

SHORT COMMUNICATION

**Oxidation of dibenzothiophene as a model substrate for the removal of organic sulphur from fossil fuels by iron(III) ions generated from pyrite by *Acidithiobacillus ferrooxidans***

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*Abstract:* Within this paper a new idea for the removal of organically bonded sulphur from fossil fuels is discussed. Dibenzothiophene (DBT) was used as a model compound of organic molecules containing sulphur. This form of (bio)desulphurization was performed by an indirect mechanism in which iron(III) ions generated from pyrite by *Acidithiobacillus ferrooxidans* performed the abiotic oxidation. The obtained reaction products, dibenzothiophene sulfoxide and dibenzothiophene sulfone, are more soluble in water than the basic substrate and the obtained results confirmed the basic hypothesis and give the possibility of continuing the experiments related to application of this (bio)desulphurization process.

*Keywords:* *Acidithiobacillus ferrooxidans*, iron(III) ion, DBT, oxidation, desulphurization.

INTRODUCTION

Among the various classes and numerous kinds of sulphur-containing organic compounds identified in fossil fuels the most represented is DBT, dibenzothiophene, and its derivatives. Therefore, this compound can be considered to be the model substrate of organically bonded sulphur in fossil fuels.<sup>1</sup> Thermodynamic computings showed that desulphurization of DBT is possible at pH 2.5 by the action of iron(III) ion generated by *Acidithiobacillus ferrooxidans* from pyrite, whereby sulphur is oxidized to sulphates, and the desulphurized DBT is transformed into forms more soluble in water.<sup>2</sup>

The scientific hypothesis of DBT removal from fossil fuels by the action of iron(III) ion generated by *A. ferrooxidans* is based on the following idea: "To con-

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vert DBT into a (water soluble) sulphur-free form by oxidation with bacterially generated–regenerated iron(III) sulphate from pyrite!" The hypothesis is schematically shown in Fig. 1.

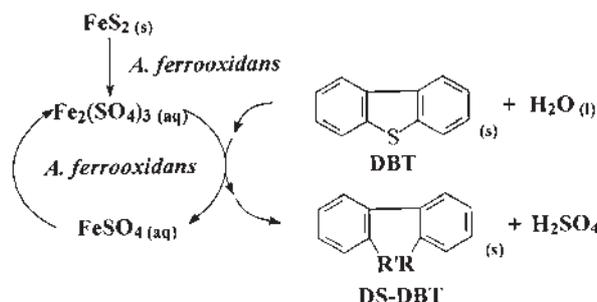
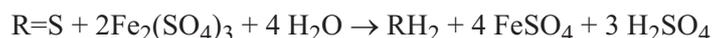


Fig. 1. Schematic presentation of hypothesis. DS-DBT – Desulphurized DBT R = R' = H and/or OH.

The hypothetical molecular chemical equation resulting from the hypothesis diagram has the following form:



Thermodynamic computations of DBT desulphurization ( $\text{R}=\text{S}$ ) to biphenyl ( $\text{RH}_2$ ) by the action of iron(III) sulphate according to this equation indicate that the Gibbs energy change of this process under standard conditions (unit activity and 298 K) and at pH 2.5 has the value  $\Delta G_{2.5}^0 = -168 \text{ kJ mol}^{-1}$ .<sup>3-7</sup> This means that the process can be spontaneously developed, being one of the proofs that theoretically the hypothesis is correct.

The presence of pyrite as the source of iron(III) ion (oxidant) together with DBT should favour the oxidation of thiophenic sulphur.

In the case the hypothesis is correct, this form of (bio)desulphurization would be performed by an indirect mechanism in which biogenously generated iron(III) ions would perform the abiotic oxidation.

The obtained iron(II) ions are included again in the "ferrous–ferric cycle" and thereby the cycle would be closed.<sup>5</sup>

#### EXPERIMENTAL

The basic model system contained 9K<sup>8\*</sup> iron-free medium with suspended DBT (25 mg/L) and pyrite concentrate (purity approx. 85 %; pulp density 2.0 % – equivalent to 9 gFe/L). The biotic tests were inoculated with a biomass of pure microbial culture isolated from the copper sulphide mine in Bor (Serbia), identified as *A. ferrooxidans*<sup>9</sup> (designation: V). The starting number of microorganisms was approx.  $10^9 \text{ mL}^{-1}$ . As the control, the same mixture but sterilized at 121°C (designation: S) was used. Uninoculated solution was used as a blank probe (designation: B). Desulphurization of DBT was tested by the shake-flask testing technique<sup>10</sup> with an initial pH of 2.5 and at a temperature of 28 °C for 30 d. Subsequently, solutions were prepared for analytical and structural investigations [multiple extraction with ethyl acetate (EtOAc) in an ultrasonic bath for 30 min] which is described elsewhere.<sup>2</sup>

\* Original designation from the cited literature of medium for the growth of *A. ferrooxidans*, which originally contained 9 g of iron(II) per liter.

*Analytical methods*

UV spectrophotometry vs. EtOAc; FT-IR spectra. KBr pellet (approx. 1:100); NMR spectra.  $^1\text{H-NMR}$  in chloroform-*d* (at 200 MHz).  $^{13}\text{C-NMR}$  in DMSO-*d*<sub>6</sub> (at 50 MHz), ambient temperature; Gas chromatography (GC) with FID; GC-MS. GC equipped with a split/splitless injector (1:99) operated at 244 °C. Transfer line at 270 °C, coupled to a mass spectrometer. Iron source temperature 170 °C, EI, 70 eV, 0.1 mA.

## RESULTS

All analytical data (UV, FT-IR and NMR spectra, not shown here) indicate changes in the structure of the DBT molecules. GC-MS proved the presence of DBT molecule oxygen derivatives as an intermediate in the desulphurization process.

On the basis of MS Library NIST 02, Software Version 2.0d, and quantitative GC analysis, DBT derivatives were detected, as shown in Table I.

TABLE I. Proportion of DBT and oxidation products from different model systems

Model system	B	S		V		
Compound	DBT	DBT	DBT-O <sub>2</sub> <sup>a</sup>	DBT	DBT-O <sup>b</sup>	DBT-O <sub>2</sub>
% <sup>c</sup>	100	92	8	38	22	40

<sup>a</sup>DBT-O<sub>2</sub>: dibenzothiophene sulfone (dibenzothiophene *S,S*-dioxide); <sup>b</sup>DBT-O: dibenzothiophene sulfoxide (dibenzothiophene *S*-oxide); <sup>c</sup> % in relation to the initial concentration of DBT

In the model system with viable microorganisms, 62 % of the extracted DBT was in the oxidised state.

The obtained gas chromatographs of the model system with pertaining to DBT and its derivative structures and their *m/z* values based on mass spectrometry are presented in Figs. 2-4.

The presence of the DBT-O<sub>2</sub> signal in the sterilized model system shows that oxidation of DBT had nevertheless occurred to a certain extent, which is due to abiotic oxidation by residual iron(III) ion present in extracellular polymeric substances (EPS) of *A. ferrooxidans*.<sup>11</sup>

This fact indicates that DBT oxidation is of a completely abiotic type resulting from the action of iron(III) ions generated from pyrite in the biotic model system. The absence of the DBT-O signal in the sterile model system indicates that the limiting reaction is just the occurrence of this compound, while the following oxidation step to DBT-O<sub>2</sub> is considerably faster.

The obtained reaction products are more soluble in water than is the basic substrate. DBT-O is approx. 320 times more soluble than DBT and DBT-O<sub>2</sub> about 6 times, thereby directly reducing the concentration of organically bonded sulphur in fossil fuels by dissolving the more polar compounds resulting from oxidation by iron(III) ion.<sup>12</sup>

The results obtained confirm the basic hypothesis and give the possibility of continuation of experiments related to the application of this (bio)desulphurization process.

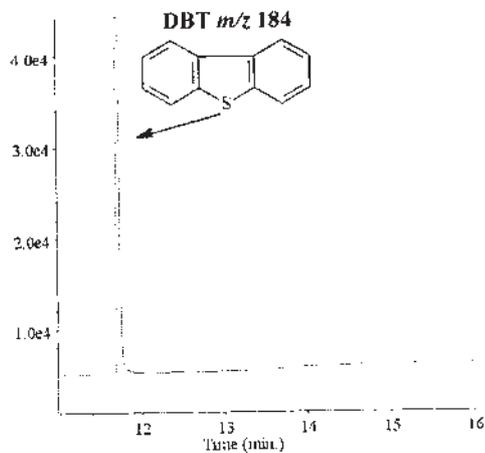


Fig. 2. Gas chromatogram of the products obtained with the Model system B.

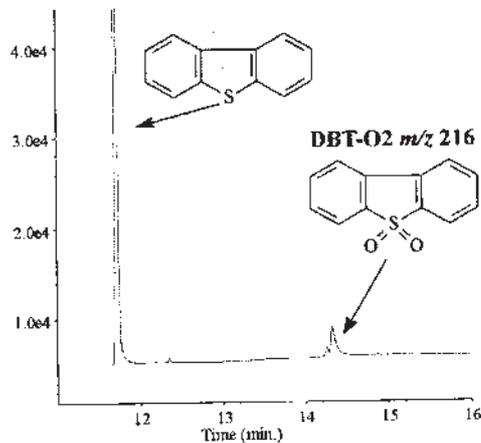


Fig. 3. Gas chromatogram of the products obtained with the Model system S.

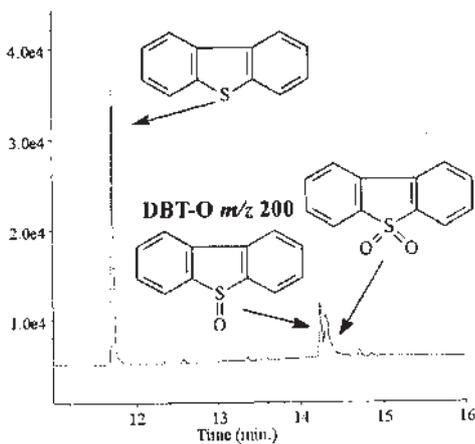


Fig. 4. Gas chromatogram of the products obtained with the Model system V.

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## ИЗВОД

ОКСИДАЦИЈА ДИБЕНЗОТИОФЕНА КАО МОДЕЛ-СУПСТРАТА ЗА  
ИЗДВАЈАЊЕ ОРГАНСКОГ СУМПОРА ИЗ ФОСИЛНИХ ГОРИВА ДЕЈСТВОМ  
ГВОЖЂЕ(III)-ЈОНА ГЕНЕРИСАНОГ ИЗ ПИРИТА ПОМОЋУ *Acidithiobacillus*  
*ferrooxidans*

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Основа овог рада је нова идеја за издвајање органски везаног сумпора из фосилних горива. Дибензотиофен је употребљен као модел-једињење органских молекула са сумпором који су присутни у фосилним горивима. Овај нови процес (био)десулфуризације се остварује индиректним механизмом, где се дејством *Acidithiobacillus ferrooxidans* из пирита генеришу гвожђе(III)-јони, који даље абиотички оксидују органски везани сумпор. Добијени реакциони производи дибензотиофен-сулфоксид и дибензотиофен-сулфон су вишеструко растворљивији у води у односу на почетно једињење. Добијени резултати потврђују основну хипотезу и дају могућност наставка експеримената за примену овог (био)десулфуризационог процеса.

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