

Decolorization of synthetic dyes by hydrogen peroxide with heterogeneous catalysis by mixed iron oxides

Petr Baldrian^{a,*}, Věra Merhautová^a, Jiří Gabriel^a, František Nerud^a,
Pavel Stopka^b, Martin Hrubý^c, Milan J. Beneš^c

^a *Laboratory of Biochemistry of Wood-rotting Fungi, Institute of Microbiology AS CR, Vídeňská 1083, 14220 Prague 4, Czech Republic*

^b *Institute of Inorganic Chemistry AS CR, 25068 Řež, Czech Republic*

^c *Institute of Macromolecular Chemistry AS CR, Heyrovského nám. 2, 16206 Prague 6, Czech Republic*

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Abstract

Heterogeneous catalysts based on magnetic mixed iron oxides (MO-Fe₂O₃; M: Fe, Co, Cu, Mn) were used for the decolorization of several synthetic dyes (Bromophenol Blue, Chicago Sky Blue, Cu Phthalocyanine, Eosin Yellowish, Evans Blue, Naphthol Blue Black, Phenol Red, Poly B-411, and Reactive Orange 16). All the catalysts decomposed H₂O₂ yielding highly reactive hydroxyl radicals, and were able to decolorize the synthetic dyes. The most effective catalyst FeO-Fe₂O₃ (25 mg mL⁻¹ with 100 mmol L⁻¹ H₂O₂) produced more than 90% decolorization of 50 mg L⁻¹ Bromophenol Blue, Chicago Sky Blue, Evans Blue and Naphthol Blue Black within 24 h. The fastest decomposition proceeded during the first hour of the reaction. In addition to dye decolorization, all the catalysts also caused a significant decrease of chemical oxygen demand (COD). Individual catalysts were active in the pH range 2–10 depending on their structure and were able to perform sequential catalytic cycles with low metal leaching.

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1. Introduction

Decolorization of synthetic dyes as potential environmental pollutants attracted considerable attention in the past two decades. Two main approaches have been developed for the remediation of dyes containing effluents. Bioremediation techniques utilize the abilities of various types of microorganisms to decolorize synthetic dyes. Although especially white-rot fungi were tested for dye decolorization, the use of bioremediation is limited mainly due to the complexity of the biological process that results in a low speed of degradation [1]. High degradation rates can only be achieved with purified microbial enzymes, e.g. laccase or peroxidase [2,3]. The second approach utilizes many alternative chemical and physical-chemical methods such as, e.g. TiO₂ photolysis [4–6], ZnO photolysis [5], ultraviolet light and ultrasonic treatment [7,8], wet air oxidation [9] or ozonization [10]. Most of them are of

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

One of the suitable solutions to cope with the problem seems to be the use of catalytic oxidation with hydrogen peroxide. The most widely used catalytic process for dyes decolorization is Fenton oxidation [11,12] including several modifications, e.g. with the use of suitable ligands of metals [13,14]. Recently, several copper- and cobalt-based Fenton-like systems for homogeneous catalytic decomposition of hydrogen peroxide and production of hydroxyl radicals were described. They take advantage of simple organic molecules, e.g. organic acids or amino acids, to increase the oxidative performance of Cu/H₂O₂ to degrade synthetic dyes or nonpolar organic compounds [1,15–18]. 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 comes from the requirement of catalyst recovery or separation. In many cases, catalyst separation from the reaction mixture is technically and/or economically unfeasible. Moreover, many

* Corresponding author.

E-mail address: baldrian@biomed.cas.cz (P. Baldrian).

active homogeneous catalysts, including transition metal ions and their complexes are toxic and are thus potentially environmentally problematic. Under these circumstances, the development of heterogeneous catalytic processes is the most suitable solution.

So far, heterogeneous catalysis for degradation of synthetic dyes or other organic compounds by hydrogen peroxide has been described with systems that employ classical Fenton oxidation with iron or iron powder or granulated Fe-hydroxide [19,20], silica-supported complexes of Cu, Ni, and Co [21,22], zeolite-immobilized metals ions [23–27], metal pillared clay [28], or metals bound to a polymeric support [29–32] including polymeric metalloporphyrins containing different transition metals [33,34]. Transition metals used include Fe(III), Cu(II), Co(II), Mn(II) and Ni(II). Unfortunately, the requirements of visible light for photocatalysis, unsuitable pH-dependence of activity [19,21,22] or the need to perform the catalysis in two steps – sorption and degradation [20,35] – limits the use of these processes for industrial effluents. Several catalysts, including the polymer-supported metal chelates described previously [32] exhibit high adsorption of dyes (Baldrian et al., unpublished data) and are thus inapplicable. Systems based on ion-exchange binding usually suffer from leaching of bound metals and systems immobilized in the form of a slurry are not always easy to separate from other components of the reaction mixture.

The aim of this study was to characterize catalytic effect of heterogeneous magnetically separable iron mixed oxides (Co(II), Cu(II), Mn(II) ferrite and magnetite) on decolorization of synthetic dyes by hydrogen peroxide.

2. Experimental

2.1. Preparation and characterization of catalysts

Magnetic oxides were prepared by precipitation of the mixture of Fe(III) and M(II) chlorides in a molar ratio of Fe(III)/M(II) = 2 with the surplus of base by a modified procedure according to Refs. [36–39] to obtain magnetic products. Precipitation of the solution of FeCl₃ (0.0915 mol L⁻¹) and appropriate M(II) chloride (0.057 mol L⁻¹) was carried out at 70 °C under vigorous stirring. Afterwards, the reaction mixture was kept at 90 °C for 1 h. Magnetite was prepared with aqueous ammonium hydroxide as a base (13.3 mol L⁻¹, molar ratio [NH₃]/[Fe(III)] = 10) from Fe(III) and Fe(II) chlorides. Ferrites (Co, Cu, Mn) were prepared by precipitation with aqueous NaOH as a base (6 mol L⁻¹, [NaOH]/[Fe(III)] = 8). Precipitates were repeatedly washed with water and the suspension was then evaporated in vacuum and ground with a mortar and pestle to obtain dry catalyst. Magnetic oxides are composed of aggregates of primary nanoparticles (20–30 nm; Fig. 1) and contain approximately 4.2–4.3 mmol g⁻¹ of Co, Cu, or Mn.

2.2. Catalytic systems

The synthetic dyes Bromophenol Blue (Aldrich, dye content 95%), Chicago Sky Blue 6B (CSB; Aldrich, dye content 50%, CI 24410), Evans Blue (Aldrich, dye content 85%, CI 23860),

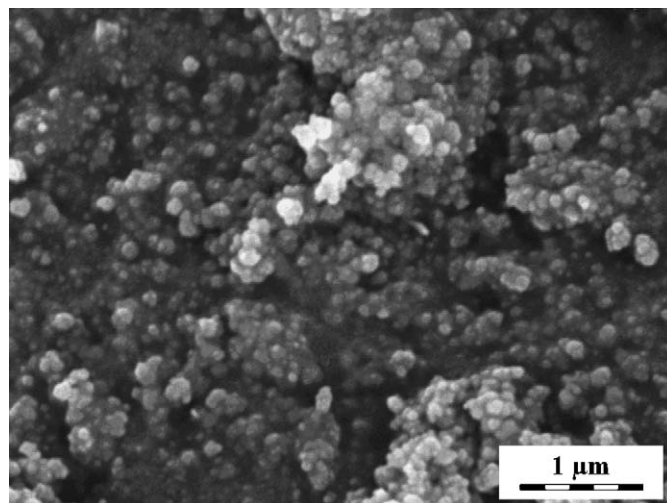


Fig. 1. Mn ferrite, Scanning Electron Microscopy (JSM 6400, Jeol, Japan).

Cu Phthalocyanine (Aldrich, dye content 99%), Eosin Yellowish (Aldrich, dye content 80%, CI 45380), Naphthol Blue Black (NBB; Aldrich, dye content 80%, CI 20470), Phenol Red (Aldrich, dye content 95%), Poly B-411 (Sigma, dye content 65%), and Reactive Orange 16 (Aldrich, dye content 50%, CI 17757) were used.

The dry catalysts (1.25–25 mg mL⁻¹) were combined with synthetic dyes (50–500 mg L⁻¹) in water and the reaction was started by adding hydrogen peroxide (100 mmol L⁻¹). The reactions proceeded at 30 °C in the dark with slow agitation. At each sampling time, the catalyst was separated either by centrifugation (~30 s) or magnetically and the supernatant was immediately used for analysis. It was decided not to stop the reaction by the addition of a quenching agent because this interfered with the analysis of the reaction mixture. In the experiments with the pH-dependence of decolorization, the pH values of catalysts in 20 mM NaCl were adjusted with HCl and NaOH, respectively, to pH 2–12 before hydrogen peroxide addition. The pH in pH-nonadjusted systems was 6.6 for CoO·Fe₂O₃, 6.8 for CuO·Fe₂O₃, 6.5 for FeO·Fe₂O₃, and 6.0 for MnO·Fe₂O₃. After the reaction the catalysts were separated either by centrifugation or magnetically and washed with 20 mM aqueous NaCl for further reuse.

2.3. Dye decolorization and COD estimation

Visible spectra of the reaction mixture samples were recorded using a microplate Spectra Max Plus 384 reader (Molecular Devices, USA). The degree of decolorization was expressed as the percent decrease of absorbance at absorption maxima of the particular dyes – 590 nm for Bromophenol Blue, 615 nm for Chicago Sky Blue, 630 nm for Cu Phthalocyanine, 515 nm for Eosin Yellowish, 605 nm for Evans Blue, 615 nm for Naphthol Blue Black, 430 nm for Phenol Red, 590 nm for Poly B-411, and 495 nm for Reactive Orange 16, respectively. Dye solutions were also combined with metal oxide catalysts in the absence of H₂O₂ and dye adsorption to the catalysts was determined. COD was determined using standard methods for the examination of water and wastewater [40]. Potassium

hydrogen phthalate (PHP) was used as a standard for the calculation of oxygen demand. The theoretical oxygen demand of PHP is 1.176 mg oxygen demand per milligram PHP [40].

2.4. Electron paramagnetic resonance (EPR) measurements

EPR spectra were recorded with E-540 Spectrometer X-Band (Bruker-Biospin, Germany). The following conditions were used while recording the spectra: microwave power 20 mW, magnetic modulation amplitude 0.2 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. WinEPR (Bruker-Biospin, Germany) program was used for spectra recording, handling and evaluation. 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 Fig. 5. The catalyst was applied in the form of slurry after H_2O_2 and DMPO addition.

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

The concentration of H_2O_2 was determined with xylenol orange and sorbitol [41]. $\bullet\text{OH}$ radicals produced by the catalysts were detected by the method based on their reaction with deoxyribose [40]. The reaction mixture consisted of the catalyst (25 mg mL^{-1}), hydrogen peroxide (100 mmol L^{-1}) and deoxyribose (2.8 mmol L^{-1}). 500 μL aliquots of the reaction mixture were taken and the reaction was stopped by the addition of 500 μL thiobarbituric acid (10 mg mL^{-1} in 50 mmol L^{-1} NaOH) and 500 μL of trichloroacetic acid (28 mg mL^{-1}). The deoxyribose degradation product reacted with thiobarbituric acid during subsequent 30 min incubation at 80 °C with the resulting formation of pink color. The product of the reaction was quantified with UV-vis 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) in a 10 mm optical length cuvette.

Concentrations of metal ions were determined using flame atomic absorption spectrophotometer (AI 1200, Aurora Instruments, Canada) after appropriate dilution.

3. Results

3.1. Decolorization and adsorption of the dyes

Decolorization of 50 mg L^{-1} CSB was tested with different initial contents of the catalysts. Both the decolorizations after 1 h (see Fig. 2) and after 24 h incubation increased with increasing catalyst concentration in the range of 1.25–25 mg mL^{-1} , however, decolorization over 80% was detected after 24 h incubation even with the lowest catalyst concentrations. The decolorization of CSB was very fast, 30–70% decolorization being recorded after a mere 5 min of incubation (Fig. 3). After 24 h, decolorization with $\text{CoO}\cdot\text{Fe}_2\text{O}_3$, $\text{CuO}\cdot\text{Fe}_2\text{O}_3$, and $\text{FeO}\cdot\text{Fe}_2\text{O}_3$ was almost complete (over 93%), while $\text{MnO}\cdot\text{Fe}_2\text{O}_3$ was slightly less effective (81%).

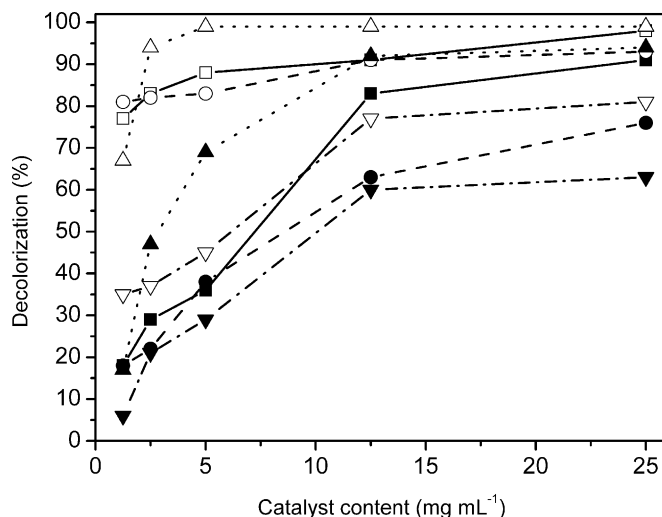


Fig. 2. Effect of catalyst content on the decolorization of 50 mg L^{-1} Chicago Sky Blue after 1 h and 24 h of incubation. Catalyst: $\text{CoO}\cdot\text{Fe}_2\text{O}_3$ (full squares 1 h; open squares 24 h), $\text{CuO}\cdot\text{Fe}_2\text{O}_3$ (full circles 1 h; open circles 24 h), $\text{FeO}\cdot\text{Fe}_2\text{O}_3$ (full triangles 1 h; open triangles 24 h), and $\text{MnO}\cdot\text{Fe}_2\text{O}_3$ (full inverted triangles 1 h; open inverted triangles 24 h).

The degree of decolorization decreased with increasing dye concentration, although at 500 mg L^{-1} CSB the decolorization was still 65% with $\text{CoO}\cdot\text{Fe}_2\text{O}_3$, 79% with $\text{CuO}\cdot\text{Fe}_2\text{O}_3$, 60% with $\text{FeO}\cdot\text{Fe}_2\text{O}_3$, and 58% with $\text{MnO}\cdot\text{Fe}_2\text{O}_3$.

Twenty-four hours decolorization of nine synthetic dyes (50 mg L^{-1}) was tested with all catalysts (25 mg mL^{-1}). The decolorization efficiency differed significantly among the dyes and the catalysts (Table 1). $\text{CuO}\cdot\text{Fe}_2\text{O}_3$ and $\text{FeO}\cdot\text{Fe}_2\text{O}_3$ were the most efficient catalysts with all the dyes tested while $\text{MnO}\cdot\text{Fe}_2\text{O}_3$ was almost ineffective except with Chicago Sky Blue, Naphthol Blue Black and Phenol Red. More than 90% decolorization was achieved with Bromophenol Blue, Chicago Sky Blue, Evans Blue and Naphthol Blue Black. The lowest decolorization was observed in the case of Poly B-411 (less

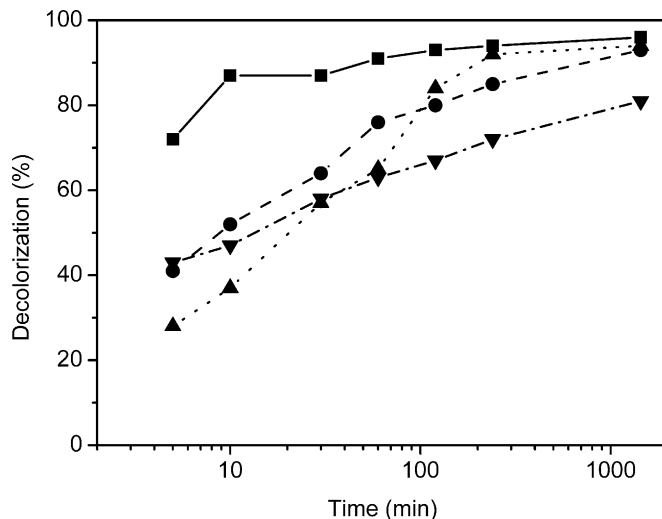


Fig. 3. Time course of decolorization of Chicago Sky Blue (50 mg L^{-1}) in the presence of 25 mg mL^{-1} of catalysts and 100 $\text{mM H}_2\text{O}_2$. Catalyst: $\text{CoO}\cdot\text{Fe}_2\text{O}_3$ (squares), $\text{CuO}\cdot\text{Fe}_2\text{O}_3$ (circles), $\text{FeO}\cdot\text{Fe}_2\text{O}_3$ (triangles), and $\text{MnO}\cdot\text{Fe}_2\text{O}_3$ (inverted triangles).

Table 1

Decrease of color after 24-h treatment of synthetic dyes (50 mg L^{-1}) with 25 mg mL^{-1} catalysts

Dye	Decolorization/adsorption (%)			
	CoO·Fe ₂ O ₃	CuO·Fe ₂ O ₃	FeO·Fe ₂ O ₃	MnO·Fe ₂ O ₃
Bromophenol Blue	2 (0)	48 (15)	99 (9)	0 (0)
Chicago Sky Blue	93 (9)	95 (8)	98 (10)	91 (6)
Cu Phthalocyanine	70 (3)	75 (18)	92 (18)	19 (7)
Eosin Yellowish	25 (2)	53 (17)	85 (15)	12 (0)
Evans Blue	73 (16)	92 (9)	99 (18)	8 (2)
Naphthol Blue Black	68 (8)	95 (13)	93 (16)	75 (0)
Phenol Red	85 (4)	86 (12)	81 (0)	63 (0)
Poly B-411	0 (0)	7 (1)	38 (0)	0 (0)
Reactive Orange 16	21 (2)	86 (21)	77 (6)	6 (0)

The values represent total decrease of color in supernatant after catalyst removal, adsorption of dye to the catalysts is indicated in parentheses.

than 40%) and only FeO·Fe₂O₃ caused significant decolorization of Eosin Yellowish. Adsorption of dye to the catalysts accounted for less than 18% of the total color removal in all cases (Table 1).

To test the ability of the catalysts to decrease chemical oxygen demand, Naphthol Blue Black was selected as the dye with the highest COD (1.80 mg oxygen per milligram NBB, i.e. approximately 70 mol oxygen per mol NBB). About 500 mg L^{-1} of the dye was incubated with 25 mg mL^{-1} of the particular catalyst and 100 mmol L^{-1} H₂O₂. Incubation with CoO·Fe₂O₃ resulted in 92% decolorization and 67% reduction of COD; the corresponding values were 97% and 85% for CuO·Fe₂O₃, 88% and 53% for FeO·Fe₂O₃, 75% and 58% for MnO·Fe₂O₃, respectively. The COD decrease corresponds to the consumption of 0.477–0.766 mg O₂ per litre.

3.2. Decomposition of hydrogen peroxide and formation of hydroxyl radicals

The highest rate of hydrogen peroxide decomposition was observed in the initial minutes of the reaction, which corresponds to the course of decolorization (Fig. 4). All hydrogen peroxide was decomposed within 2–24 h depending on the catalyst type. Decomposition of H₂O₂ was accompanied by the production of hydroxyl radicals. The highest concentrations were detected after 10–30 min of the reaction depending on the catalyst, and their presence was detected for more than 4 h. The highest production of hydroxyl radical was detected with CuO·Fe₂O₃ and the lowest with FeO·Fe₂O₃. Spin trapping experiments with DMPO also confirmed the production of hydroxyl radicals by the heterogeneous catalysts (Fig. 5). It seems that the metal ions on the surface of the catalyst first form a complex with hydrogen peroxide. The hydroxyl radical probably forms within this bound complex and can later oxidise synthetic dyes or other organic compounds. The formation of ligand-metal-radical complexes follows from the slight difference in magnetic field in the EPR spectra of hydroxyl radicals formed by different catalysts (Fig. 5) [16]. In addition to hydroxyl radicals, the presence of nitroxyl radicals

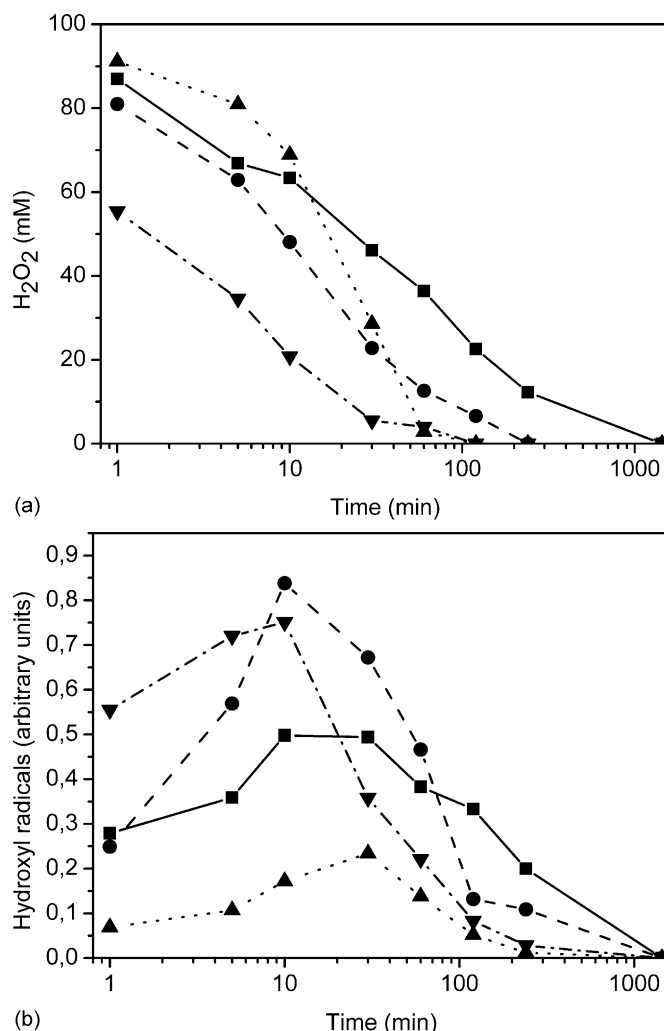


Fig. 4. Time course of hydrogen peroxide concentration (a) and production of hydroxyl radicals (b) during the incubation with 25 mg mL^{-1} catalysts and 100 mM hydrogen peroxide. Catalyst: CoO·Fe₂O₃ (squares), CuO·Fe₂O₃ (circles), FeO·Fe₂O₃ (triangles), and MnO·Fe₂O₃ (inverted triangles).

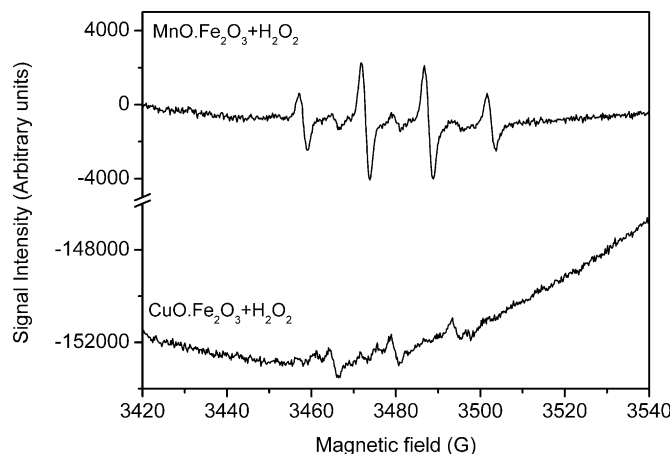


Fig. 5. EPR spectra of spin adducts of DMPO produced by heterogeneous catalysts CuO·Fe₂O₃ and MnO·Fe₂O₃. The reaction was initiated by the addition of H₂O₂. The reaction mixture contained 25 mg mL^{-1} catalyst, 100 mM H₂O₂ and 300 mM DMPO and proceeded at 25°C in the dark.

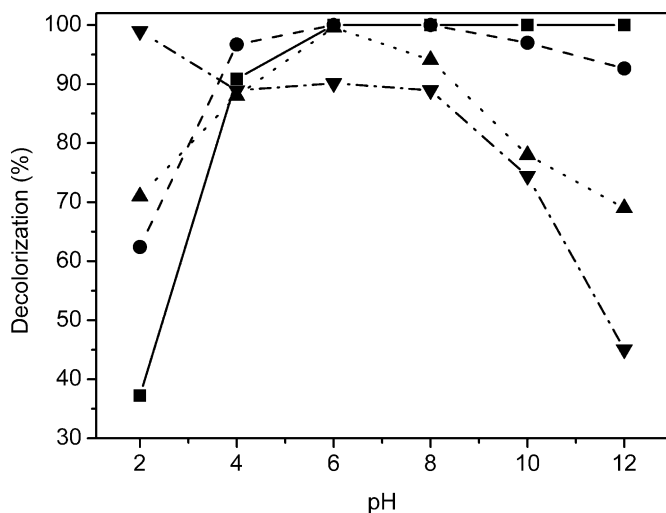


Fig. 6. Effect of pH on the decolorization of 50 mg L⁻¹ CSB after a 24-h incubation in the presence of 25 mg mL⁻¹ catalyst and 100 mM hydrogen peroxide. Catalyst: CoO·Fe₂O₃ (squares), CuO·Fe₂O₃ (circles), FeO·Fe₂O₃ (triangles), and MnO·Fe₂O₃ (inverted triangles).

presumably originating from the air dissolved in water was also detected by EPR.

3.3. Properties and stability of the catalysts

The decolorization of synthetic dyes by the catalysts was pH dependent. All of them exhibited high decolorization in the range of pH 4–8 (Fig. 6). The Co- and Cu-containing catalysts were also active at higher pH up to 12, while the performance of FeO·Fe₂O₃ and MnO·Fe₂O₃ decreased. MnO·Fe₂O₃ exhibited high decolorization at pH 2 where all other catalysts were less effective. Dye adsorption to the catalyst did not change significantly with the pH value (data not shown).

The catalysts exhibited remarkable stability of performance and low metal loss. No decrease in decolorization efficiency was observed during five 72-h cycles of CSB (50 mg L⁻¹) decolorization using 25 mg mL⁻¹ of all four catalysts tested. Metal loss in five subsequent catalytic cycles ranged 0.1–0.4 mg L⁻¹ for Co, 0.4–1.6 mg L⁻¹ for Cu, less than 0.5 mg L⁻¹ for Fe and 0.1–0.7 mg L⁻¹ for Mn, corresponding to 0.002–0.030% of the total metal.

4. Discussion

In this work we demonstrated that iron oxide (magnetite) and mixed iron oxides (Cu, Co, Mn ferrites) are effective catalysts of oxidative decolorization of dyes with hydrogen peroxide. This confirms the earlier reports about the use of magnetite for the catalytic epoxidation of alkenes and their ability to decompose H₂O₂ and oxidise simple organic compounds [42–46]. The catalysis reported here was fast and the catalysts exhibited no loss of performance in subsequent reaction cycles and low metal leaching. The experiments demonstrated that approximately up to 8% of O₂ contained in H₂O₂ present in the reaction mixtures participated in the oxidation of dyes and a high COD decrease can be

achieved in a relatively broad pH interval. Furthermore, the ferromagnetic character of the catalysts could possibly be used to make its separation from the treated solutions even more simple.

We used dyes from the groups of sulfoftaleins (Bromophenol Blue), azodyes (Chicago Sky Blue, Evans Blue, Reactive Orange 16, Naphthol Blue Black), fluorescein derivatives (Eosin Yellowish), triphenylmethanes (Phenol Red), phthalocyanines (Cu Phthalocyanine) and anthraquinones (poly B-411) to evaluate influence of structure on degradability (see Fig. 7 for structures). Chicago Sky Blue was most easily decolorized under the catalysis of all oxides used in our study, most likely due to anisidine moiety in its structure which is very easy to oxidise. Naphthol Blue Black and Phenol Red were slightly less degraded also with all catalysts employed. Evans Blue was decolorized efficiently with CuO·Fe₂O₃ and FeO·Fe₂O₃, less efficiently with CoO·Fe₂O₃ and only very little with MnO·Fe₂O₃. This behaviour is most likely caused by selective chelating properties of this dye. Also in the case of Cu Phthalocyanine MnO·Fe₂O₃ was almost inactive. Reactive Orange was well degraded under the catalysis of CuO·Fe₂O₃ and FeO·Fe₂O₃, less with CoO·Fe₂O₃ and insignificantly with MnO·Fe₂O₃, which is the same pattern as for Evans Blue, most likely due to the presence of the same chelating moiety (*o*-hydroxyazoaromate). Eosin Yellowish and Bromophenol Blue were degraded well with FeO·Fe₂O₃, a little bit with CuO·Fe₂O₃ while CoO·Fe₂O₃ and MnO·Fe₂O₃ were almost inactive. Poly B-411 exhibited the highest stability being decolorized slightly with FeO·Fe₂O₃, negligibly with CuO·Fe₂O₃ and not at all with CoO·Fe₂O₃ and MnO·Fe₂O₃. Comparison of stabilities against oxidative degradation thus shows that all azodyes and triphenylmethane dyes were oxidised more easily than fluorescein type and sulfoftalein type dyes. The most stable is polymeric anthraquinone dye Poly B-411.

Several Cu-containing systems for homogeneous catalytic decomposition of H₂O₂ have recently been demonstrated [16–18]. The main advantage of Cu-mediated decomposition of hydrogen peroxide is the fact that – unlike Fe – Cu reacts with H₂O₂ as both Cu(II) and Cu(I) and hydroxyl radicals are produced in both cases [47]. However, the catalytic performance of a methacrylate-based metal-containing heterogeneous catalyst for PAH degradation was similar with Fe, Cu, and Co [32] and the same was found in the present study. All oxides used catalyzed the decomposition of hydrogen peroxide and the formation of hydroxyl (•OH) radicals. The extent of peroxide to hydroxyl radical conversion was however different for the particular oxides. The highest yield was detected with CuO·Fe₂O₃ and the lowest with FeO·Fe₂O₃, but the highest catalytic activity for decolorization of all dyes had FeO·Fe₂O₃ followed by CuO·Fe₂O₃ and CoO·Fe₂O₃. Thus the catalytic activity of oxides for the decolorization of dyes was probably not closely and directly connected with the formation of reactive hydroxyl radicals. The production of other reactive oxygen species can also play a role as well as the chelation of dyes on the oxides [9,20]. However, the extent of adsorption represented only a minor fraction of the total amount of dye in this study and it is even less important during dye

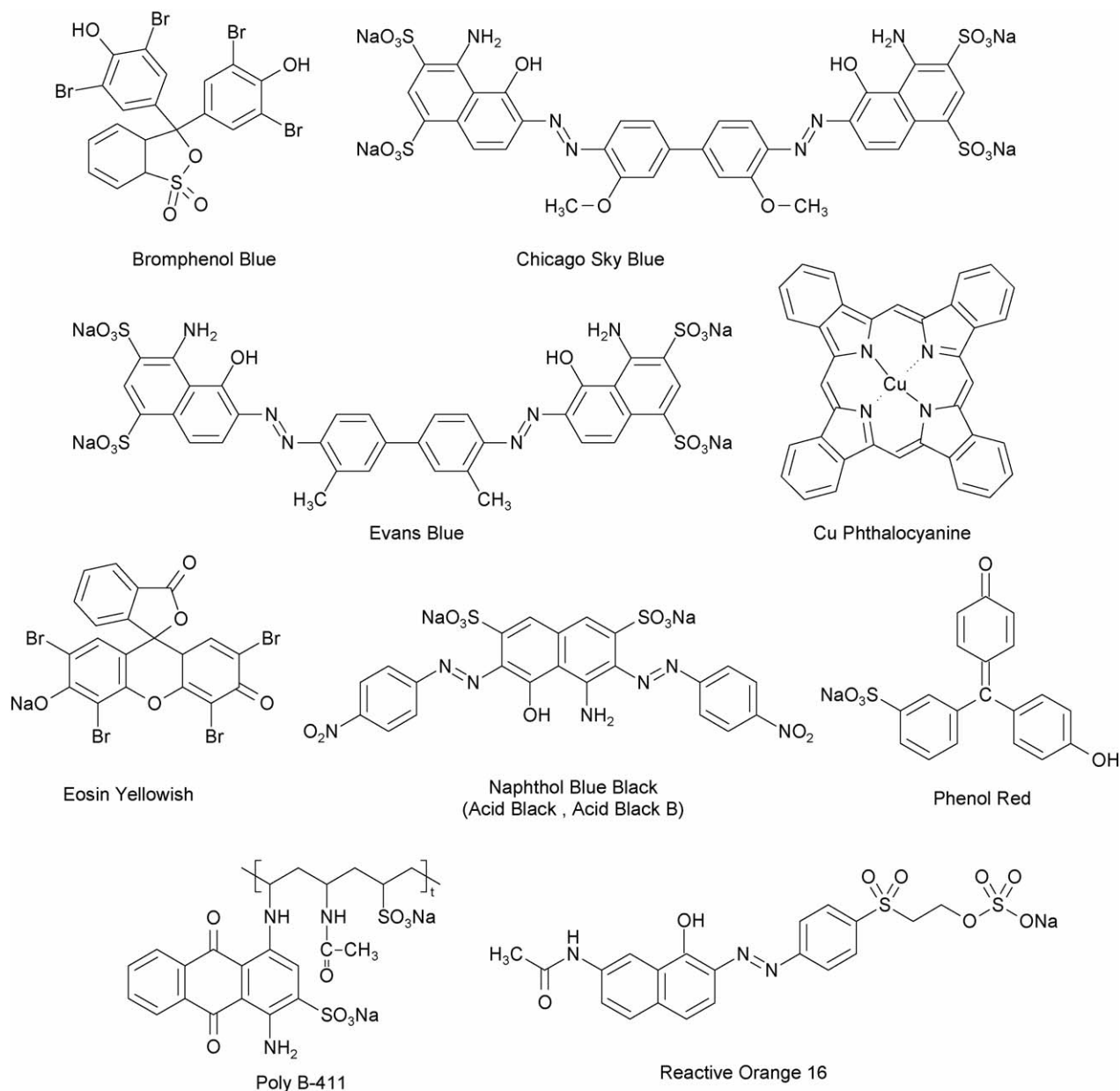


Fig. 7. Chemical structures of synthetic dyes.

decolorization in subsequent catalytic cycles since the adsorption equilibria are already reached in the first cycle.

The concentration ranges for heterogeneous catalysts of dye degradation range from a few milligrams, e.g. in case of metalloporphyrins [34] until grams per litre [19,48]. Concentrations of catalysts reported in this study are relatively high, but this disadvantage is overcome with easy separation and stable activity in subsequent catalytic cycles.

The pH profile of activity is one of the most important properties of catalytic performance. However, several efficient heterogeneous catalysts reported so far suffer from a narrow range of pH optima. Fe powder combined with H₂O₂ performed fast decolorization of dyes only at pH 2–3 [19], while silica and alumina-supported metal complexes decolorized indigo carmine and pyrocatechol violet only at pH 10–12 [21,22]. In

contrast, catalysts reported in this study were effective over a broad pH range.

5. Conclusions

Heterogeneous iron oxides – magnetite a Co, Cu and Mn ferrites – catalyze decomposition of hydrogen peroxide giving partly hydroxyl radicals. They catalyze oxidative degradation of selected dyes connected with decolorization. The catalysts retained their activity in repeated catalytic cycles and were active over a broad pH range. Compared to the homogeneous catalytic processes for dye decolorization, the catalysts described in this work offer the advantages of simple recovery from the treated solution, repeated use and a very low input of metals into the treated solutions.

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