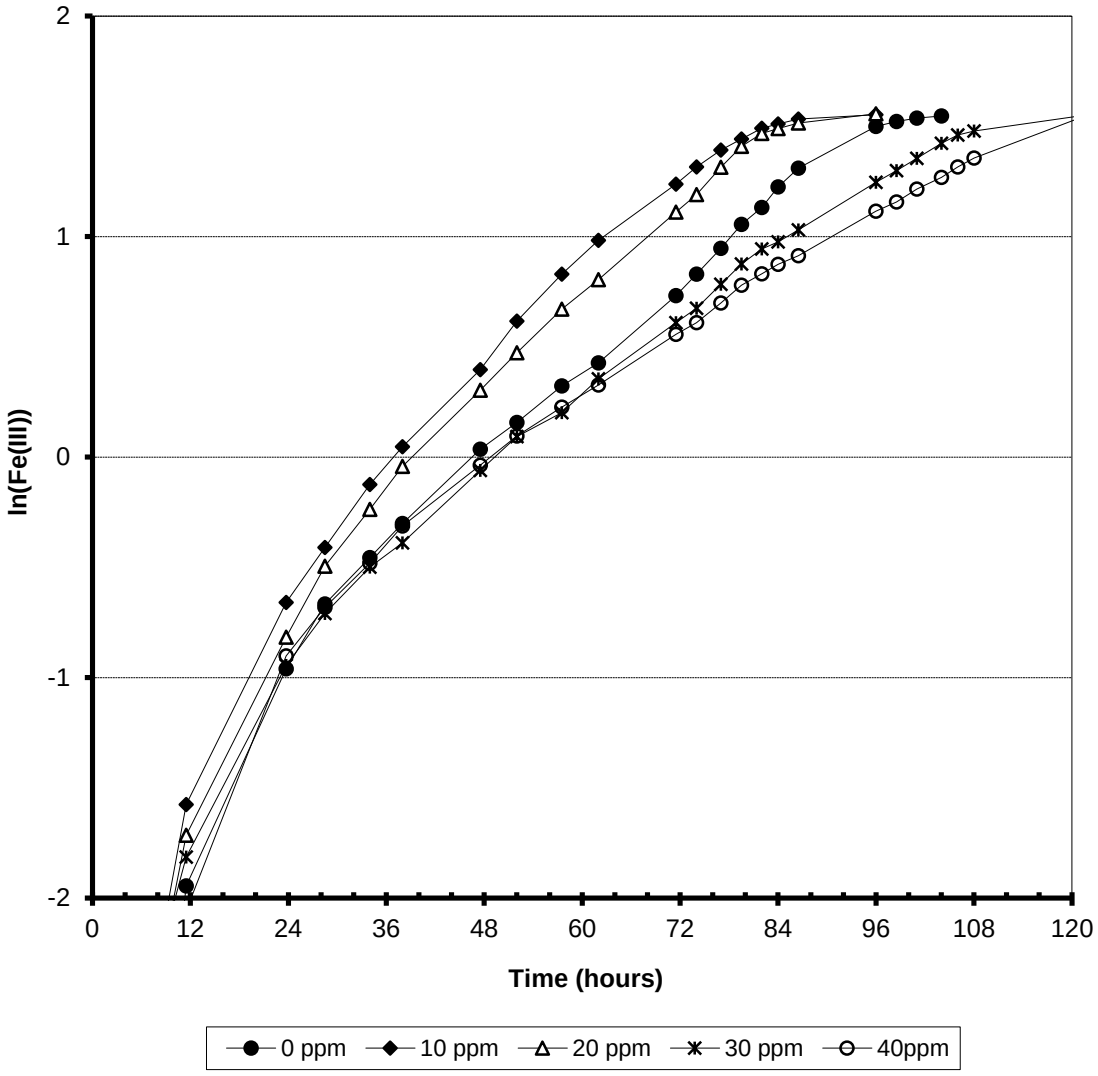

2
1
0
-1
-2
ln(Fe(III))
0
12
24
36
48
60
72
84
96
108
120
Time (hours)
0 ppm
10 ppm
20 ppm
30 ppm
40ppm

Figure 3

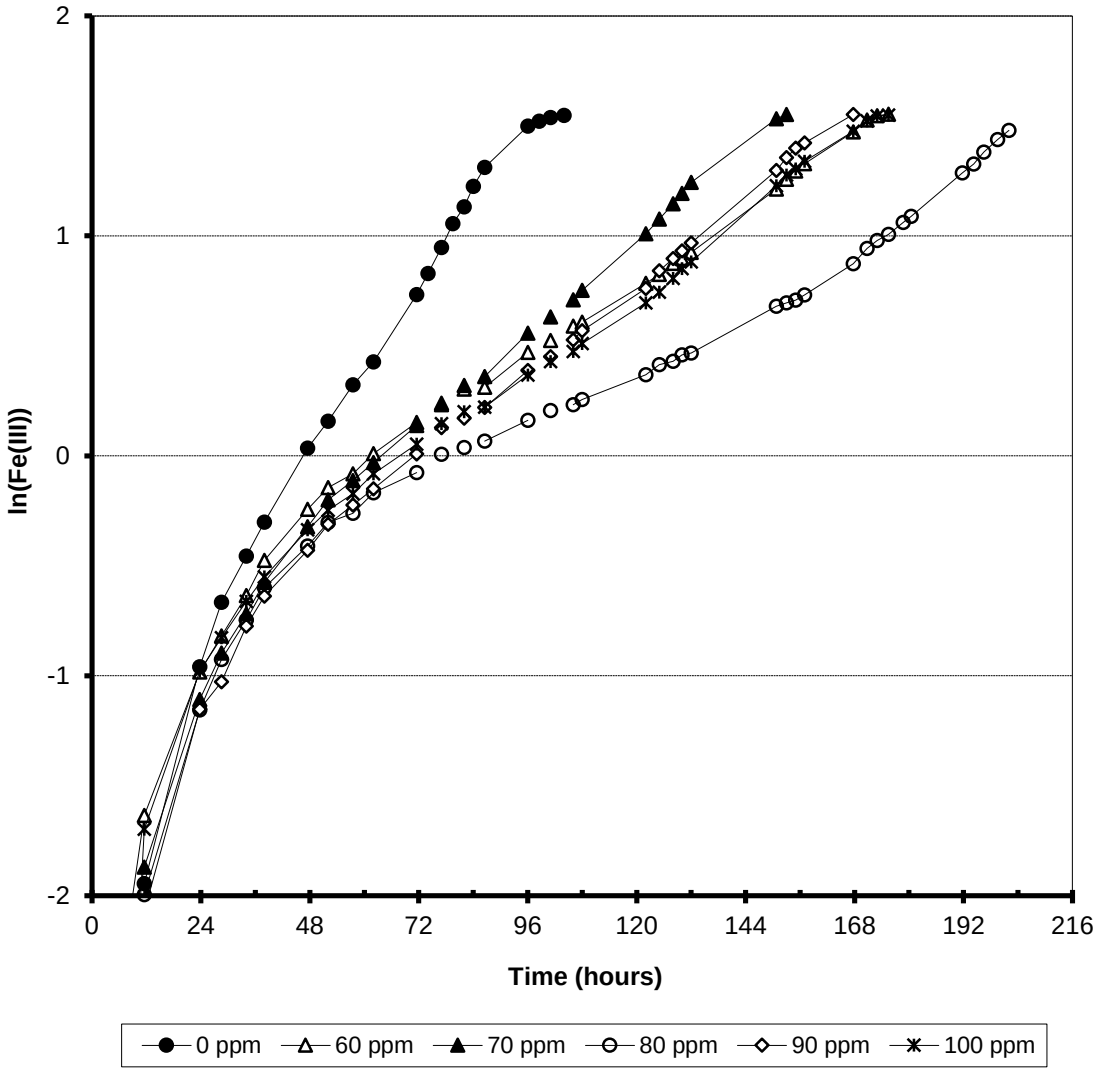

2
1
0
-1
-2
ln(Fe(III))
0
24
48
72
96
120
144
168
192
216
Time (hours)
0 ppm
60 ppm
70 ppm
80 ppm
90 ppm
100 ppm

Figure 4

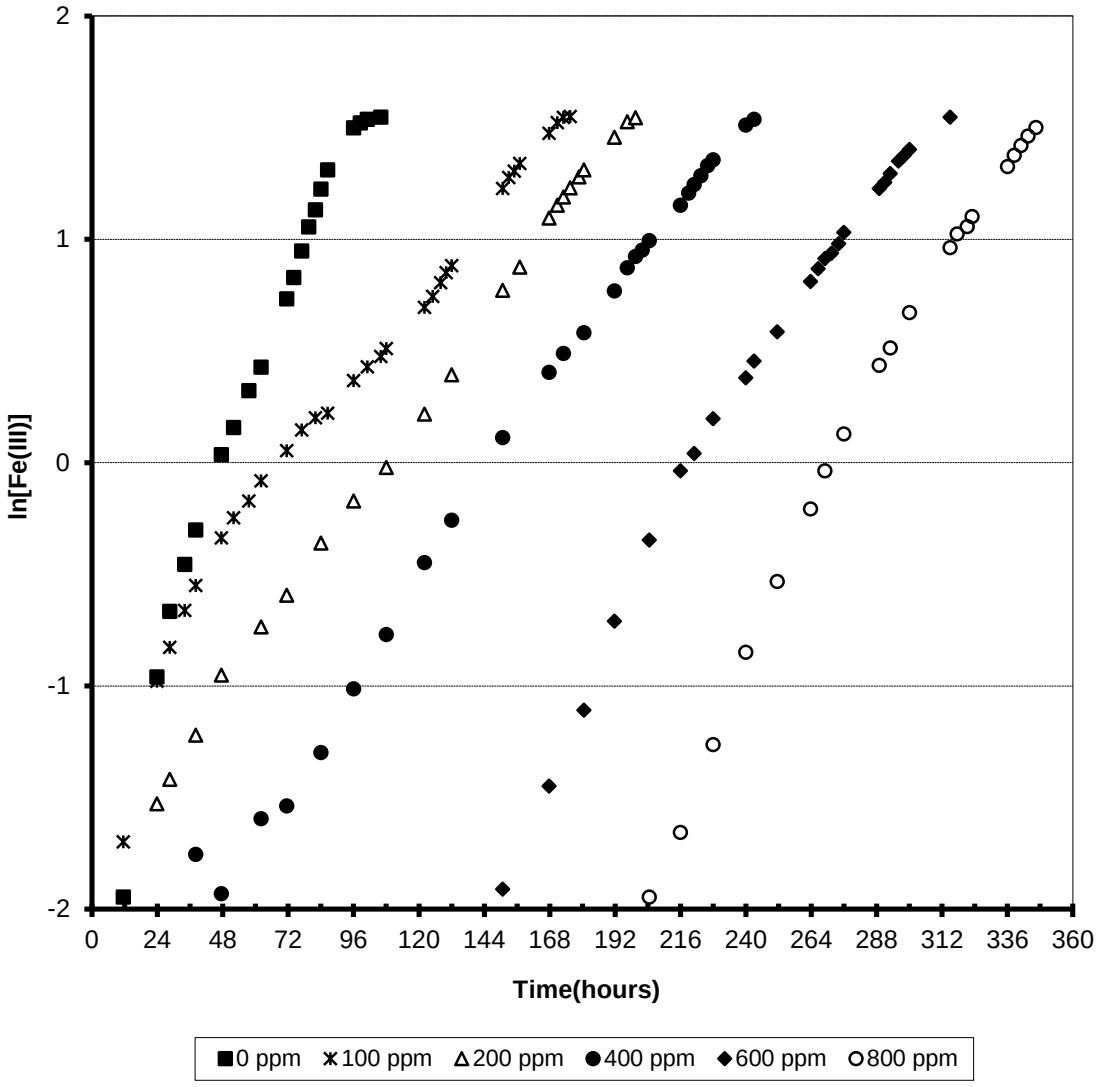

2
1
0
-1
-2
ln[Fe(III)]
0
24
48
72
96
120
144
168
192
216
240
264
288
312
336
360
Time(hours)
0 ppm
100 ppm
200 ppm
400 ppm
600 ppm
800 ppm

Figure 5

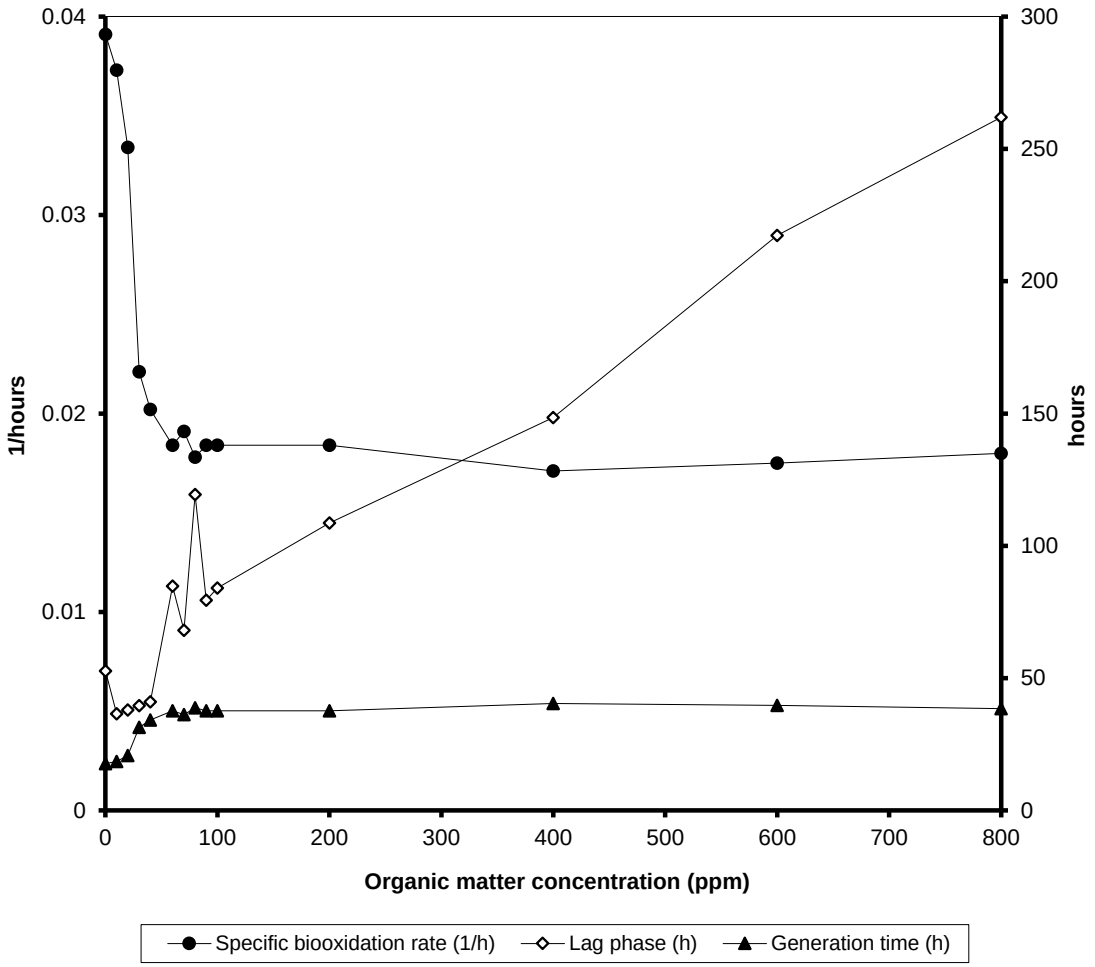
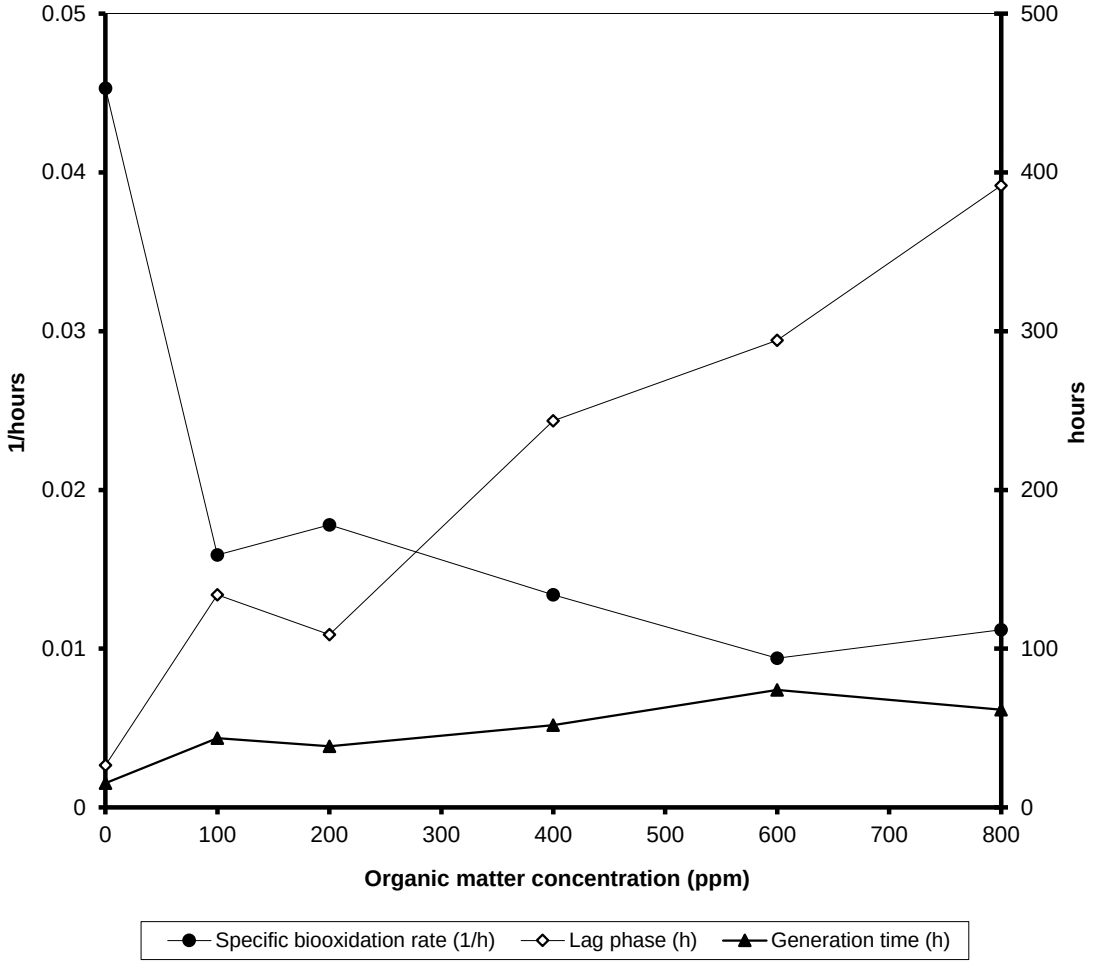

0.04
0.03
0.02
0.01
0
1/hours
300
250
200
150
100
50
0
hours
0
100
200
300
400
500
600
700
800
Organic matter concentration (ppm)
Specific biooxidation rate (1/h)
Lag phase (h)
Generation time (h)

Figure 6


0.05
0.04
0.03
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0.01
0
1/hours
500
400
300
200
100
0
hours
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100
200
300
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500
600
700
800
Organic matter concentration (ppm)
Specific biooxidation rate (1/h)
Lag phase (h)
Generation time (h)

Figure 7

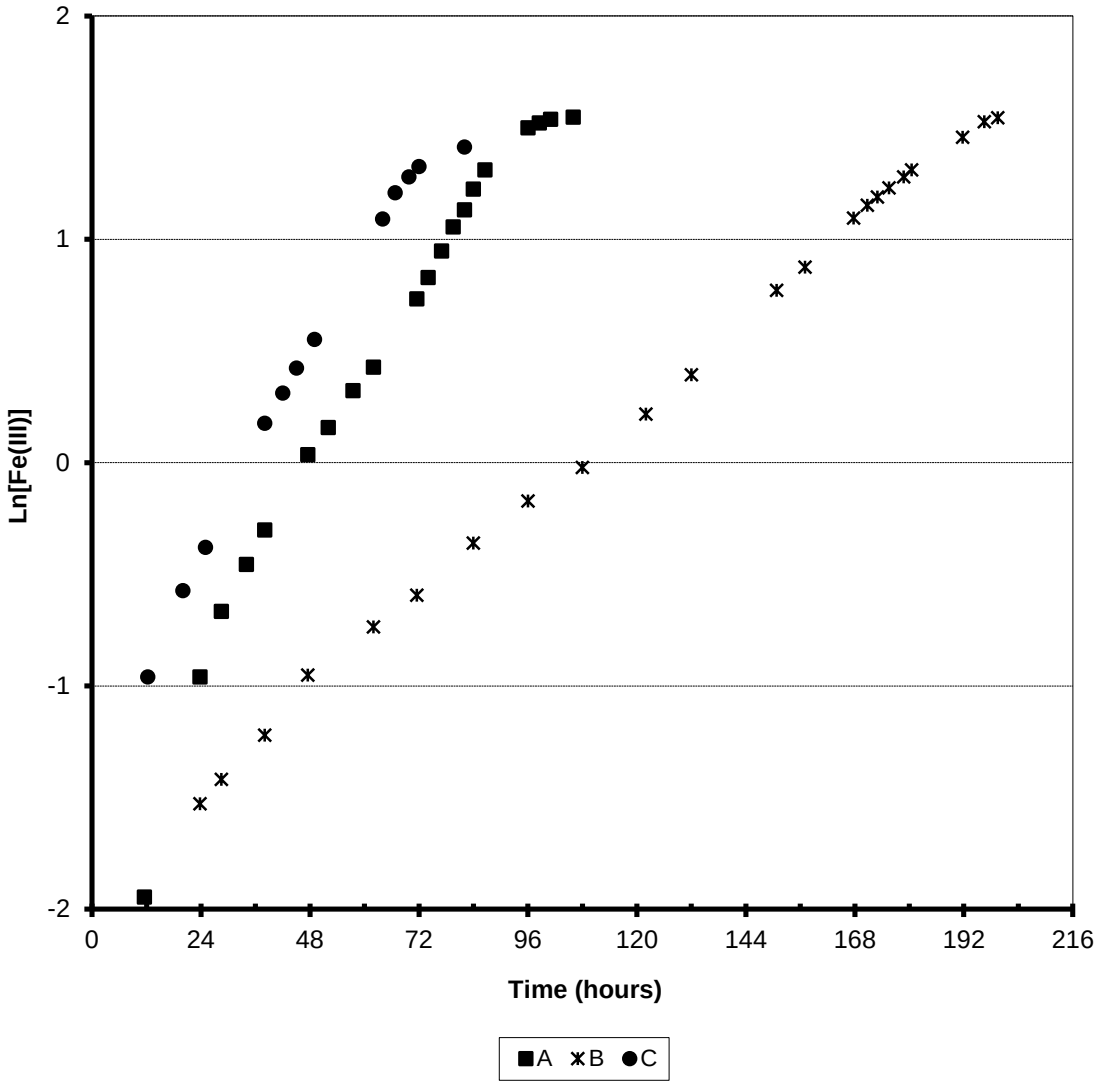
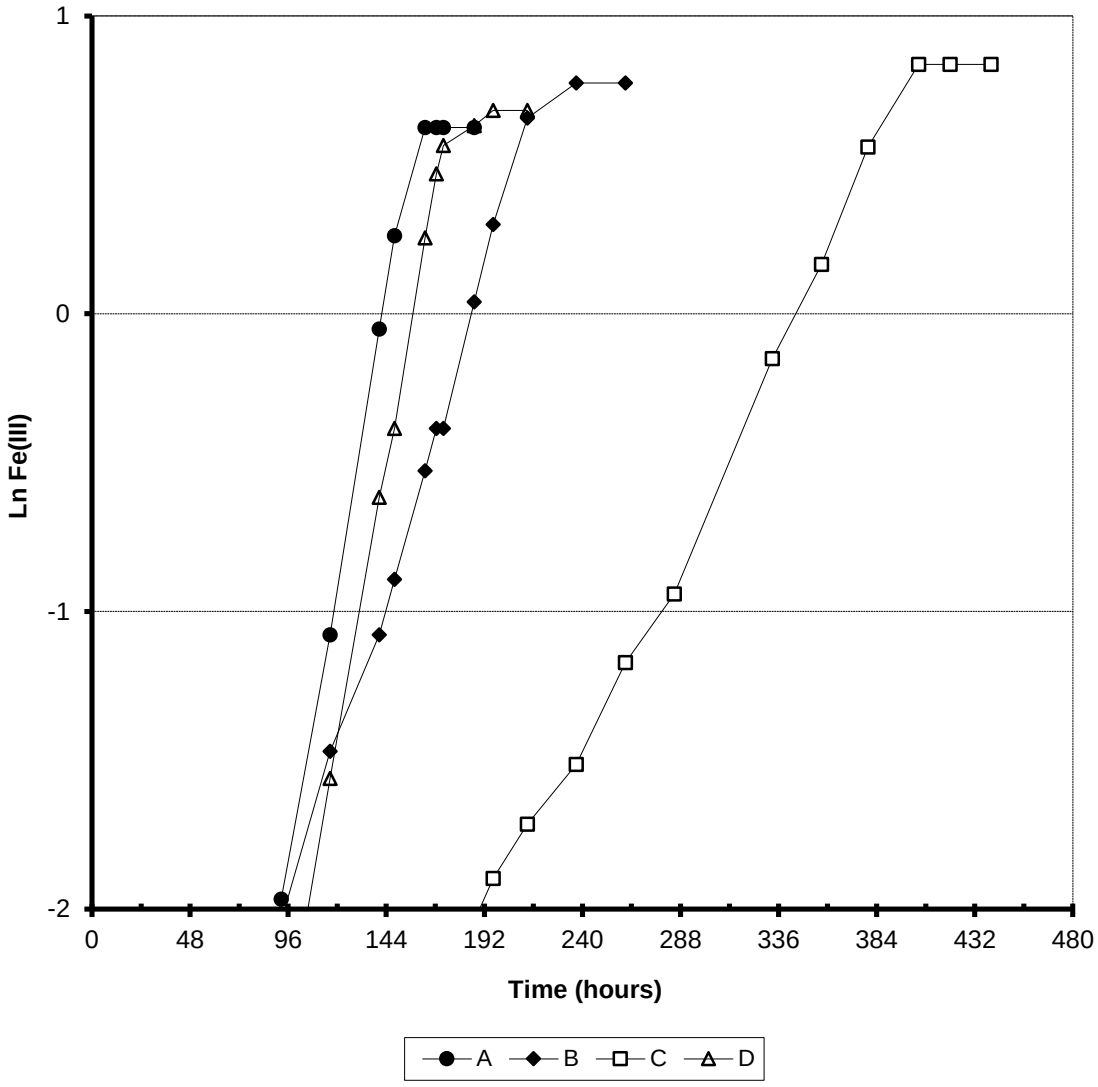


Figure 8


1
0
-1
-2
Ln Fe(III)
0
48
96
144
192
240
288
336
384
432
480
Time (hours)
A
B
C
D