

Degradation of Polycyclic Aromatic Hydrocarbons by the Copper(II)–Hydrogen Peroxide System

J. GABRIEL, V. SHAH, K. NESMĚRÁK, P. BALDRIAN, F. NERUD*

Laboratory of Biochemistry of the Wood-rotting Fungi, Institute of Microbiology, Academy of Sciences of the Czech Republic, 142 20 Prague 4, Czechia

fax +420 2 475 2384

e-mail nerud@biomed.cas.cz

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ABSTRACT. A non-enzymic system containing CuSO₄ (10 mmol/L) and hydrogen peroxide (100 mmol/L) was used for the degradation of three polycyclic aromatic hydrocarbons: phenanthrene, fluoranthene, and pyrene (all at 10 mmol/L). The

system degraded the compounds rapidly and efficiently. After 1 d at room temperature, more than 80 % of pyrene, phenanthrene, and fluoranthene disappeared. Several products are formed during the reaction including a black precipitate.

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants found in numerous aquatic and terrestrial ecosystems. Bacterial and fungal species are capable of PAHs degradation (Cerniglia 1992; Paszczynski and Crawford 1995). However, microorganisms degrade PAHs to a limited extent due to the physico-chemical properties of these compounds: low water solubility and the tendency to be adsorbed to the organic fraction of soil or sediments. Bacterial species require preconditioning – the cells must be pre-exposed to a significant concentration of the particular pollutant to induce the synthesis of degradative enzymes. The degradation of PAHs by white-rot fungi is at least in part a consequence of the mechanisms used by these microorganisms for lignin degradation (Field *et al.* 1993). In the case of laccase, PAHs degradation is based on nonspecific free radical mechanisms (Majcherczyk and Johannes 2000). An alternative approach for remediation is the use of free radicals-generating reactions. The role and participation of reactive oxygen species generated by different systems in living cells as well as in the degradation processes has recently been described (Sigler *et al.* 1999). Generation of radicals is also the basis of the Fenton reaction and related processes, including the reaction of copper(II) and hydrogen peroxide (Kocha *et al.* 1997). Such an artificial system can overcome the major disadvantages of microbial biodegradation – slow reaction rate and high costs. In this work, we used the system composed of copper(II) and hydrogen peroxide for the degradation of pyrene, phenanthrene and fluoranthene.

Acetonitrile solutions of phenanthrene, fluoranthene and pyrene (10 mmol/L) and their mixture containing each of the compounds at 10 mmol/L were incubated with CuSO₄ (10 mmol/L) and hydrogen peroxide (100 mmol/L) at room temperature. All experiments were done in triplicate and the reaction mixtures were analyzed after 1 d on a Hewlett Packard 1090 liquid chromatograph. Separations were performed isocratically at 25 °C with an analytical column Hypersil PAH 5 μ (150 × 4.6 mm). The mobile phase was acetonitrile–water (9 : 1, *V/V*), the flow rate was 0.5 mL/min and the compounds were detected at 230 nm.

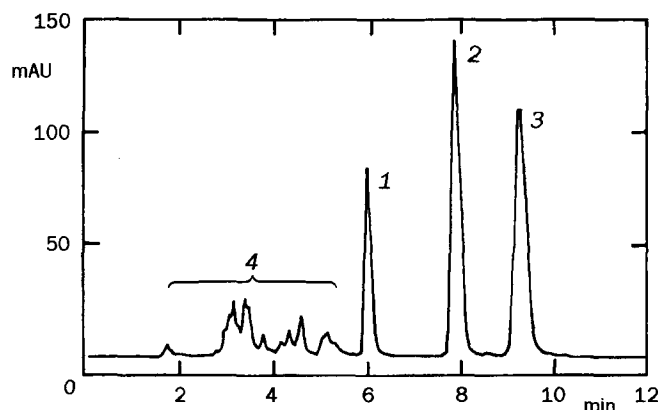
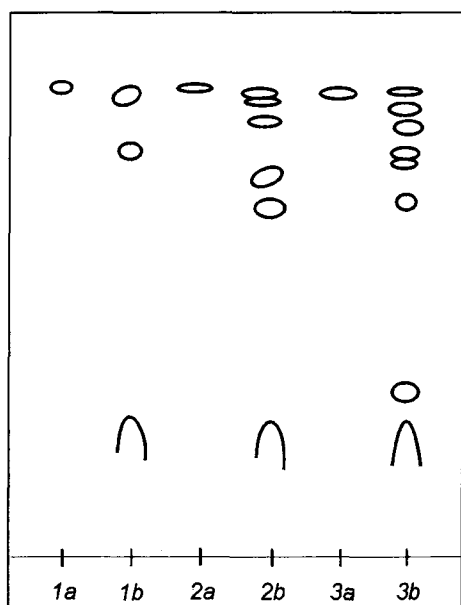
Thin layer chromatography of the oxidation products was performed with Silufol (UV 254; *Kavalier*, Czechia) silicagel sheets. Two different solvent systems, chloroform–methanol (48 : 1, *V/V*) and benzene–acetic acid–water (125 : 74 : 1, *V/V/V*) were used for the development of samples (Menn *et al.* 1993). Spots were visualized under UV light. The UV spectrum of the water-insoluble precipitate was recorded after washing with 0.5 mol/L HCl and subsequent solubilization in toluene on 8453 DAD UV–VIS spectrophotometer (*Hewlett-Packard*).

More than 80 % of phenanthrene, fluoranthene, and pyrene was degraded by the Cu^{II}–hydrogen peroxide system within 1 d (Table I). Many different products are formed during the reaction (Fig. 1). In addition to HPLC, TLC analysis also confirmed the presence of various products for each compound. A better resolution of polar products which remained at or near the origin of the TLC with the chloroform–methanol system, was achieved with benzene–acetic acid–water as a mobile phase (Fig. 2). In all cases the color of the reaction mixture turned dark and a black precipitate was formed. Most precipitate was formed in the case of pyrene. The precipitate was soluble neither in water nor in 0.5 mol/L HCl, but was soluble in toluene. The UV spectrum of the precipitate dissolved in toluene was similar to that of pyrene (Fig. 3).

*Corresponding author.

Table I. HPLC analysis of PAHs (10 mmol/L each) after 1 d incubation with the Cu^{II}-hydrogen peroxide system

Compound	t_R^a min	Peak area, AU min		Degradation %
		control	1 d	
Phenanthrene	6.03	3.28	0.66	80
Fluoranthene	7.70	7.52	0.75	90
Pyrene	9.31	8.15	0.98	88

^aRetention time.**Fig. 1.** HPLC analysis of mixture of PAHs after degradation: 1 – phenanthrene, 2 – fluoranthene, 3 – pyrene, 4 – products; analysis was done with a Hypersil PAH 5 μ (150 \times 4.6 mm) column, mobile phase acetonitrile–water (9 : 1, *V/V*), flow rate 0.5 mL/min, UV detection at 230 nm; AU – arbitrary units.**Fig. 2.** TLC chromatogram of PAHs before (a) and after (b) degradation in benzene–acetic acid–water (125 : 74 : 1) as a mobile phase; 1 – phenanthrene, 2 – fluoranthene, 3 – pyrene.

Similarly to microbial degradation, chemical oxidation of PAHs with the studied system led to the formation of polar compounds. Thus Menn *et al.* (1993) described the oxidation of phenanthrene to 1-hydroxy-2-naphthoic acid by *Pseudomonas fluorescens* and formation of *trans*-4,5-dihydropyrenediol was the result of pyrene transformation by the white-rot fungus *Pleurotus ostreatus* (Bezalel *et al.* 1996).

The use of iron and hydrogen peroxide (Fenton reaction) for PAHs degradation has been studied for a long time. The production of reactive oxygen species and PAHs degradation has been reported (Saxe *et al.* 2000). Kawahara *et al.* (1995) reported more than 80 % removal of PAHs by Fenton reagent from polluted soil samples. The system based on another transition metal – copper(II) and hydrogen peroxide is also based on the generation of hydroxyl radicals (Kocha *et al.* 1997). This system has already been shown to degrade protein molecules (Lee and Sok 2000). The main advantage of the use of Cu instead of Fe is the higher stability of Cu²⁺ ions in comparison with Fe²⁺ ions, that oxidize rapidly to Fe³⁺.

In conclusion, a fast and effective system degrading higher aromatic hydrocarbons has been described. The use of the Cu^{II}-hydrogen peroxide system provides an alternative to the biological approach for degradation of PAHs.

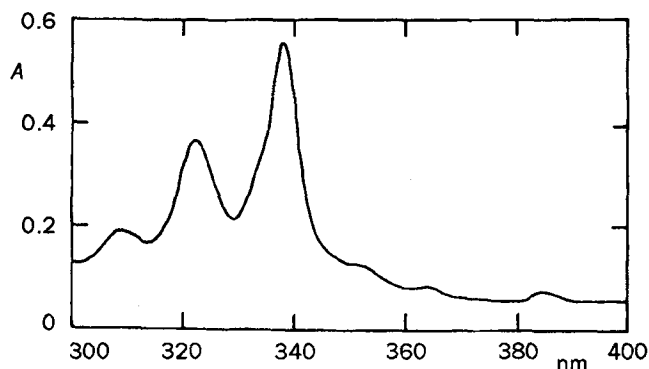


Fig. 3. UV spectrum (absorbance A) of the toluene-solubilized black precipitate formed during the incubation of pyrene with the $\text{Cu}^{\text{II}}\text{-H}_2\text{O}_2$ system.

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