DECOLOURISATION OF AN ANTHRAQUINONE DYE

WITH COPPER COMPLEXES

Romana Šuláková[c], Ana M. F. Oliveira –Campos[b] , Radim Hrdina[c] ,
Graça M. B. Soares[a]

[a] Departmento de Engenharia Têxtil, Universidade do Minho, 4800-058 Guimarães, Portugal

[b] Centro de Química, IBQF, Universidade do Minho, 4710-320 Braga, Portugal

[c] Department of Organic Technology, University of Pardubice, Studentská 95, Pardubice, Czech Republic

KEYWORDS

Oxidation of textile dyes, redox catalyst, chitosan, immobilization

ABSTRACT

Nowadays the research is focused on ecological friendly catalysts to be used in dyes decolourisation as an important target in the textile industry.

In the presented work some copper complexes were prepared by immobilization of Cu (II) on the chitosan matrix. The oxidation of model acid dye ANTD (anthraquinone dye) with hydrogen peroxide catalyzed by these Cu complexes has been investigated and the kinetic of ANTD oxidation was measured. It was found, that the reactivity of catalyst was in the relation with the amount of copper incorporated in the complex. The rate of the oxidative reaction depends also on the concentration of hydrogen peroxide in the reaction solution.

Prepared copper complexes were compared in the dye decolourisation efficiency. In the best reaction conditions the anthraquinone dye decolourisation was over 95 %.

Obtained results leads us to assume that heterogeneous redox catalysis process could be relatively easy, cheap and useful way to remove textile dyes from wastewater effluents.

1. Introduction

The purification of wastewaters from organic pollutants such as organic dyes is very important target in the textile industry.

The extensive research has been dedicated to develop ecological friendly oxidative catalyst based on the some natural polymers as chitosan serving as a catalysts support matrix [1, 2]. Chitosan is formed through N-deacetylation of the chitin, one of the most abundant polysaccharides found in the nature, obtained from crab or shrimp shells and fungal mycelia. The difference between cellulose and chitosan is that the 2-hydroxy group of the cellulose has been replaced with an amine group [1]. From the chemical point of view, chitosan is a cationic polyelectrolyte with the general formula:
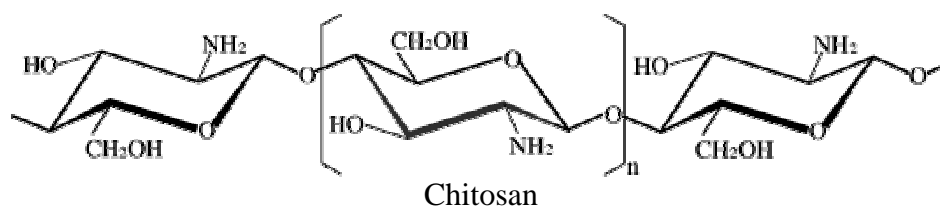
Chitosan

The biodegrability of chitosan is well known, which is an advantage factor to use that in environmental applications. The presence of different nucleofilic functional groups (OH, NH_2) and high nitrogen content of chitosan predicts the ability to sorbs metal ions through several mechanisms including ion exchange or chelation, depending on the metal and pH of the solution [2]. Hydrophilic chitosan-supported catalysts could be useful for oxidation processes of the fine organic synthesis, such as oxidation of terminal olefins, catechols and catecholamines in water [3].

Chitosan is readily soluble in various acidic solvents, whereas chitin is insoluble in water. Chitosan dissolves when the electrostatic repulsion corresponding to cationic charges are more important than the attractive interactions such hydrogen bonding or hydrophobic interactions. The solubility is also favoured by the hydratation of various sites, mainly those that are charged. In aqueous media lower than pH 6.5 the amino group of chitosan acquires a proton and ionises positively [4]. Chitosan has a pKa about 6.2 [5]. The study of the interactions of metallic ions with chitosan is well-developed [1,2,3,6,7].

The copper ion is bonded with chitosan monomer trough one amino group and two hydroxyl groups, the formation depends on the pH as described by Domard [7] (Fig. 1).

The aim of this study is the preparation of copper chitosan catalysts, which could be allowance to the mimic oxidases. For this reason was as an ion chosen copper (II). Catalysts were prepared by coprecipitation and complexation Cu (II) in the bulk of chitosan and were studied on the degradation of antraquinone textile dye.
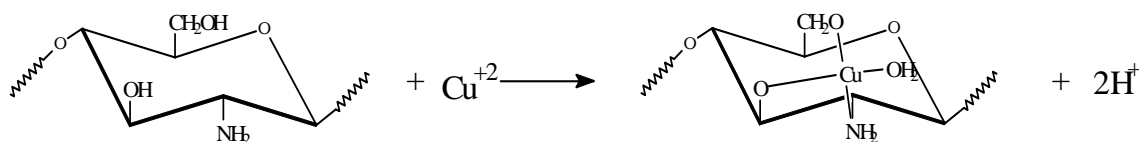

**Figure 1.** Formation of copper complex from chitosan

2. Materials and Methods

2.1 Reagents

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

$CuCl_2.2H_2O$ salt, NaOH, HCl, and H_2O_2 solutions were purchased from Fluka AG (Germany) as analytical grade reagents.

Anthraquinone blue dye of the formula $C_{20}H_{15}N_3O_8S_2$ (M = 489.47) was purchased from Synthesia (Czech Republic).
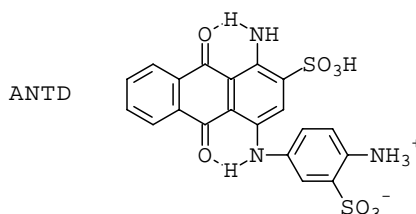
2.2 Preparation of chitosan copper catalysts [3]

Chitosan 1.5 wt% (0.32 g) was dissolved in 0.1M HCl (20 ml) at room temperature, and stirred until the formation of a clear solution. The calculated amount of $CuCl_2.2H_2O$ (0.1 to 0.5 wt% Cu) was added and the mixture was stirred for next 30 minutes. Solution of complex was dropped into 0.1M NaOH solution (300 ml) with immediate coagulation of drops into the spherical globules. Particles with diameter approximately 4-5 mm were filtered off and repeatedly washed with water until neutral pH. After this globules were air-dried at room temperature for 48 hours.

2.3 FTIR analyses

The dry catalysts were analysed by FTIR spectroscopy with a Thermo Nicolet 360 Spectrophotometer in the range of 4000-600 cm^{-1} and resolution 36 cm^{-1}. The samples were measured without preparation using Avantar Multi-Bounce ATR.

2.4 Cyclic voltammetry

Cyclic voltammetry experiments were performed at laboratory temperature with Potentistat type DT 21101 and Waveform generator Hi-Tek Instruments England. A conventional single-compartment cell, equipped with three-electrode configuration, was employed. All the measurements were done in 25 ml of 0.01M KCl. A saturated calomel electrode (SCE) was used as a reference electrode, and Pt electrode as a counter-electrode. Cyclic voltammetry of solid complex B was done by measurement of redox potential on the modified carbon electrode. Electrode covered with complex was prepared by dipping electrode into the liquid complex solution, after that into the 0,1M NaOH for 20 min and exposed to air for 20 min.

For measurement of liquid complex and acidic solution $CuCl_2.2H_2O$ was into the 25 ml of 0.01M KCl added 3 ml of sample. Carbon electrode was used as a working electrode. All with according ration of copper (11.27 %).

The potential shown in the cyclic voltammetry curve vs. SCE, the half-wave potential was calculated using $E=1/2(E_A-E_C)$, where E_A and E_C are the peaks of anodic oxidation and cathodic reduction.

### 2.5 Catalytic oxidation of anthraquinone dye (ANTD)

Anthraquinone dye ANTD (0.001 mmol) was dissolved in 50 ml of water. The catalyst (0.05 g) was added to the dye solution and then hydrogen peroxide (0.047 mmol, 0.5 ml 30 % aqueous solution). Then pH of the solution was adjusted (pH 4.5, 5.2, 6.0, 7.7, 10.0) and the mixture was stirred at room temperature ($25^{o}C$) for 2 hours. Comparative test was done under the same reaction conditions but without H_2O_2.

The dye destruction was determined by the monitoring of absorbance at wavelength 604 nm using a Unicam UV2 spectrophotometer.

3. Results and discussion

3.1 Redox potentials of copper

The oxidative destruction of a dye with hydrogen peroxide in the presence of Cu(II) catalyst (complex) can be described by the following reaction scheme (Fig.2), where L (ligand) represents a functional group of chitosan ($-NH_2$, $-OH$). Standard reductive potential for hydrogen peroxide is 1,776 V [8].

$$H_2O_2 + 2\ H^+ + 2\ e^- \rightleftharpoons 2\ H_2O \quad E^0 = 1.776\ V$$
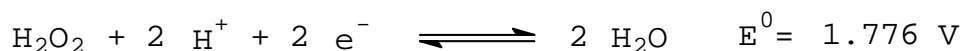
In this reaction scheme can not be forgotten, that air oxygen is also the oxidative specie, of course, less reactive then hydrogen peroxide:

$$O_2 + 4\ H^+ + 4\ e^- \rightleftharpoons 2\ H_2O \quad E^0 = 1.229\ V$$
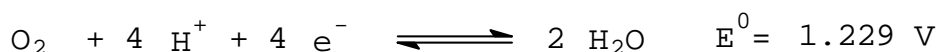
At normal experimental conditions (atmospheric pressure, laboratory temperature 298.15 K) the solubility of oxygen O_2 in water is X_l (mole fraction solubility) $= 1.671*10^{-4}$ [8].

Standard reductive potential for Cu^{2+} ions (aqua ions) is declared:

$$Cu^{2+} + e^- \rightleftharpoons Cu^+ \quad E^0 = 0.153\ V$$

This redox potential should be different in the complex. It is known from the literature [9], that the difference between standard reductive potential of "free" Cu^{2+} ion and complexed Cu^{2+} ion is in a direct relation with the logarithm of complex constant (K_{compl}):

$$E^o (Cu^{2+})\ -\ E^o (Cu^{2+}_{compl}) = RT.F^{-1}.\ln (K^{Cu(II)}_{compl} / K^{Cu(I)}_{compl})$$
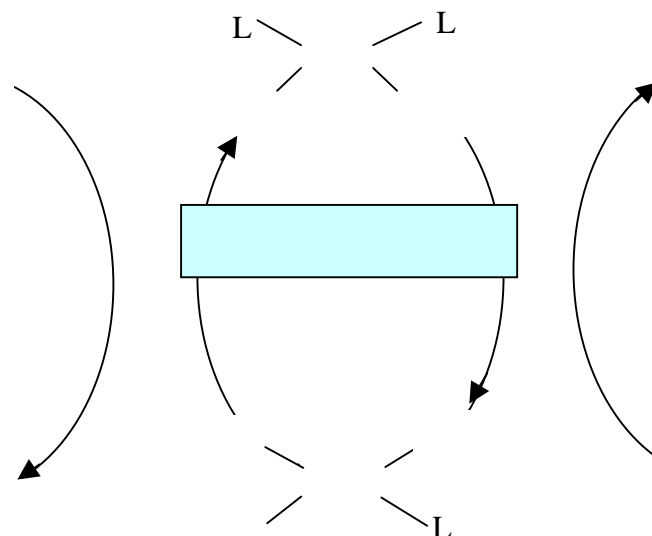
Figure 2. Catalytic oxidation of dye

The cyclic voltagrams obtained by a quick scan (250mV/s) of the solutions and cyclic voltagram of complex coated electrode are shown in figure 3.

Resulting redox potentials for the **acidic** solution of $CuCl_2$ were 0.463 V and for dissolved complex 0.425V. Carbon electrode coated with complex B had a potential 0.381 V. From the values of redox potential we found that the heterogeneous complex is weaker oxidant than dissolved complex or free ions of Cu^{2+} in the acidic solution.
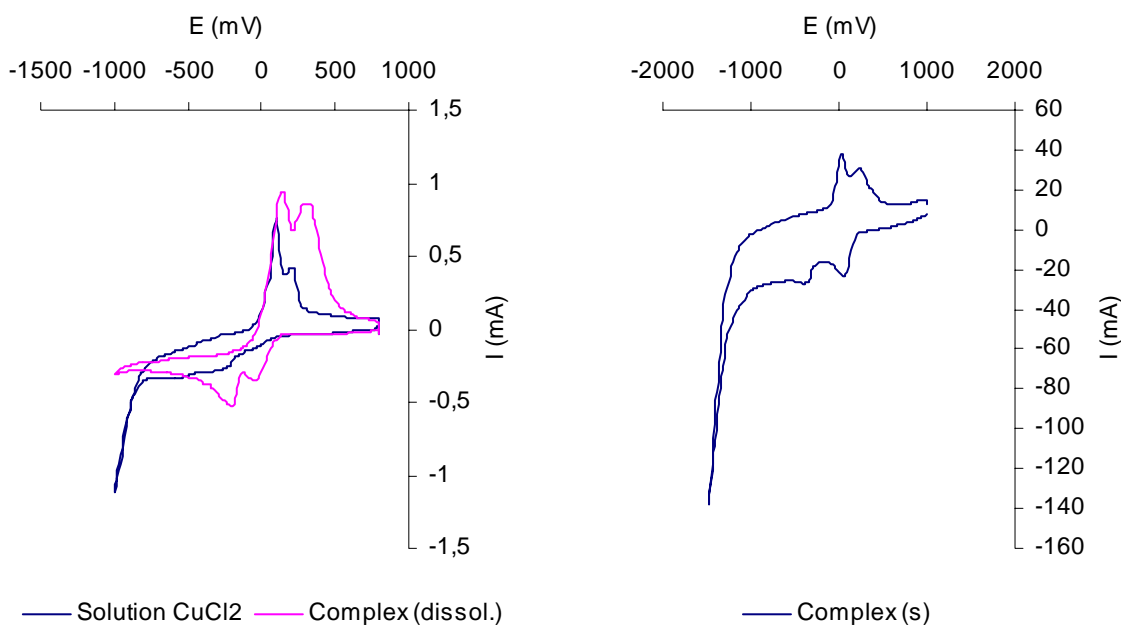

Figure 3. Cyclic voltagrams of solution $CuCl_2$, liquid and solid complex

Account these results we could declare that the rate of dye destruction is not given only by reactivity (effect of reductive potential) of the oxidant but also with the concentration of the reactants on the surface of solid catalyst, which is higher than the concentration in solution.

3.2 Sorption properties of complex

It's seen that the adsorption properties depend on the content of copper. Low loaded complex could adsorb more substrate because of high content of free NH_2 groups. The results of the reaction without hydrogen peroxide are shown in the table 2. The large molecule of the dye is softly adsorbed by chitosan (3.4 % of dye from aqueous solution).

The sorption isotherms were studied on the complex B by usual isotherms equations such as Freundlich and Langmuir.

Langmuir isotherm:
$$\theta = \frac{K.[D]}{1+K.[D]}$$

Freundlich isotherm:
$$\theta = K.[D]^a$$

Where θ is relative coverage which is done with the fraction of adsorbed dye and maximum of adsorbed dye, **[D]** is a concentration of the dye on the surface and **K, a** are the isotherms constant.

Our sorption fits to the Freundlich isotherm, where constants were determined $a=1$ and $K=1177$.

3.3 Catalytic activity of copper complexes

Catalytic activity of a copper complex strongly depends on the content of Cu^{2+} ions and on the sorption capacity of this heterogeneous complex. Basic problem is that copper ions are bonded with amino groups of chitosan, which are also responsible for the dye adsorption. It means high content of Cu^{2+} ions in complex (defined as mole of Cu^{2+} per gram of complex) increases actual concentration of Cu^{2+} in the oxidation process, but contrary decreases the actual amount of adsorbed dye. The result is that the maximal reaction rate of oxidation should be achieved at some optimal concentration of Cu^{2+} in the complex.

Thus, Cu(II)-chitosan complexes were prepared with different amount of copper ion in the polymer matrix (Tab. 1). The percent content of copper was calculated assuming the resulting mass of dry complex and initial added amount of $CuCl_2.2H_2O$ (% = 100.mass of $CuCl_2.2H_2O$/mass of dry complex).

Table 1. Prepared Cu-Chitosan complexes

Complex	Cu/chitosan (%)	Mole of Cu(II)/g of catalyst (mole.g-1)
A	6,15	0,09693
B	11,27	0,17762
C	14,28	0,22506
D	20,91	0,32955

FTIR spectra of complexes and chitosan are shown in the figure 4. We can see the increase of absorbance (A-C) in the range between 3700-3000 cm^{-1}. This broad absorption peak is typical for –OH and –NH$_2$ groups in the polymer. Thus, the amount of complexed (bonded) copper in the polymer is in the direct proportion with the decreasing of the peak.

The incorporation of copper into the chitosan causes the formation of the stable complexes. Ion Cu^{2+} has ability to form planar complexes, where copper has coordination number 4.
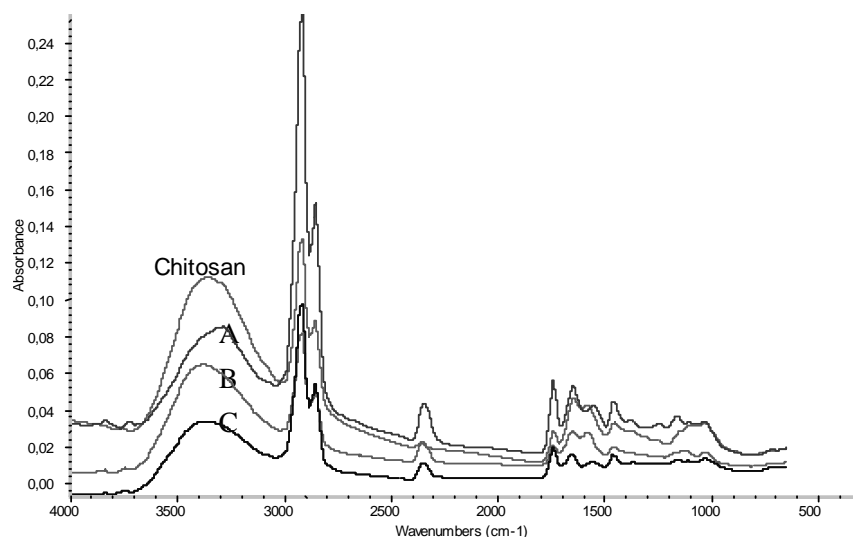

Figure 4. FTIR spectra of Cu-chitosan complexes (A – C)

Chitosan has pK$_a$ 6.2 [5] it means that at lower pH (when its amine groups are protonated) is soluble in water. For this reason electrostatic chitosan properties are pH responsive [1] and pH conditions assumes a large importance in a catalytic process. Acid conditions were found to be the more favourable to the catalytic oxidation of ANTD. The reason is in the following equilibria (Fig. 5), where anionic dye (ANTD) has high affinity to chitosan matrix.
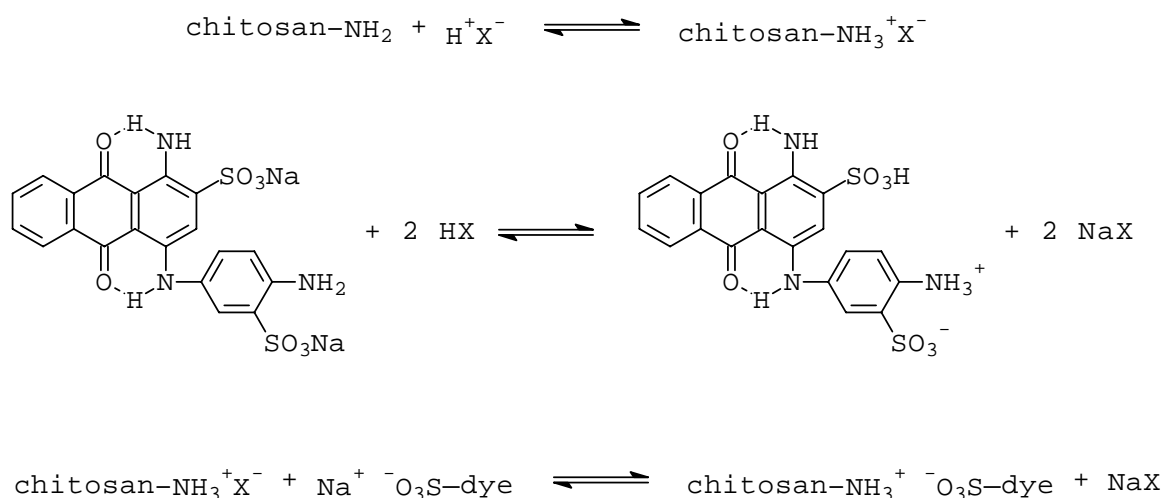
chitosan–NH$_2$ + H$^+$X$^-$ $\rightleftharpoons$ chitosan–NH$_3$$^+X^-$

Figure 5. The ion exchanges in the reaction mixture

All prepared catalysts A-D were tested on the efficiency of ANTD decolourisation. This model dye is water-soluble anthraquinone dye. ANTD is the typical example of a blue dye used in the textile industry and it was chosen, since anthraquinone dye is resistant against oxidative species. For example, this dye is oxidised with hydrogen peroxide in aqueous solution in 120 min only from 1.21 %.

The oxidative catalytic activity of copper complexes was firstly tested at the different reaction pH (Fig. 6).
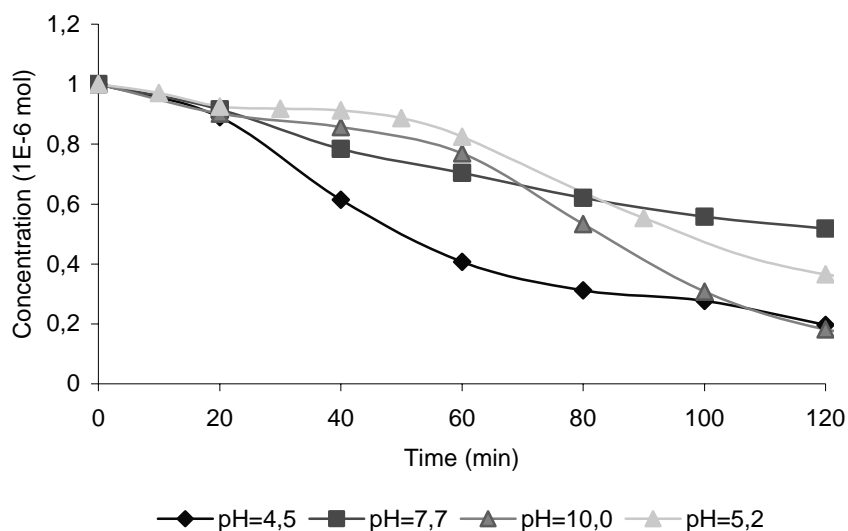

Figure 6. Decolourisation at different pH using catalyst C

From the results and the knowledge of chitosan behaviour we can say that optimal reaction pH is 5.6-6, because at lower pH the chitosan complex is easily dissolved.

The efficiency of complex A-D were tested at reaction pH 5.6, results are in the table 2 and figure 7. It's known that the copper ion bonded with chitosan monomer trough one amino group and two hydroxyl groups, so the formation of the complex depends on the pH and of course on the sorption [7]. The optimal content of Cu^{2+} incorporated in chitosan matrix is around 11 % (catalyst B), where the balance between content of metal and adsorption properties is most favorable.

Table 2. Decolourisation of ANTD with complexes A-D (reaction pH 5.6)

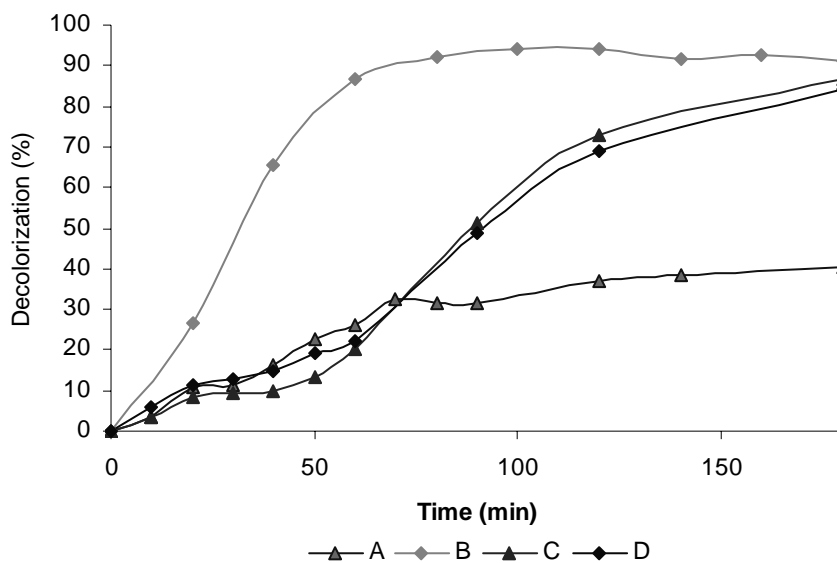|	% ANTD decolourisation			
	Reaction time 120 min		Reaction time 180 min	
	Concentration of hydrogen peroxide		Concentration of hydrogen peroxide	
Catalyst	0 mmol	0,047 mmol	0 mmol	0,047 mmol
A	17.68	36.81	25.15	40.55
B	**14.68**	**94.14**	**28.86**	**91.21**
C	9.91	73.02	11.85	86.51
D	5.67	68.99	6.72	84.18

Figure 7. Decolourisation using complexes A-D

The influence of concentration of hydrogen peroxide was tested on the catalyst C. The relationship between initial rate and the concentration of hydrogen peroxide was determined (Fig. 8). From the curve we can see that hydrogen peroxide concentrations up to 0.047 mM had no influence on the reaction rate. In the top of it, the amount of hydrogen peroxide has the decisive effect on the stability of the complex and consequently on its recovery and reusing.
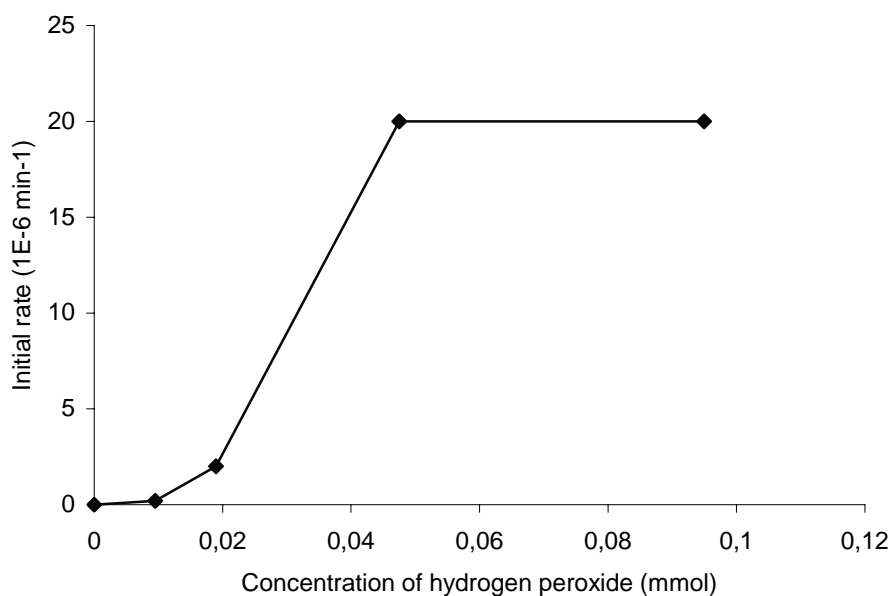

Figure 8. Influence of concentration of hydrogen peroxide

3.4 Kinetics studies

The catalytic treatment of wastewater with hydrogen peroxide has very complicated mathematical description, where we should note the adsorption, desorption of the dye in the catalyst, diffusion of the reactants and chemical reactions as an oxidation of the dye and reoxidation of catalyst. For the formal description of the kinetics we used for different Cu-chitosan catalysts the kinetic pseudo 1st order ($A=e^{-kt}$). The reaction rate constant **k** was determined from the linear plot of logarithmic concentration of the dye with time
$lnA= k.t +lnA_0$ (where **A** is a concentration of the dye in the solution, A_0 is a starting concentration and **t** is the time). Obtained results are summarized in the table 3.

Table 3. Kinetics of pseudo first order for complexes A-D

Catalyst	$k\ (s^{-1})$
A	0,0000950
B	0,0004933
C	0,0001317
D	0,0001317

In accordance with table 2, we can see that the oxidative degradation of the dye is fastest using catalyst B. If hydrogen peroxide is not present in the reaction mixture, the catalyst is reoxidized by the air oxygen, but this reaction is extremely slow, in days.

4. Conclusions

Results reported at this poster are a part of a large project devoted to the degradation of textile dye pollutants.

The heterogeneous system consists from copper-chitosan complex and hydrogen peroxide is promising for the degradation of the textile dye. Total decolourisation of the model anthraquinone dye was achieved using the copper-chitosan complex B with 11.27 % of Cu^{2+} and laboratory temperature (25°C).

The best pH for antraquinone dye degradation is acidic; at higher pH the reactions are producing different products. By catalytic and stability reasons, the pH 6 was the most convenient for the oxidation of ANTD.

The amount of hydrogen peroxide has a crucial influence on the stability and following reusing of the complex. The optimal concentration of H_2O_2 is about 0.03-0.04 mmol.

References

[1]   M. N. V. Ravi Kumar, Reactive & Functional Polymers 2000,46,1-27; A review of chitin and chitosan applications.

[2]   [M. Ruiz, A.M. Sastre, E. Guibal, Reactive & Functional Polymers 2000,45,155-173; Palladium sorption on glutaraldehyde-crosslinked chitosan.

[3]   A.V. Kucherov, N.V. Kramareva, E.D: Finashina, A.E. Koklin, L.M. Kustov, Journal of Molecular Catalysis A: Chemical 2003,198,377-389; Heterogenized redox catalysts on the basis of the chitosan matrix 1. Copper complexes.

[4]   M.R. Julia, E. Pascaul and P.Ezra, J.S.D.C. 2000; Influence of the molecular mass of the chitosan on shrink-resistance and dyeing properties of chitosan treated wool.

[5]   R. F. Taylor, Protein immobilization – fundamentals and applications, 1991.

[6]   L. Dambies, C. Guimon, S. Yiacoumi, E. Guibal, Colloids and Surfaces A: Physicochemical and Engineerinf aspects 2001,177,203-214; Characterization of metal interactions with chitosan by X-ray photoelectron spectroscopy.

[7]   A. Domard , Inter. J. Biol. Macromol., 1987, 9, April; pH and c.d. measurements on a fully deacetylated chitosan: applications to Cu- polymer interactions.

[8]   CRC Handbook of Chemistry and Physics, 78th Edition, 1997-1998, CRC Press, New York.

[9]   Physical Chemistry, A. Tockstein, Pardubice 1977.