

Degradation of polycyclic aromatic hydrocarbons by hydrogen peroxide catalyzed by heterogeneous polymeric metal chelates

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Abstract

Chelating sorbents with 8-hydroxyquinoline (**IVa**), 8-hydroxyquinoline-5-sulfonic acid (**IVb**), and tris(2-aminoethyl)amine (**VI**) ligands immobilized on macroporous methacrylate matrix were prepared and saturated with Co(II), Cu(II), and Fe(II). All these chelates catalyze cleavage of H₂O₂ yielding highly reactive hydroxyl radicals. All were able to degrade by this mechanism polycyclic aromatic hydrocarbons (anthracene, benzo[a]pyrene and benzo[k]fluoranthene). The most effective catalysts **IVa-Fe**, **IVb-Fe**, and **VI-Cu** (25 mg with 100 μmol H₂O₂) performed complete decomposition of 33 μg anthracene and benzo[a]pyrene during one 7-day catalytic cycle at 25 °C. The fastest decomposition proceeded during the 1st day of incubation; 75% of anthracene and 74% of benzo[a]pyrene were decomposed by **IVb-Co** within the first 24 h. More than 25% decomposition within the 1st day was also achieved with **IVb-Fe**, **VI-Cu**, **IVa-Cu**, and **VI-Co** for anthracene and more than 30% benzo[a]pyrene was decomposed by **IVb-Fe**, **VI-Cu**, **IVa-Cu**, and **IVb-Cu** during the same period. 1,4-Anthracenedione was the main product of anthracene oxidation by all catalysts. The catalysts were stable at pH 2–11 depending on their structure and able to perform sequential catalytic cycles without regeneration.

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1. Introduction

The ever-stricter regulations in the treatment of liquid waste containing organic contaminants accelerated the research of methods for efficient effluent treatment. Removal of nonpolar contaminants including polycyclic aromatic hydrocarbons (PAH) is particularly complicated, since such wastes, e.g. the extracts from contaminated soils, are not readily degraded by conventional methods and must be sometimes treated in the presence of organic solvents due to the limited water-solubility of these compounds [1].

Two main approaches have been developed for the remediation of PAH-polluted water. Bioremediation techniques utilize abilities of various types of microorganisms to degrade PAH [2–5]. Although especially white-rot fungi were tested for PAH degradation under laboratory as well as natural conditions, the use of bioremediation is limited due to inherent toxicity of PAH-containing wastes and complexity of the biological process that results in a low speed of degradation [6,7]. High degradation rates can only be achieved with purified microbial enzymes, e.g. laccase or peroxidase [8].

Many alternative chemical and physical–chemical approaches for PAH degradation have been proposed, e.g. gamma radiolysis [9], ultraviolet light [10–12], ultrasonic treatment [13], or ozonation [14,15]; most of them are of

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limited use due to high operation costs and/or the need for a special equipment.

One of the suitable solutions to cope with the problem seems to be the use of catalytic oxidation. The use of an adaptable catalyst can reduce the energy consumption of treatment processes such as wet oxidation or wet peroxidation [16,17]. The most widely used catalytic process for PAH degradation is Fenton-based oxidation [6,15,18–22]. In our previous works we described several copper- and cobalt-based Fenton-like metal/ligand systems for homogeneous catalytic decomposition of hydrogen peroxide and production of hydroxyl radicals. Pyridine, succinic acid, glucaric acid and D-arabinono-1,4-lactone were shown to increase the oxidative performance of $\text{Cu}/\text{H}_2\text{O}_2$ and degrade polycyclic aromatic hydrocarbons [23,24]. In contrast to the Fenton reagent, which is the most effective under acidic conditions (pH 2–4), oxidation by cobalt- and copper-based systems proceeds in the pH range 3–9 and can thus be interesting from the practical point of view.

The main shortcoming of homogeneous catalytic processes ensue from requirement of catalyst recovery or separation. In many cases, catalyst separation from the reaction mixture is technically and/or economically unfeasible. Moreover, many active homogeneous catalysts, including transition metal ions and their complexes are toxic thus are potential environmental problem. Under these circumstances, it is desirable to develop heterogeneous catalytic procedures where the catalysts are easily separable.

Recently, heterogeneous wet peroxidation systems have been described using metal- or metal complex-loaded ion-exchange carrier [25–28], zeolite-immobilized Fe(III) or Cu(II) ions [29–31], Al–Fe pillared clay [32], transition metals nonspecifically bound to polymeric support [33–35] or soluble polymer-bound metal–phthalocyanine complexes [36]. Transition metals used include Fe(III), Cu(II), Co(II), and Ni(II). Most of the heterogeneous catalysts described so far, however, have some limitations for practical use. Systems based on ion-exchange binding usually suffer from leaching of bound metals or metal-like complexes while systems immobilized in the form of a slurry are not always easy to separate and in some cases increased temperature or pressure was necessary to obtain reasonable reaction rate.

The aim of this study was oxidative degradation of polycyclic aromatic hydrocarbons using hydrogen peroxide catalyzed by heterogeneous polymeric chelates of selected metals (Fe(II), Cu(II), and Co(II)). Two types of ligands giving stable chelates with these ions were immobilized by chemical bond on support to prevent the leakage of the metal to the effluent: 8-hydroxyquinoline and its sulfoderivative and tris(aminoethyl)amine. Macroporous poly(glycidylmethacrylate-*co*-ethylenedimethacrylate) was used as a support enabling simple immobilization of ligands. The catalytic effects of chelates of ligands in solution were compared with those of chelates immobilized on support.

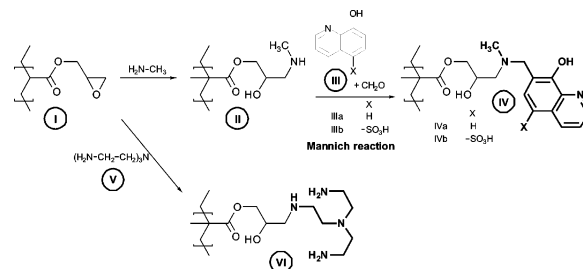


Fig. 1. Addition of ligand groups to the polymeric chain of poly(glycidyl methacrylate-*co*-ethylene dimethacrylate).

2. Experimental

2.1. Preparation and characterization of heterogeneous catalyst

The chelating sorbent with 8-hydroxyquinoline immobilized on methacrylate support (**IVa**) was prepared by modified two-step reaction from macroporous poly(glycidylmethacrylate-*co*-ethylenedimethacrylate) (**I**) [37] by aminolysis with methylamine followed by Mannich reaction with formaldehyde using the procedure described in [38] (Fig. 1). The epoxide group content in **I** was 2.8 mmol g^{-1} , particle size of the starting material was in this case 200–1000 μm , specific surface area: $55 \text{ m}^2 \text{ g}^{-1}$ and pore volume 1.5 mL g^{-1} . The content of 8-hydroxyquinoline moieties in **IVa** was 1.46 mmol g^{-1} dry matter (calculated from the difference in N analysis before and after Mannich reaction). The conversion of the amino group by Mannich reaction was 85%. The equilibrium sorption capacity for Cu^{2+} in acetate buffer pH 4.75 was 0.54 mmol g^{-1} dry matter.

The chelating sorbent with 8-hydroxyquinoline-5-sulfonic acid immobilized on methacrylate support (**IVb**) was prepared by a procedure described for immobilized 8-hydroxyquinoline (see above) using the same molar amount of 8-hydroxyquinoline-5-sulfonic acid instead of 8-hydroxyquinoline (Fig. 1). The content of 8-hydroxyquinoline-5-sulfonic acid in dry **IVb** was 0.50 mmol g^{-1} according to S analysis (1.60% S). The equilibrium sorption capacity for Cu^{2+} in acetate buffer pH 4.75 was 0.73 mmol g^{-1} dry matter.

The chelating sorbent with tris(2-aminoethyl)amine immobilized on methacrylate support (**VI**) was prepared by the following procedure: the glycidyl methacrylate-*co*-ethylene dimethacrylate beads (5.0 g, 14 mmol epoxide, 200–100 μm size) were allowed to stay in tris(2-aminoethyl)amine (25 mL, 167 mmol) for 2 days at room temperature. After that the sorbent was washed with methanol and water. The content of **V** in dry **VI** was 1.22 mmol g^{-1} dry **VI** according to N analysis (6.85% N). Epoxy group conversion was 53%. The equilibrium sorption capacity for Cu^{2+} in aqueous ammonium hydroxide (0.5 mol L^{-1}) was 0.81 mmol g^{-1} dry matter.

Support with covalently bound ligands was saturated with Co(II), Cu(II), or Fe(III) forming stable complexes with **IIIa**, **IIIb**, and **V** groups. The saturation was accomplished by incubation of **IVa**, **IVb**, or **VI** with buffered metal salt solutions.

The removal of metal ions was performed by repeated incubation of metal-containing catalyst with hydrochloric acid (2 mol L^{-1}).

Wet weight – dry sucked – of the catalysts are used in this study to prevent possible, sometimes irreversible, changes during air-drying. The dry weights corresponding to wet weight of **IVb**, **IVa**, and **VI** are 43.2 ± 2.0 , 41.4 ± 2.0 , and $35.9 \pm 1.8\%$, respectively.

The pH of complexes in 20 mM NaCl were adjusted with HCl and NaOH, respectively to pH 0.5–11 for pH stability estimations of **IVa**, **IVb**, and **VI** complexes with Co, Cu, and Fe. The amount and percentage of metal ions liberated from the complexes was estimated.

2.2. Catalytic systems

In nonsupported homogeneous systems, 50 mmol L^{-1} **IIIa**, **IIIb**, and **V**, respectively, were combined with 100 mM hydrogen peroxide and CoCl_2 , CuSO_4 , or FeCl_3 . One-hundred and twenty millimoles per liter of metal salts were used, the amount of metal was approximately corresponding to the amount bound to ligand-PMA at 2.5% (w/v). The reaction proceeded at 25°C in the dark.

In supported heterogeneous system, 2.5% (w/v) **IVa**, **IVb**, or **VI**, saturated with Co(II), Cu(II), or Fe(II), were combined with 100 mM hydrogen peroxide in water. The reaction proceeded at 25°C in the dark.

In the experiments with polycyclic aromatic hydrocarbon degradation, the heterogeneous polymeric metal chelate catalysts were combined with 100 mM hydrogen peroxide in water:acetone (1:1, v/v) containing 33 ppm anthracene, benzo[a]pyrene, or benzo[b]fluoranthene. Treatments used as controls: **IVb** + H_2O_2 (without metal), H_2O_2 only and PAH only (without H_2O_2). The reaction proceeded at 25°C in the dark.

2.3. High-performance liquid chromatography

Degradation of polycyclic aromatic hydrocarbons was followed by RP-HPLC. The analyses were performed on an HP 1090 L HPLC instrument (Hewlett-Packard, The Netherlands) using LiChrospher PAH column ($250 \text{ mm} \times 4 \text{ mm}$, particle diameter $5 \mu\text{m}$; Merck, Germany). Acetonitrile and water (9:1) mixture was used as mobile phase in isocratic mode, flow rate 1 mL min^{-1} . Analyses were performed at 35°C with DAD/UV detection of the compounds at 230 nm (benzo[k]fluoranthene) and 250 nm (anthracene and benzo[a]pyrene). All compounds were eluted from the column during a 30 min run under the conditions described. Degradation rate of PAHs refers to signals obtained with samples with no addition of oxidation system components.

2.4. EPR measurements

EPR spectra were recorded on E-540 Spectrometer X-Band (Bruker, Germany). Following conditions were used

while recording the spectra: microwave power 20 mW, modulation amplitude 0.02 mT, attenuation 20 dB, time constant 0.5 s, scan speed 0.3 mT/min, calibration standard $\text{Cr}^{3+}/\text{MgO}$ and 25°C . The program used for spectra recording, handling and evaluation as WinEPR (Bruker, Germany). 5,5-Dimethyl-1-pyrroline-*N*-oxide (DMPO) was used as a radical-trapping agent. The reaction system of the EPR experiments is described in the legend to the respective figures. The catalyst was ground with a mortar and pestle before use and applied in the form of slurry after H_2O_2 and DMPO addition.

2.5. Estimation of hydrogen peroxide, hydroxyl radicals and metal ions

The concentration of H_2O_2 was estimated using xylenol orange and sorbitol [39]. The method based on the reaction of deoxyribose with $\bullet\text{OH}$ radicals was used to detect the production of $\bullet\text{OH}$ radicals by the catalyst [40]. The reaction mixture consisted of the catalyst (2.5%, w/v), hydrogen peroxide (100 mmol L^{-1}) and deoxyribose (2.8 mmol L^{-1}). Five-hundred microliter aliquots of the reaction mixture were taken and the reaction was stopped by the addition of $500 \mu\text{L}$ thiobarbituric acid (1%, w/v in 50 mmol L^{-1} NaOH) and $500 \mu\text{L}$ of trichloroacetic acid (2.8%, w/v). The deoxyribose degradation product reacted with thiobarbituric acid during subsequent 30 min incubation at 80°C , with the resulting formation of a pink colour. The product of the reaction was quantified by spectrophotometry ($\lambda = 532 \text{ nm}$) after dilution with an equal amount of water. The amount of $\bullet\text{OH}$ radicals detected was expressed in absorbance units (A).

Concentrations of metal ions were analysed using flame atomic absorption spectrophotometer (AAS, Aurora Instruments, Canada) after appropriate dilution.

3. Results

3.1. Preparation of chelating supports

The macroporous poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) was used as a carrier for covalent modification by metal-chelating ligands (Fig. 1). The ligands were selected due to their ability to chelate metal ions and the ability to form covalent bonds with the polymeric chain without the loss of metal-chelating abilities. Reactive epoxide of support bind directly **V** (epoxide conversion 53%). **IIIa** and **IIIb** were immobilized by two-step reaction. In the first step epoxide reacted with methylamine (conversion 92%) and then are bound by Mannich reaction **IIIa** or **IIIb**. Variant with drying agent binding equilibrium water was used to enhance conversion; whereas for **IIIa** is conversion from amino group 85%, for **IIIb** it is only 25%.

Table 1

Decomposition of hydrogen peroxide catalyzed by free and support-bound 8-hydroxyquinoline, 8-hydroxyquinoline-5-sulfonic acid and tris(aminoethyl)amine metal chelates

Metal	Ligand type	H ₂ O ₂ decomposition (%)		
		Free ligand	Bound ligand	
		3 h	3 h	24 h
Co	8-Hydroxyquinoline (IIIb)	2.7	84.7	99.5
	8-Hydroxyquinoline-5-sulfonic acid (IIIa)	0.0	68.3	100.0
	Tris(aminoethyl)amine (V)	100.0	24.1	54.1
Cu	8-Hydroxyquinoline (IIIb)	93.8	6.6	19.9
	8-Hydroxyquinoline-5-sulfonic acid (IIIa)	97.9	26.0	44.4
	Tris(aminoethyl)amine (V)	61.1	14.3	42.1
Fe	8-Hydroxyquinoline (IIIb)	96.2	44.2	86.2
	8-Hydroxyquinoline-5-sulfonic acid (IIIa)	96.4	54.0	99.1
	Tris(aminoethyl)amine (V)	95.5	9.0	26.8

3.2. Decomposition of hydrogen peroxide by metal complexes with 8-hydroxyquinoline, 8-hydroxyquinoline-5-sulfonic acid, and tris(aminoethyl)amine as ligands

IIIa, **IIIb**, and **V** were selected as compounds forming stable chelates with catalytically active transition metal ions due to the fact that these compounds can be covalently bound to organic or inorganic support. The decomposition of hydrogen peroxide with **IIIa**, **IIIb**, and **V** and Co(II), Cu(II) and Fe(III) ions proceeded in the water-slurry system since the complexes are water-insoluble. All complexes except **IIIa-Co** were able to decompose hydrogen peroxide (Table 1), however, the decomposition with **IIIb-Co** was only 2.7%.

Compared to free metal–ligand complexes, the decomposition of H₂O₂ with PMA-bound metal–ligand complexes proceeded more slowly with the notable exception of **IVb-Co** and **IVa-Co** (Table 1). Three of the catalysts tested decomposed hydrogen peroxide completely within 24 h. This is a good result when the lower rate of diffusion in the macroporous beads of the catalyst is taken into account.

3.3. Properties and stability of the catalysts

The carriers with covalently bound **IIIa**, **IIIb** or **V** turned from white to white-yellow when without metals to orange (**IVb-Cu**, **IVa-Cu**, **VI-Cu**), green (**IVb-Co**, **IVa-Co**), light blue (**VI-Co**), black (**IVb-Fe**, **IVa-Fe**) or beige (**VI-Fe**) when saturated with metal ions. Metal contents in the saturated catalysts varied widely in the range of 30–400 $\mu\text{mol g}^{-1}$, d.w. (Table 2). **VI-Fe** and **VI-Co** exhibited the lowest metal contents with 30 and 117 $\mu\text{mol g}^{-1}$, d.w. The pH of the catalysts in distilled water was 3.5–3.7 for bound Fe(III), 4.0–4.7 for Cu(II) and 5.8–8.8 for Co(II). During one catalytic cycle, the catalysts lost different amounts of bound metal (Table 2). Especially the copper-containing catalysts lost significant amounts of metal (30–52%) during one cycle. On the other hand, **IVa-Co**, **IVb-Co**, and **IVb-Fe** lost less than 5% of the bound metal. In most

Table 2

Reaction pH, metal contents in heterogeneous polymeric metal chelate catalysts and metal loss during one cycle of hydrogen peroxide decomposition

Catalyst	pH	Metal content ($\mu\text{mol g}^{-1}$, d.w.)	Metal loss (% cycle ⁻¹)	
			Total (%)	Irreversible (%)
IVa-Co	8.8	333	4	4
IVb-Co	7.7	253	<1	<1
VI-Co	5.8	117	31	<1
IVa-Cu	4.1	241	42	37
IVb-Cu	4.7	181	30	4
VI-Cu	4.0	249	51	<1
IVa-Fe	3.5	392	8	<1
IVb-Fe	3.6	190	5	<1
VI-Fe	3.7	30	9	<1

cases, the catalyst could be loaded again with the same amount of metal, however, in the case of **IVa-Cu**, the loss of bound Cu(II) was irreversible and lost metal could not be replaced.

The catalysts were further tested for decomposition of hydrogen peroxide in subsequent catalytic cycles. Each cycle proceeded for 24 h. The H₂O₂ decomposition efficiency decreased during the experiment with all catalysts tested (Fig. 2). The highest total H₂O₂ decomposition was observed for **IVa-Co** and **IVb-Co**. The decrease of activity was probably at least partially due to metal loss between the cycles, since the catalysts recovered their original H₂O₂ decomposition rate after metal supplementation.

The binding of metals to the respective ligands was pH dependent. Whereas at alkaline or weakly acidic conditions the metal was firmly bound to the ligand, metal binding by the ligands decreased with the decrease of pH (Fig. 3). At pH 3, 0.8% of Cu was liberated from **VI-Cu**, 2.6% Co from **IVa-Co** and 6.5% Co from **IVb-Co**. The iron-containing complexes were more stable under acidic conditions, with only 0.7 or 1.0% Fe liberated from **IVa-Fe** or **IVb-Fe** at pH 2. More than 50% of bound metals was liberated from all complexes tested at pH 0.5 and complete removal was possible using 1 M HCl.

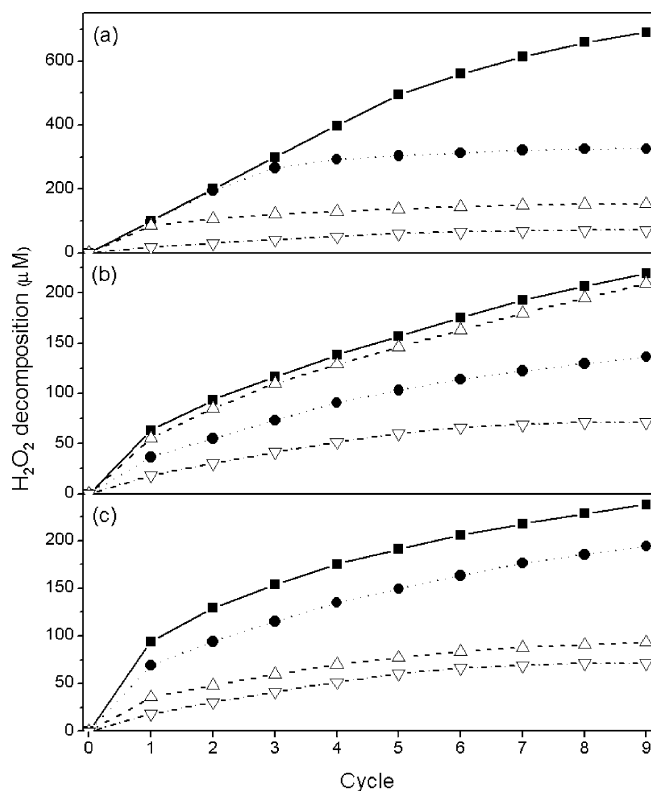


Fig. 2. Hydrogen peroxide decomposition by heterogeneous catalysts containing Co (panel a), Cu (panel b), and Fe (panel c) during nine sequential catalytic cycles. One-hundred parts per million of hydrogen peroxide was incubated with 2.5% (w/v) heterogeneous polymeric metal chelate catalysts and 100 mM hydrogen peroxide at 25 °C, one cycle lasted for 24 h. Catalysts: **IVa** + metal (squares), **IVb** + metal (circles), **VI** + metal (up triangles), **IVb** (down triangles; control treatment without metal).

The decomposition of hydrogen peroxide by all catalysts is accompanied by the production of hydroxyl radicals. The highest production of hydroxyl radical was detected in **IVa-Fe** and **IVb-Fe**. Spin trapping experiments with DMPO

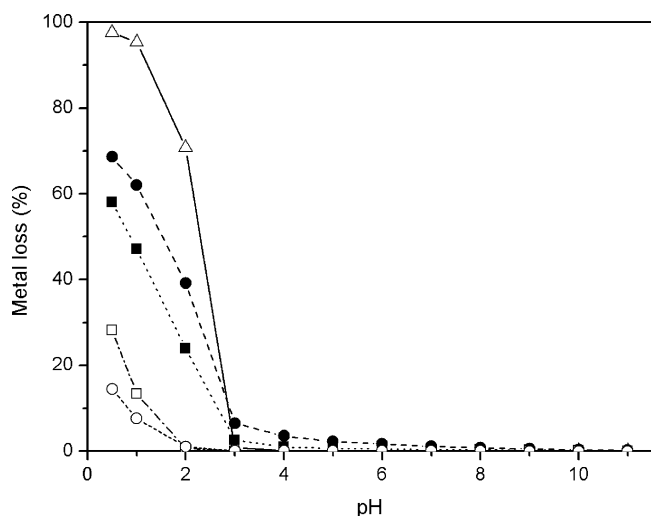


Fig. 3. pH stability of heterogeneous catalysts **IVa-Co** (full squares), **IVb-Co** (full circles), **VI-Cu** (triangles), **IVa-Fe** (open squares), and **IVb-Fe** (open circles): amount of metal lost during the incubation at pH 0.5–11.

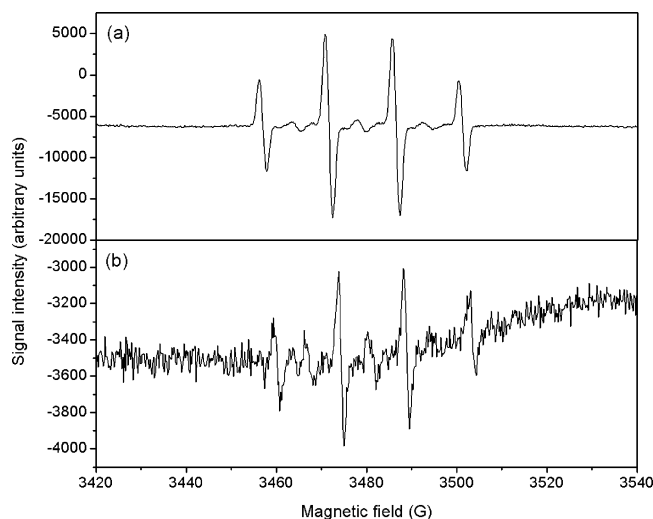


Fig. 4. EPR spectra of spin adducts of DMPO produced by heterogeneous catalysts **IVb-Fe** (a) and **VI-Cu** (b). The reaction was initiated by the addition of H_2O_2 . The reaction mixture contained 2.5% (w/v) homogenized PMA-based catalyst, 100 mM H_2O_2 and 300 mM DMPO and proceeded at 25 °C in the dark.

(Fig. 4) also confirmed the production of hydroxyl radicals by the heterogeneous polymeric metal chelate catalysts. It seems that the Cu–ligand complex bound to the catalyst first forms a complex with Cu hydrogen peroxide. The hydroxyl radical probably forms within this bound complex and can later oxidize PAH or other organic compounds. The formation of ligand–Cu(II)–radical complexes follows from the slight difference in magnetic field in the ESR spectra of hydroxyl radicals formed by heterogeneous and homogeneous catalysts (Fig. 4, [41]).

3.4. PAH decomposition

All catalytic systems decomposed anthracene, benzo[a]pyrene and benzo[b]fluoranthene in a mixture containing 33 ppm of all three compounds. The most effective catalytic systems were **IVa-Fe**, **IVb-Fe**, and **VI-Cu** that performed complete decomposition of anthracene and benzo[a]pyrene during the 7-day treatment (Fig. 5). The fastest decomposition proceeded during the first 2 days of incubation; 75% of anthracene and 74% of benzo[a]pyrene were decomposed by **IVb-Co** within the first 24 h. More than 25% decomposition within the 1st day was also achieved with **IVb-Fe**, **VI-Cu**, **IVa-Cu**, and **VI-Co** for anthracene and >30% benzo[a]pyrene was decomposed by with **IVb-Fe**, **VI-Cu**, **IVa-Cu**, and **IVb-Cu** during the same period. Only some catalysts caused statistically significant decrease of benzo[b]fluoranthene, namely **IVa-Fe**, **IVb-Fe**, **VI-Cu**, and **IVa-Cu** (Fig. 5). The specific oxidation rates ranged 5–50 $\text{nmol min}^{-1} \text{mmol}^{-1}$ of metal in the case of anthracene and benzo[a]pyrene and 2–10 $\text{nmol min}^{-1} \text{mmol}^{-1}$ for benzo[b]fluoranthene.

After the first cycle of PAH degradation, all catalysts were washed extensively with water/acetone (1:1) and used

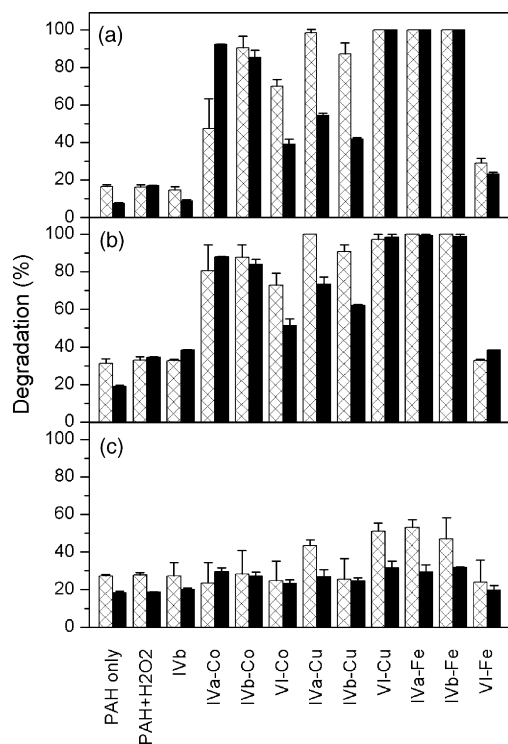


Fig. 5. Degradation of anthracene (a), benzo[a]pyrene (b) and benzo[b]fluoranthene (c) by heterogeneous catalysts. A mixture of 33 ppm anthracene, 33 ppm benzo[a]pyrene, and 33 ppm benzo[b]fluoranthene was incubated with 2.5% (w/v) heterogeneous catalysts and 100 mM hydrogen peroxide d at 25 °C. Data from two subsequent 7-days cycles; cycle one (hatched) and cycle two (black). The data represent averages and standard errors of three replicate reactions.

for the second cycle of PAH decomposition under the same conditions. Most catalysts exhibited the same or similar efficiency as in the first cycle, however, in **IVb-Cu**, **IVa-Cu**, and **VI-Co** the amount of degraded PAH in the second cycle dropped considerably (Fig. 5).

1,4-Anthracenedione was estimated in the reaction mixture during anthracene degradation as one of the probable products of anthracene oxidation. 1,4-Anthracenedione was found in all catalytic systems tested (Table 3), but not in controls (PAH and H₂O₂ with or without **IVb**). Anthracene oxidation was accompanied by the strictly parallel production of 1,4-anthracenedione ($R^2 = 0.964$). The amount of 1,4-anthracenedione produced was proportional to the amount of anthracene degraded at a molar ratio of 0.51, which indicates that there is probably at least one more product of anthracene degradation, and secondly, that 1,4-anthracenedione is not degraded by the catalysts. No major products were detected after degradation of benzo[a]pyrene and benzo[b]fluoranthene.

4. Discussion

Several Cu-containing systems for homogeneous catalytic decomposition of H₂O₂ have recently been demon-

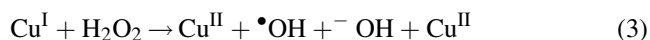
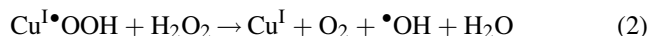
Table 3

Time course of anthracene (ANT) degradation and 1,4-anthracenedione (ANQ) production by heterogeneous catalysts

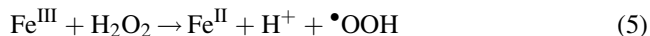
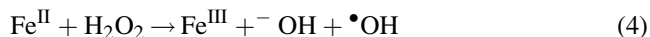
Catalyst	Compound	Time (day)			
		1	2	3	7
IVa-Co	ANT	27.5 ± 2.8	24.4 ± 1.0	23.5 ± 0.4	17.6 ± 5.3
	ANQ	2.3 ± 0.9	5.2 ± 0.4	8.7 ± 3.1	10.9 ± 5.0
IVb-Co	ANT	8.3 ± 2.2	4.2 ± 1.9	3.4 ± 0.0	3.2 ± 2.1
	ANQ	15.4 ± 1.3	18.1 ± 0.0	19.4 ± 0.0	20.4 ± 0.5
VI-Co	ANT	24.7 ± 0.4	19.5 ± 1.0	17.3 ± 0.8	10.1 ± 1.2
	ANQ	4.8 ± 0.3	8.4 ± 0.6	10.7 ± 0.6	16.0 ± 0.1
IVa-Cu	ANT	22.2 ± 2.3	8.1 ± 0.0	7.0 ± 4.2	0.6 ± 0.6
	ANQ	7.0 ± 1.0	13.1 ± 0.0	14.4 ± 1.0	20.3 ± 0.1
IVb-Cu	ANT	26.1 ± 0.4	20.4 ± 1.5	15.4 ± 1.5	4.3 ± 2.0
	ANQ	3.9 ± 0.5	6.8 ± 0.2	10.4 ± 0.9	18.0 ± 0.8
VI-Cu	ANT	21.9 ± 0.2	10.3 ± 2.2	1.0 ± 1.0	0.0 ± 0.0
	ANQ	6.8 ± 0.4	12.9 ± 0.4	19.2 ± 0.5	21.4 ± 0.1
IVa-Fe	ANT	26.5 ± 2.2	17.8 ± 2.2	6.2 ± 0.6	0.0 ± 0.0
	ANQ	3.3 ± 1.1	6.5 ± 1.2	12.3 ± 1.1	15.4 ± 0.3
IVb-Fe	ANT	21.6 ± 1.9	15.0 ± 1.6	7.6 ± 0.5	0.0 ± 0.0
	ANQ	6.6 ± 1.0	11.1 ± 1.2	11.7 ± 2.8	20.3 ± 1.1
VI-Fe	ANT	30.0 ± 0.6	27.4 ± 0.4	26.5 ± 0.5	23.8 ± 0.9
	ANQ	1.9 ± 0.1	2.5 ± 0.1	3.2 ± 0.1	4.3 ± 0.1

Thirty-three parts per million of anthracene was incubated with 2.5% (w/v) catalysts and 100 mM hydrogen peroxide for 7 days at 25 °C. The data are in ppm and represent averages and standard errors of three replicate reactions.

strated [23,24]. The main advantage of Cu-mediated decomposition of hydrogen peroxide is the fact that Cu reacts with H₂O₂ as both Cu(II) and Cu(I) and hydroxyl radicals are produced in both cases [42]:



In the case of iron, the Fenton process, both ferrous and ferric ions also react with H₂O₂ [30]:



However, the process is pH-dependent and hydroxyl radicals are produced only in reaction (4). Moreover, reaction (5) is rate-limiting and the process is fast only as long as ferrous ions are readily available. In the case of chelated Co(II), the generation of hydroxyl radicals proceeds in a reaction analogous to reaction (4) [43]. In the case of heterogeneous catalysis demonstrated in this study the difference in kinetic behaviour of Co, Cu, and Fe containing catalysts was not observed.

The production of 1,4-anthracenedione and phthalic acid during the oxidation of anthracene by homogeneous copper-ligand-hydrogen peroxide systems was described previously [24]. 1,4-Anthracenedione was also the major product of anthracene degradation in this study. The

transformation of PAH molecules to water-soluble quinones is the most typical result of PAH oxidation and it opens the pathway for its further degradation including bacterial biodegradation.

The lower PAH degradation by some of the catalysts during the second catalytic cycle is most probably due to the leaching of metals from the catalysts (mainly the copper-containing ones). The decrease of hydrogen peroxide decomposition in subsequent catalytic cycles has probably the same cause. In the case of iron, also the low rate of Fe(III)–Fe(II) cycling can contribute to the lowering of hydrogen peroxide degradation during 24 h of reaction time. The specific reaction rates are lower than in the case of PAH degradation by purified enzymes or other AOPs [8]. However, the main drawbacks of these processes—the use of free metals in homogeneous systems and chemical instability of enzymatic preparations are overcome by metal immobilization to a chemically stable support. Among the catalysts tested, **IVa-Co** and **IVb-Co** combined high PAH degradation, high decomposition of hydrogen peroxide in subsequent cycles and low metal leaching from the catalysts and seem to be the most promising for further research or use. The consequences of a slow leaching of metals from the supports could possibly be minimized by including an ion-exchange step in the treatment procedure.

Since hydroxyl radicals are produced during the catalytic decomposition of hydrogen peroxide, it is highly probable that other organic compounds (synthetic dyes, phenols, etc.) could possibly be degraded using the catalysts. The ESR experiments documented that UV-irradiation can further increase the production of hydroxyl radicals by the heterogeneous catalysts.

5. Conclusions

Heterogeneous methacrylate-based polymeric metal chelates were prepared and the degradation of PAH was demonstrated. The catalysts retained their activity in repeated catalytic cycles and were active in a broad pH range. To our knowledge this is the first report of heterogeneous catalysis of PAH peroxidation. Compared to the homogeneous catalytic processes for PAH oxidation [24], the catalysts described in this work offer the advantages of simple recovery from the treated solution and repeated use. The main disadvantage of homogeneous catalysis – input of heavy metals into treated solutions – was solved by metal immobilization.

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