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Dyes and Pigments 73 (2007) 19–24
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Oxidation of azo textile soluble dyes with hydrogen peroxide in the presence of Cu(II)–chitosan heterogeneous catalysts

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Received 20 May 2005; received in revised form 26 September 2005; accepted 7 October 2005
Available online 28 November 2005

Abstract

Cu(II)–chitosan complexes were used as heterogeneous catalysts for degradation of five model azo textile dyes in aqueous solution with hydrogen peroxide. The most efficient catalyst contained 3.6% Cu^{2+} and the optimal reaction conditions were pH 7.0 and 50 mM of hydrogen peroxide. The rate of decolourisation was found to be directly dependent on the dye and hydrogen peroxide concentrations in the reaction mixture. Azo dyes containing the nitro group in their molecule were easier to oxidise than those lacking this group. Using optimal reaction conditions, 91.5% decolourisation of dye **III** (4×10^{-5} mol L^{-1}) was obtained after about 20 min of reaction. However, 180 min were needed to decolorize about 85% of similar concentration of dye **I**. The only chemical structural difference is one nitro group on *para* position in relation to the azo bond.

Keywords: Chitosan; Oxidation; Catalyst; Textile; Dyes

1. Introduction

Textile dyes are an important class of synthetic organic compounds and are therefore common industrial pollutants. They are produced in large scale and may enter the environment during production or later on during textile dyeing. Due to the stability and solubility of modern dyes, conventional treatment methods for industrial wastewater are ineffective, resulting in an intensely coloured discharge from the treatment facilities. Thus, there is a need for developing new methods that are effective and acceptable in industrial use in eliminating dyes from waste streams at the source [1–11].

During the past few decades, there has been increasing interest in solutions using natural polymers as immobilization matrixes for various purposes [12–18]. Chitin, a polysaccharide found as a structural component of crab or shrimp shells and fungal mycelia, is one of the most abundant naturally occurring polymers.

Chitosan is derived from chitin by deacetylation. Due to the various desirable properties of this polyelectrolyte such as hydrophilicity, biocompatibility, low toxicity, chemically inert characteristics and high mechanical strength, it has found applications in areas from pharmaceutical, environmental and biotechnological [10,12,19]. The presence of nucleophilic functional groups, such as hydroxyl and amino and its high nitrogen content imparts the ability to adsorb metal ions through several mechanisms including ion exchange or chelation, depending on the metal type and pH of solution used [10,19–24].

The copper ion is bonded to the chitosan monomer through one amino group and two hydroxyl groups forming planar complexes with coordination number 4 [10,12].

Chitosan is soluble in water at acid pH and the electrostatic properties of chitosan are pH responsive. Thus, pH plays an important role in chitosan-based catalysts processes [5,16,19–22].

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doi:10.1016/j.dyepig.2005.10.004

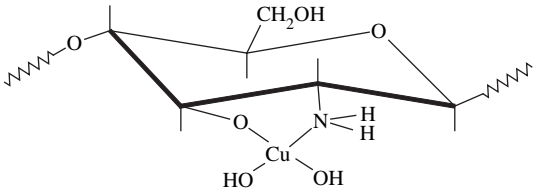


Fig. 1. Cu(II)–chitosan catalysts.

Kucherov and co-workers conducted studies using homogeneous Cu/chitosan, heterogeneous bulk Cu/chitosan and heterogeneous egg-shells catalysts, Cu/chitosan/SiO_2. These catalysts were successfully tested for oxidation of isomeric *o*- and *p*-dihydroxybenzene to the corresponding quinones by air [28].

To date, the focus of previous reports was the sorption capacities of the chitosan. In our previous work it was found that Cu(II)–chitosan complexes (Fig. 1) can catalyse the total decolourisation of anthraquinone textile dye with hydrogen peroxide, at pH 6 and at room temperature in 120 min [22].

The present work aims to extend the decolourisation study to the more important textile-dyes class, the azo dyes.

2. Experimental

2.1. Chemicals

H-acid (1-amino-8-hydroxy-naphtalene-3,6-disulfonic acid), aniline ($H_2N–C_6H_5$), 4-nitroaniline and sulfamic acid (NH_2SO_3H) were purchased from Sigma (Germany).

Chitosan from crab shells (deacetylation degree of amino groups 85%) was obtained from Sigma (Germany) and was used without further purification.

$NaNO_2$, $CuCl_2 \cdot 2H_2O$, NaOH, HCl, and H_2O_2 were analytical grade reagents, purchased from Fluka AG (Germany).

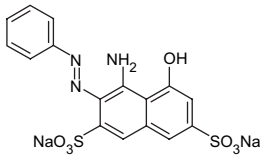
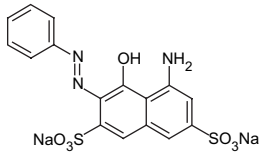
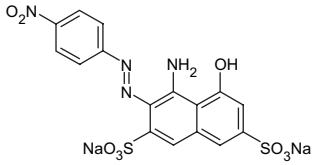
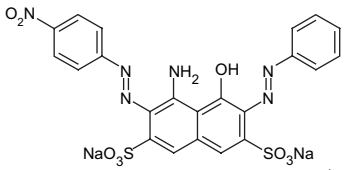
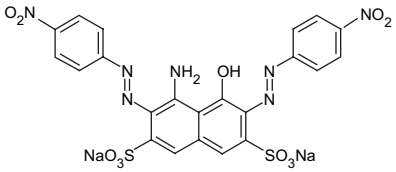
2.2. Dyes

Azo dyes **I**–**V** (Table 1) were synthesized by known methods using aniline and 4-nitroaniline as primary amine and H-acid as secondary component [25]. Thus, the preparation was the consequence of diazotization of primary amine and the coupling reaction of prepared diazonium compound with H-acid.

2.3. Preparation of the catalysts

The preparation process of catalyst **A**–**D** was similar to the method described by Kucherov and co-workers [28]. Chitosan (0.32 g) was dissolved in 0.1 M HCl (20 cm^3) at room temperature and stirred until a clear solution was formed. Solid $CuCl_2 \cdot 2H_2O$ (as indicated in Table 2) was added and the mixture was stirred for 30 min. This solution was poured into 0.1 M NaOH (300 cm^3), resulting in the coagulation of catalyst into spherical globules. Catalyst particles with diameter approximately 4–5 mm were filtered off and repeatedly washed with water until neutral pH. The globules were dried and used for the decolourisation of dyes.

Table 1
The molecular structure of prepared dyes

Dye	**Structure** (written in the azo form)
I	
II	
III	
IV	 Acid Black 1, C.I. 20470.
V	

The content of copper in dry catalyst was determined by the atomic absorption analysis in Research Institute of Organic Syntheses a.s. Pardubice. Thus, the samples of catalyst (**A**–**D**) were digested with microwave digestion system MLS 1200 using H_2SO_4, HNO_3 and H_2O_2 in two steps and measured by flame atomic absorption spectrometer PU 9400X (PHILIPS).

Cyclic voltammetry experiments were performed at laboratory temperature with Potentiostat type DT 21101 and Waveform generator Hi-Tek Instruments England. All the determinations were carried out in 25 cm^3 of 0.01 M KCl. A saturated calomel electrode (SCE) was used as a reference electrode and the Pt electrode as a counter-electrode. Cyclic voltammetry of the solid complex **B** was done by measurement of redox potential on the modified carbon electrode. The modified electrode was prepared by dipping the carbon electrode into the solution containing the complex, then into 0.1 M NaOH for 20 min and finally exposing to air for 20 min.

Table 2
Prepared Cu(II)–chitosan complexes

Complex	Copper content in dry catalyst (mass %)	Preparation of catalyst $CuCl_2 \cdot 2H_2O$/1 g chitosan (g)
A	2.3 ± 0.0	0.0615
B	3.6 ± 0.1	0.1125
C	4.1 ± 0.1	0.1428
D	6.6 ± 0.1	0.2093

2.4. Sorption analysis

The adsorption process on the complexes was studied by the known equations to describe how adsorbates interact with adsorbent [27]. The Freundlich and Langmuir isotherm equations were used, where θ is the relative coverage which is done with allotment of adsorbed dye and maximum of adsorbed dye, [**D**] is the concentration of the dye on the surface, K and a are the isotherm constants.

$$\text{Langmuir isotherm}: \quad \theta = (K[\mathrm{D}])/(1 + K[\mathrm{D}])$$

$$\text{Freundlich isotherm} \quad \theta = K[\mathrm{D}]^a$$

2.5. Oxidation of the dyes

The dye (**I**–**V**, 0.04 mM) was dissolved in acetic–acetate buffer (20 mM, 25 cm^3). The dry catalyst (**A**–**D**, 0.05 g) was added to the dye solution followed by hydrogen peroxide (35% aqueous solution). The reactions were performed without stirring at room temperature (25 °C) for 2–6 h. Comparative tests were repeated under the same conditions without H_2O_2. The kinetics of dye oxidations was monitored with the decrease of absorbance for each dye with a Unicam UV2 spectrophotometer.

3. Results and discussion

3.1. Effect of copper ion in the polymer matrix of chitosan

Cu(II)–chitosan complexes (**A**–**D**) were prepared with different amounts of copper ion in the polymer matrix (Table 2). The prepared globules were dried and used for the oxidation of dyes.

The best decolourisation results were obtained with complex **B** for all the tested dyes **I**–**V**. Table 3 shows these results for dye **III** as an example.

Two significant conclusions can be derived from the obtained results. The first is that the hydrogen peroxide is needed to regenerate Cu(II) during reduction/oxidation decolourisation process.

The second is that the copper sorption during the formation of the complex blocks part of the chitosan amino groups. Then low copper loaded complexes can adsorb more substrate (dye) because of their higher content of free NH_2 groups. The control reaction, without hydrogen peroxide, showed that 4% of the dye was adsorbed by chitosan. The catalytic activity of a copper complex depends strongly on the content of Cu^{2+} ions and on the adsorption capacity of this heterogeneous complex. These results are consistent with the conclusions of Gemeay and co-workers [8] who confirmed the dependence of the oxidative degradation of Indigo Carmine dye with hydrogen peroxide, catalyzed by supported metal complexes, on the amount of complex loads per gram of dry catalyst, the redox potential of the metal ions, and the supporting surface. All these factors act together and the net effect depends on factor which is more pronounced.

Table 3
Decolourisation of dye **III** (initial concentration was 4×10^{-5} M, pH 6, 25 °C) with catalyst after 100 min of reaction time

Catalyst	Decolourisation (%)	
	Without H_2O_2	Initial concentration of H_2O_2 (0.233 M)
A	17.60	36.83
B	14.74	95.24
C	10.10	69.57
D	5.07	52.77

The problem, as referred before, is that the copper ions are bonded with amino groups of chitosan, which are also responsible for dye adsorption. A high content of Cu^{2+} ions in the complex increases the concentration of Cu^{2+} in the oxidation process, but on the other hand decreases the amount of adsorbed dye. Therefore, the maximal oxidation rate should be achieved at an optimal concentration of Cu^{2+} in the chitosan matrix. This is about 3.6% for catalyst **B**, wherein the balance between the metal content and adsorption capacity is most favourable. Similar results were found for anthraquinone dye in our previous studies [22].

Since "free" aqueous Cu^{2+} ions can also serve as homogenous catalyst of dye oxidation, the decolourisation of Dye **III** was done at the same reaction conditions. The degree of decolourisation was only 36.21%.

Cyclic voltammetry experiments showed that the redox potential of the carbon electrode coated with the complex **B** was 0.381 V, which is lower than the redox potential (0.463 V) for an acidic solution of $CuCl_2$. Conclusion is that complex **B** is a weaker oxidant than Cu^{2+} ions in an acidic solution. Based on comparison of above redox potentials, it appears that the process of dye decolourisation is not only related to the redox potential of the catalyst but also to the concentration of the dye adsorbed on the catalyst.

The adsorption process on the surface of heterogeneous complex **B** was studied by the Freundlich and Langmuir isotherm equations. As shown in Fig. 2, our data fit better the Freundlich isotherm, where isotherms constants a and K are 1 and 1176.50×10^3 mol^{-1}, respectively. For the Langmuir isotherm, K is 1250×10^3 mol^{-1}.

3.2. The influence of pH and hydrogen peroxide concentration on the oxidation process

The oxidative catalytic activity of the copper complex **B** was tested at different pH values and the optimal reaction

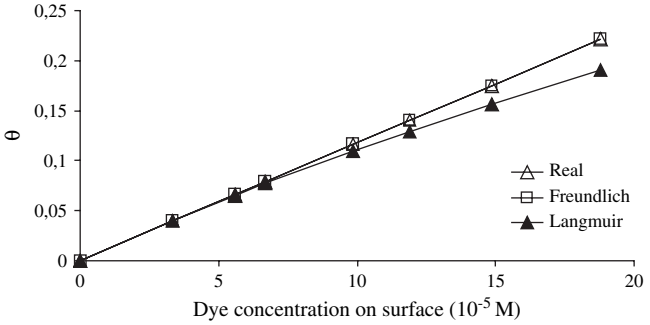


Fig. 2. Relative coverage in relation to the concentration of dye on the surface of the catalyst.

pH was found to be 7. Nevertheless lower pH values (for example pH 5.5 and 6.0) were found to be the most favourable for the catalytic oxidation of the dyes. This is due to the equilibrium where the anionic dye has higher affinity to the chitosan matrix at acidic pH. Unfortunately the catalyst is more soluble at acidic pH, which leads to the loss of catalyst during the decolourisation process.

The effect of hydrogen peroxide concentration was studied in the range of 46.53–279.18 mM. It was found that the initial reaction rate increases with the hydrogen peroxide concentration (Fig. 3). But, after 50 mM of hydrogen peroxide, it was observed that the stability of catalyst was compromised (see Section 3.2.1). Based on these results, the optimal concentration was assumed to be 50 mM, the higher hydrogen peroxide concentration that allows us to reuse the catalyst.

The catalytic process of decolourisation with hydrogen peroxide has a complex mathematical description. In the present case one can assume that the dye (**D**) is completely dissolved in water and the catalyst is in the form of particles; the dye is partly adsorbed on the surface of the catalyst, where dye-SO_3^- ^+H_3N-chitosan is formed; the adsorbed dye is oxidised with Cu^{2+} bound to the catalyst (complex); the Cu^+ ions are "re-oxidised" with H_2O_2. The formed product is desorbed into the solution.

The kinetic model was simplified by the neglecting of inductive period in the process (the incorporation of time t_0; Fig. 4).

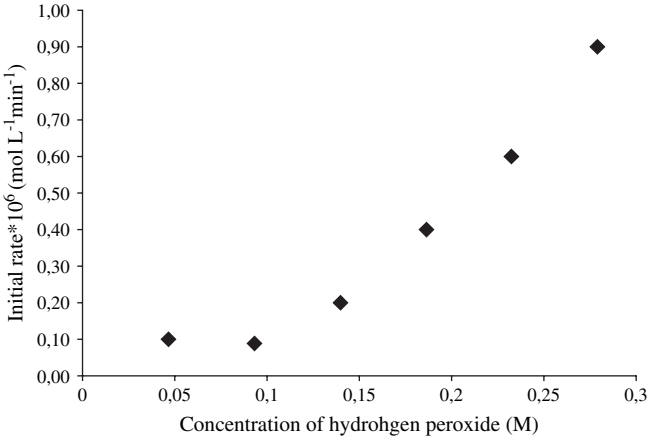


Fig. 3. Influence of hydrogen peroxide concentration on initial rate of dye degradation.

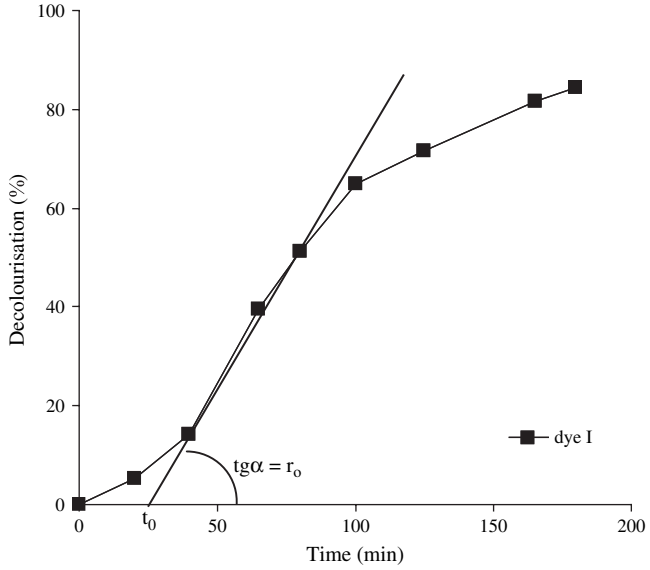


Fig. 4. Schematic determination of initial rate of azo dye **I** decolourisation.

The reaction rate (r) of dye destruction can be described by the equation $r = k_{exp}[\mathbf{D}]^n\ [H_2O_2]^m$, where values of reaction order n and m and experimental kinetic constant k_{exp} were determined using the initial reaction rate $r_0 = k_{exp}[D]_0^n\ [H_2O_2]_0^m = [D]_0 \times (\text{decolourisation } \%)/(100 \times \Delta t)$, where $\Delta t = t - t_0$. Reaction orders were found $n = 1.06$ and $m = 1.00$ and the experimental kinetic constant was 0.9850 $dm^3\ mol^{-1}\ s^{-1}$. The conclusion is that the initial rate of dye oxidation depends directly on the dye concentration and as well as on the of the hydrogen peroxide concentration.

3.2.1. Stability of catalysts

The stability of catalyst was tested as the ratio of initial mass of catalyst and the mass of catalyst after 3 h of reaction time. It was found that the stability of catalyst depends on several parameters namely hydrogen peroxide concentration and pH. Fig. 5 shows the relationship between stability of

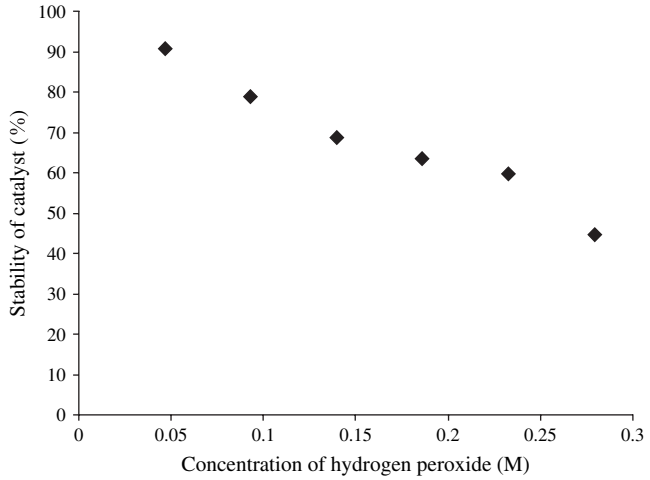


Fig. 5. Effect of hydrogen peroxide concentration on the stability of catalyst.

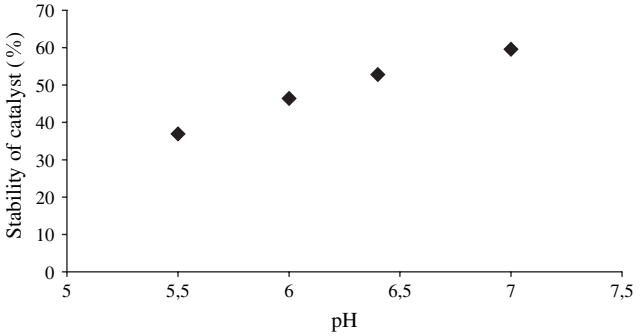


Fig. 6. Effect of pH on the stability of catalyst.

the catalyst **B** and the concentration of hydrogen peroxide in the reaction mixture.

It is obvious, that the stability of the complex decreased with the peroxide concentration.

The Fig. 6 shows the influence of pH in the range 5.5–7.0 at fixed concentration of H_2O_2 (0.050 M). The stability of catalyst increases with the pH with best results near neutrality.

These results suggest that it is possible to reuse successfully the catalyst in a new decolourisation batch.

It is also important to notice that the degree of deacetylation has direct influence on pK_a, and consequently, on its solubility, as described by Ruiz et al. [23,28,29]. Moreover, the efficiency of formed Cu(II)–chitosan catalyst will be also different.

3.3. Oxidation of azo dyes

The azo dyes **I–V** were oxidised in buffered aqueous solution of hydrogen peroxide in the presence of heterogenic catalyst **B**, where pH was 6, reaction temperature 25 °C, the initial concentration of dye was 4×10^{-5} M and the initial concentration of H_2O_2 was 0.233 M. The obtained results are depicted in Fig. 7. From the results it is obvious that the oxidative destruction of azo dyes (**III–V**) with nitro group in the *para* position to the azo group is faster in the comparison with the dyes (**I**, **II**) without this nitro group. In our opinion, the explanation of this fact is in the shifting of azo dye to its hydrazone form. It is known that the formation of the hydrazone form is facilitated by this nitro group (electron withdrawing) in the *para* position, and that hydrazone form is less stable against oxidative species [8].

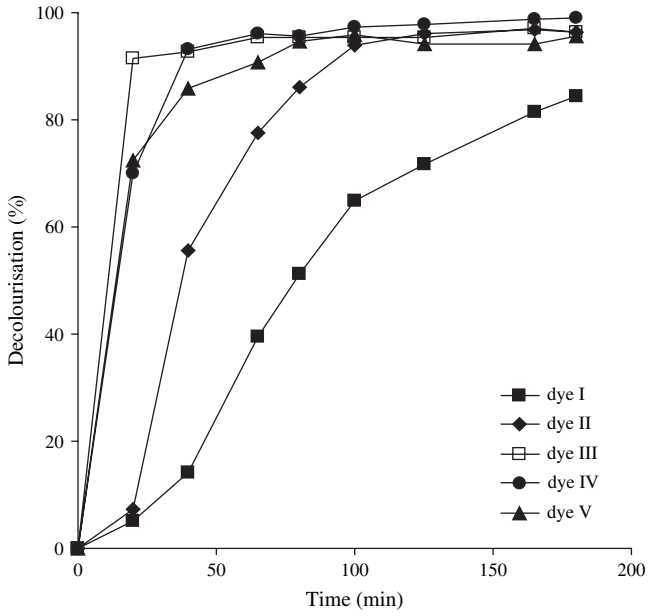


Fig. 7. Decolourisation of azo dyes.

These results are in the agreement with those obtained by Tsatsaroni [30]. The author found that the disperse dyes with nitro groups in the structure were less stable to conditions such as photo degradation.

4. Conclusions

The Cu(II)–chitosan complexes are effective heterogeneous catalysts for the decolourisation of azo dyes.

The rate of dye oxidation depends directly on the dye and hydrogen peroxide concentrations.

The optimal reaction conditions were achieved at pH 7 with 50 mM of hydrogen peroxide, 0.05 g of catalyst **B** (with 3.6% of Cu^{2+}) related to 4×10^{-5} M of dye. The pH and hydrogen peroxide concentration are crucial in the stability and reusability of the catalysts.

As these catalysts are simple, inexpensive and easily prepared, in future these method may be an alternative process for a large scale operations, namely to treat textile wastewaters.

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