

# The oxidation of hydroquinone to *p*-benzoquinone catalysed by Cu(II) ions immobilized on acrylic resins with aminoguanidyl groups: Part 1

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## Abstract

The immobilized macromolecular copper catalysts were prepared by modification of nitrile groups in acrylonitrile, vinyl acetate and divinylbenzene terpolymer using aminoguanidine carbonate and subsequent complexation with copper(II) nitrate. The activity of the catalysts was measured in the model reaction—oxidation of hydroquinone (H<sub>2</sub>Q) to *p*-benzoquinone (Q) by hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). Under the optimal conditions only main product *p*-benzoquinone (yield 98%) was obtained after 80 min. The catalytic activity and selectivity in the Cu(II)–resin system increases compared to reaction without catalyst and with native Cu(II) ions. For the best catalyst, after 10 min, initial oxidation rate increased 57 times in comparison with the same reaction without catalyst as well as 16 times in comparison with native Cu(II) ions. The oxidation reaction of H<sub>2</sub>Q showed a kinetic behaviour typical for a Michaelis–Menten mechanism. The optimal oxidation parameters in the reaction H<sub>2</sub>Q → Q are (a) H<sub>2</sub>Q:Cu(II) ratio—10:1, (b) H<sub>2</sub>O<sub>2</sub> concentration—5 × 10 (mol/l) and (c) solution pH above 5. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Oxidation catalyst; Hydroquinone to *p*-benzoquinone oxidation; Aminoguanidyl ligands with immobilized Cu(II) ions

## 1. Introduction

Heterogenized catalysts, i.e. complexes of the transition metal ions with chelating resins show usually lower catalytic activity (in most cases not exceeding 80%) than the homogeneous catalysts. Sometimes metal ions coordinated by functional groups cause high catalytic activity of formed complex in comparison with free metal ion. The metal ions of variable valence, such as copper ones, are used as reducing or oxidizing agents and can be utilised as catalyst in redox reactions. Oxidation of alcohols, phenols and

their derivatives can be carried out using atmospheric oxygen, hydrogen peroxide or others hydroxyperoxides [1].

The investigation of heterogenized catalysts concentrates on

- testing of new catalysts by using one selected model reaction, and
- obtaining desirable final product with the highest efficiency and selectivity.

In the process of catalysts selection and investigations of their catalytic activity, three groups of parameters are extremely important (1) the structure of polymer matrix and ligands (cross-linking degree, porosity and polarity, swelling, concentration

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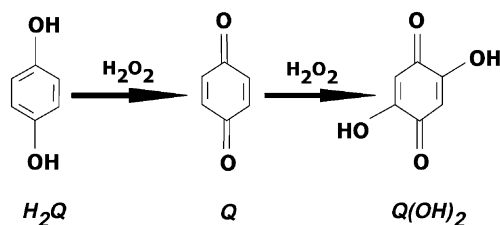


Fig. 1. Scheme of H<sub>2</sub>Q oxidation reaction.

of ligands), (2) the structure of transition metal complexes in resin system (metal ions sorption velocity, distribution coefficient, metal ion uptake, stability of complex, electronic structure of complex), (3) the parameters of model reaction (time, temperature, pH, ratio of transition metal ions to oxidized compound, kind of oxidizing agent, ratio of oxidizing agent to oxidized compound, shaking speed).

The oxidation of hydroquinone (H<sub>2</sub>Q) to *p*-benzoquinone (Q) is well known for a long time (Fig. 1). This reaction occurs with small rate without the presence of a catalyst at room temperature. Cu(II) ions accelerate this reaction. Oxidizing agent can be both oxygen and peroxides. In the case of oxidation with atmospheric oxygen it is beyond any doubt, that this is selective reaction [1]. When concentrated solutions of hydrogen peroxide are used, subsequent oxidation of reaction product (Q) to 2,5-dihydroxy-*p*-benzoquinone is possible [2,3]. If the concentration of hydrogen peroxide is in the range 10<sup>-4</sup> to 10<sup>-5</sup> M, only *p*-benzoquinone as reaction product should be formed in initial reaction stage [4].

Sato and co-workers [5,6] published the results of hydroquinone oxidation with atmospheric oxygen in the presence of catalysts such as complexes of Cu(II) with polyvinylimidazole [5] and with vinylimidazole and ethylvinyl sulphide copolymers [6]. Reoxidation of complexed Cu(I) ions was determined as the limiting process of described reaction.

The investigations of the influence of cross-linked polymer matrix and ligands structure on catalytic activity were published in 1982 by Egawa and co-workers [7]. Authors determined the catalytic activity of seven chelating resins, having different functional groups containing nitrogen, oxygen and sulphur in the oxidation of 2,6-dihydroxyphenylacetic acid and hydroquinone using atmospheric oxygen. The acrylic resin with hydrazide ligands, containing

immobilized Cu(II) ions displayed the highest catalytic activity, which did not decrease even after repeated use of the catalyst. This oxidation reaction showed a kinetic behaviour of Michaelis–Menten type that is kinetic of enzymatic reaction [7].

Butina et al. [8] observed the increase of oxidation rate of hydroquinone, using metal ions complexed on polyethyleneimines in the order Cu(II) > Co(II) > Fe(II) > Mn(II). It was found that composition of resin and ratio of polymer to amount of metal ions had an influence on oxidation degree.

Fray and co-workers [9] investigated kinetic oxidation of H<sub>2</sub>Q to Q using oxygen. 2-methylallyl L-histidinate homopolymer with Cu(II) complexes was found to be the most effective catalyst. They also considered the influence of co-ions in complexes on the sorption of Cu(II) ions. Yamashita and co-workers [10,11] tested the accelerating ability of Cu(II) complexes with 4-vinylpyridine and *N*-vinylpyrrolidinone homo- and copolymers in the oxidation reaction. Resins obtained from copolymer accelerated the oxidation reaction of H<sub>2</sub>Q over 600 times in comparison to free Cu(II) ions. Under the same conditions, Cu(II) complex with 4-vinylpyridine homopolymer caused an increase of the initial reaction rate constant only 200 times and Cu(II) complex with *N*-vinylpyrrolidinone homopolymer only just five times.

Copper complexes with polymers having siloxane matrix with pyridyl ligands were used to catalyze H<sub>2</sub>Q oxidation using oxygen in water–methanol solution [12]. Nemoto et al. [12] analysed the influence of structural characteristic of polymer ligand on catalytic properties of complex. The following were indicated as the most probable reasons of increase of catalytic activity of copper immobilized complexes (a) flexibility of siloxane matrix (possibility of conformation change of chain during Cu(II) → Cu(I) reduction), (b) substrate absorption by hydrogen bonds and (c) matrix hydrophobic effect.

This paper presents the results of investigations of catalytic activity of Cu(II) ions immobilized on acrylic resins with aminoguanidyl ligands. As a model reaction, we have used the oxidation of H<sub>2</sub>Q to Q by hydrogen peroxide in aqueous medium (Fig. 1). In the first part we have concentrated on oxidation parameters, i.e. reaction time, ratio of Cu(II) ions to oxidized compound (here H<sub>2</sub>Q), concentration of oxidizing agent (here H<sub>2</sub>O<sub>2</sub>) and reaction pH.

## 2. Experimental part

### 2.1. Preparation of catalysts

The terpolymer of acrylonitrile, vinyl acetate and divinylbenzene was obtained by suspension polymerization. More details on the preparation of this terpolymer can be found elsewhere [13,14]. Terpolymer was obtained from monomers mixture (10 wt.% DVB) diluted with 2-ethylhexanol and cyclohexanol (1:9 v/v). The ratio of monomers to diluents was 1:1 (v/v) [13]. Aminolysis of terpolymer (A) was carried out by using aminoguanidine carbonate in a boiling butanol–water mixture in presence of  $\text{Na}_2\text{CO}_3$  as described in an earlier paper [13,14].

Concentration of amino and carboxyl groups was determined as it was described in [13]. Sorption of Cu(II) was performed using batch method. Resin was swollen in distilled water. The polymer samples ( $0.5 \pm 0.001$  g) were placed in 50 ml of a buffer solu-

tion of  $\text{Cu}(\text{NO}_3)_2$ . Cu(II) solutions of concentrations  $5 \times 10^{-2}$ ,  $5 \times 10^{-3}$  and  $1 \times 10^{-4}$  mol/l were prepared at pH = 4.99 using sodium acetate buffer. After 48 h shaking the concentration of Cu(II) ions in solution was measured by atomic absorption spectrophotometry (AAS) on an AAS-30 (Perkin Elmer AAnalyst 100). Sorption of Cu(II) in mmol/g was calculated from the difference of Cu(II) concentrations in solution and confirmed by elemental analysis of copper in resin. The distribution coefficient was defined as the ratio of Cu(II) sorption in mg/g of resin to the concentration of Cu(II) ions after sorption in mg/ml of solution.

### 2.2. Oxidation reaction

Twenty-five milliliters of hydrogen peroxide solution ( $1 \times 10^{-3}$  to  $5 \times 10^{-2}$  mol/l in sodium acetate buffer; pH = 5) were mixed with 25 ml of  $\text{H}_2\text{Q}$  solution ( $4 \times 10^{-3}$  mol/l) in a polyethylene flask.

Table 1  
Characteristics of catalysts with Cu(II) ions immobilized on aminoguanidyl ligands<sup>a</sup>

KA-XY catalyst	Matrix	$Z_L$ (mmol/g)	$Z_K$ (mmol/g)	[Cu(II)] (mol/l $\times 10^4$ )	$-\text{NH}_2/\text{Cu(II)}$ (mmol/mmol)	$S_{\text{Cu(II)}}$ (mmol/g)	$K$ (ml/g)
KA-11	A-1	0.8	3.5	0.05	0.16	1.46	10
KA-12				0.5	1.62	1.04	193
KA-13				1	81	0.03	983
KA-21	A-2	1.0	1.5	0.05	0.19	0.45	3.7
KA-22				0.5	1.92	0.35	45
KA-23				1	96	0.024	10333
KA-31	A-3	1.4	2.6	0.05	0.28	0.005	0.1
KA-32				0.5	2.76	0.50	91
KA-33				1	138	0.022	14000
KA-41	A-4	1.7	2.8	0.05	0.34	0.06	1.2
KA-42				0.5	3.42	0.1	20.3
KA-43				1	171	0.03	18000
KA-51	A-5	0.3	2.1	0.05	0.065	0.03	0.6
KA-52				0.5	0.65	0.01	5
KA-53				1	32.4	0.03	16500
KA-61	A-6	2.0	3.0	0.05	0.41	1.6	13.5
KA-62a				0.5	4.10	0.90	270
KA-62b				0.5	4.10	0.7	226.4
KA-63				1	205	0.03	18200

<sup>a</sup> [Cu(II)]: initial ions concentration;  $-\text{NH}_2/\text{Cu(II)}$ : ratio of aminoguanidyl ligands to Cu(II) ions;  $K$ : distribution coefficient;  $S$ : Cu(II) loading;  $Z_L$ : concentration of aminoguanidyl ligands;  $Z_K$ : concentration of carboxyl ligands; KA-XY: symbols of catalyst, where X is a kind of support and Y denotes initial Cu(II) concentration ((1)  $5 \times 10^{-2}$  M, (2)  $5 \times 10^{-3}$  M, (3)  $1 \times 10^{-4}$  M).

Table 2

The loss of hydroquinone and initial oxidation rate ( $v_0$ ) in the oxidation reaction  $H_2Q \rightarrow Q^a$

Catalyst	Loss of $H_2Q$ after 60 min (%)	$10^7 \times v_0$ (mol/(1s))
KA-53	100	11.3
KA-32	47.5	6.9
$Cu^{2+}$	–	0.7
A	4.7	0.5
Without catalyst	2.0	0.2

<sup>a</sup> Reaction parameters:  $T = 24^\circ C$ ;  $t = 80$  min;  $pH = 4.9$ ;  $[H_2Q] = 4.0 \times 10^{-3}$  mol/l;  $[H_2O_2] = 5.02 \times 10^{-2}$  mol/l;  $[H_2O_2]:[H_2Q] = 12:6$  (molar ratio);  $[H_2Q]:[Cu(II)] = 10:1$  (molar ratio).

Next, swollen catalyst was placed in the flask and the entire mixture was shaken (100 cycles/min) for desired time at  $T = 24^\circ C$ . The concentration of unreacted  $H_2Q$  and  $Q$  was determined using SPECORD M-40 Carl Zeiss Jena at  $\lambda = 246.5$  and  $289.0$  nm, respectively.

The initial rate of reaction, called catalytic activity of catalyst ( $v_0 = \Delta[Q]/t$ ) was calculated from the concentration of  $Q$ . The loss of  $H_2Q$  ( $L_{H_2Q}$ ) is here defined as decrease of  $H_2Q$  concentration with relation to initial concentration of  $H_2Q$  expressed in weight percent ( $L_{H_2Q} = (\Delta[H_2Q]/[H_2Q]_0) \times 100\%$ ). Parameters of reaction are shown in Table 2.

### 3. Results and discussion

#### 3.1. Catalysts of KA-XY type

Polymer matrix—serving out a solid support for heterogenized catalysts—was obtained out by chemical modification of poly(acrylonitrile–vinyl acetate–divinylbenzene) terpolymer (A). The method of synthesis of resins with aminoguanidyl ligands through aminolysis of acrylonitrile groups in copolymers was described earlier [13,14]. It was found that during aminolysis, under strongly alkaline conditions, nitrile groups were converted to N-substituted amides and to carboxyl groups. Additionally, vinyl acetate mers were hydrolysed and thus swelling of resins was increased [13]. The characteristics of these resins are presented in Table 1.

In order to determine the complexing ability of the amphoteric resins, sorption of  $Cu(II)$  ions was mea-

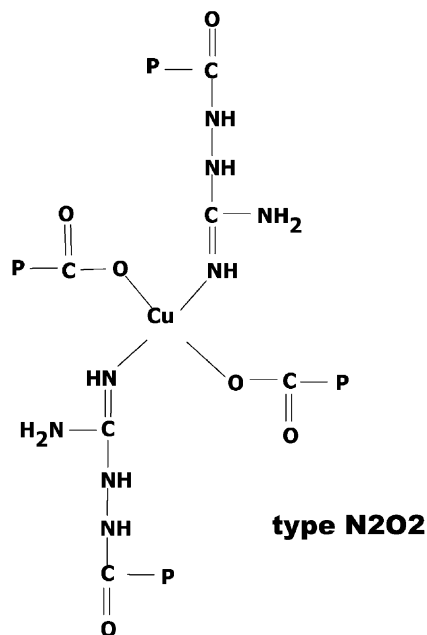
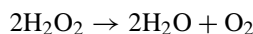


Fig. 2. Structure of  $Cu(II)$  complexes with aminoguanidyl ligands on resin at  $pH = 5$  [14].

sured. It is known that  $Cu(II)$  ions can be complexed by both carboxyl and amino groups of the resin [13]. The sorption is in the range of 0.005–1.6 mmol/g. It can be observed that a change of solution  $pH$  from 4.6 to 4.9 resulted in better sorption of  $Cu(II)$  ions from less concentrated solution ( $1 \times 10^{-4}$  M). It should be pointed out that solution  $pH$  influenced the structure of  $Cu(II)$  complexes. The presence of both the carboxyl and aminoguanidyl groups in the resin gives the possibility of different complex type formation [14]. At  $pH = 2$ , complexes of  $O_4$  type dominated; at  $pH = 5$ , complexes of  $N_2O_2$  type (Fig. 2); whereas at  $pH = 8.8$ ,  $N_4$  chelates were predominant.

#### 3.2. Oxidation of hydroquinone to *p*-benzoquinone on catalysts of KA-XY type

The catalytic properties of  $Cu(II)$  ions immobilized on resins were studied in model oxidation reaction of  $H_2Q$  to  $Q$  using hydrogen peroxide ( $H_2O_2$ ) in aqueous medium. In fact, the decomposition of hydrogen peroxide is a disproportionation reaction:



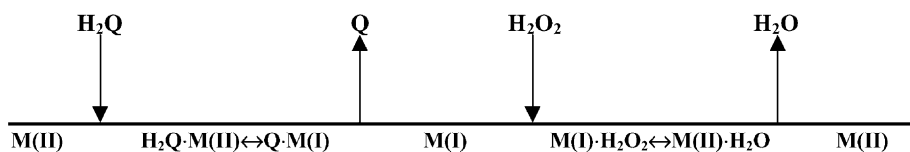


Fig. 3. Scheme of catalytic oxidation of  $\text{H}_2\text{Q}$  in the presence of transition metal complexes.

Hydrogen peroxide is simultaneously an oxidant and reducing agent. Considering this fact, the catalytic process should proceed in the following cycle (Fig. 3): (a) Attachment of a substrate, (b) Oxidation of a substrate, reduction of  $\text{Cu(II)}$  to  $\text{Cu(I)}$ , (c) Separation of a product and (d) reoxidation of  $\text{Cu(I)}$  to  $\text{Cu(II)}$ .

It should be supposed that in the decomposition of  $\text{H}_2\text{O}_2$  both chemical parts of cycle (b) and (d) overlap, because the same chemical species participate in them. Active centre containing the  $\text{Cu(II)}$  ion surrounded with ligands can occur in two forms differing in the oxidation number of metal atom. First, the substrate  $\text{H}_2\text{Q}$  is coordinated and oxidized to  $\text{Q}$ . Product of reaction ( $\text{Q}$ ) is getting free and catalytic centre undergoes reoxidation with part of second substrate— $\text{H}_2\text{O}_2$ .

### 3.3. Products of hydroquinone oxidation

The formation of  $\text{Q}$  and the product of hydroxylation reaction—2,5-dihydroxy-*p*-benzoquinone ( $\text{Q(OH)}_2$ ) can be followed spectrophotometrically. If  $\text{H}_2\text{Q}$ ,  $\text{Q}$  and  $\text{H}_2\text{O}_2$  are present only in solution after reaction, composition of products can be easily observed at characteristics absorption maxima; for  $\text{H}_2\text{Q}$ ,  $\lambda = 289 \text{ nm}$  and for  $\text{Q}$ ,  $\lambda = 246 \text{ nm}$  (Fig. 4a). Hydrogen peroxide does not interfere with these measurements because absorbance of  $\text{H}_2\text{O}_2$  solution (concentration of  $\text{H}_2\text{Q}$  is  $4 \times 10^{-4} \text{ mol/l}$ ) is about 0.01 at 246 nm and is near to zero at 289 nm. We have more complicated situation when  $\text{Q(OH)}_2$  appears as the reaction product. In this case, the absorption maximum for hydroquinone at  $\lambda = 289 \text{ nm}$  does not have analytic importance because this peak overlaps with stronger absorption peak for  $\text{Q(OH)}_2$  with maximum at  $\lambda = 302 \text{ nm}$ . The absorption peak for  $\text{Q}$  at  $\lambda = 246 \text{ nm}$  ceases to be reliable because absorbance of solution  $\text{Q(OH)}_2$  at this wavelength is almost 10 times higher than absorbance of  $\text{Q}$  (Fig. 4a).

We compare the spectra received during investigations of kinetics of  $\text{H}_2\text{Q}$  oxidation to  $\text{Q}$  without

catalyst, using copolymer and free ions  $\text{Cu(II)}$ , under the same reaction conditions (Fig. 4b). The results are presented in Table 2. In all these cases, the loss of  $\text{H}_2\text{Q}$  was very small and the peaks at 246 nm were characterized by small intensity, what made determination of  $\text{Q}$  yield impossible. Using heterogenized catalysts intensity of peak at 246 nm increases and intensity of peak at 289 nm decreases proportionally. It can be easily noticed that during oxidation  $\text{H}_2\text{Q} \rightarrow \text{Q}$  in the presence of heterogenized catalyst reaction ran with better yield and led to receiving major product ( $\text{Q}$ ) only. The initial oxidation rate ( $\nu_0$ ) in case of using the best catalyst (KA-53) increased 57 times in comparison with the same reaction without catalyst and 23 times in comparison to the reaction in the presence of resin without  $\text{Cu(II)}$  as well as 16 times compared to native copper ions. The selectivity of reaction achieved 98%.

In the next paper, we will compare the kinetics of  $\text{H}_2\text{Q}$  oxidation conducted in the presence of  $\text{Cu(II)}$  ions in complexes and other macromolecular  $\text{Cu(II)}$  complex. Further, we will compare the results of oxidation reaction for both immobilized on resins and on their low molecular analogues.

### 3.4. Influence of $\text{H}_2\text{Q}:\text{Cu(II)}$ ratio on kinetics of $\text{H}_2\text{Q} \rightarrow \text{Q}$ oxidation

In order to optimize one of the reaction parameters— $[\text{H}_2\text{Q}]:[\text{Cu(II)}]$  ratio—a series of reactions with KA-62a catalyst were carried out (Fig. 5). We found, that optimal  $[\text{H}_2\text{Q}]:[\text{Cu(II)}]$  ratio was 10:1. Using the  $\text{H}_2\text{Q}$  excess in relation to  $\text{Cu(II)}$  results in higher loss of  $\text{H}_2\text{Q}$  (yield = 53.45%) and higher initial rate ( $\nu_0 = 4.63 \times 10^{-7} \text{ mol/(l s)}$ ). Similar reaction yield was also achieved using the following  $[\text{H}_2\text{Q}]:[\text{Cu(II)}]$  ratios: 5:1, 7.5:1 and 20:1. It seems that the re-oxidation of active centres proceeds with low rate in comparison with reduction rate. On the other hand,  $\text{H}_2\text{Q}$  molecules could not reach active centres

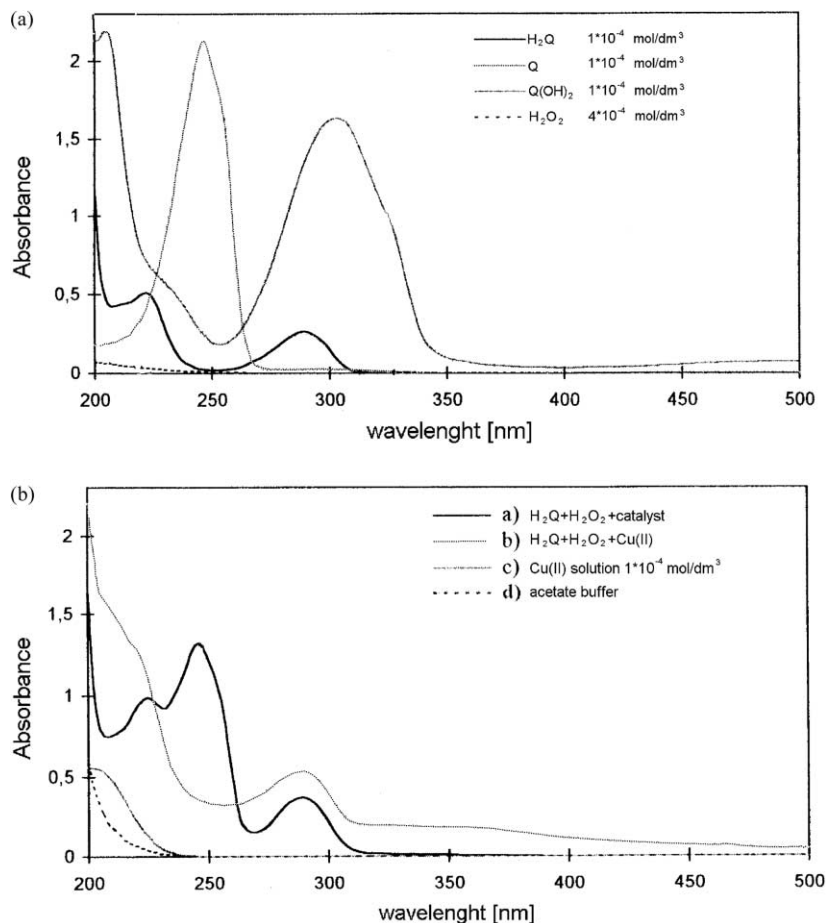


Fig. 4. UV–VIS spectra of  $H_2Q$  and products: (a)  $Q$  and  $Q(OH)_2$ ; (b) UV–VIS spectra of reaction mixture in the case of using of  $Cu(II)$ –resin catalyst and native  $Cu(II)$  ions.

because of their too large accumulation at the surface of catalyst. In case of low  $[H_2Q]:[Cu(II)]$  ratio we can suppose that the majority of active centres are not used in reaction.  $Cu(II)$  loading influences the  $H_2Q$  oxidation degree. The  $H_2Q$  loss is higher for smaller  $Cu(II)$  loading. These parameters of resin structure will be characterized in a subsequent paper.

### 3.5. Influence of hydrogen peroxide concentration on yield and initial reaction rate $H_2Q \rightarrow Q$

Basic assumption of enzymatic reaction theory is the formation of transition complex between substrate molecule and active enzyme centre. The complex

resolves freeing reaction product and reproducing enzyme catalytic centre.

Kinetics of enzymatic transformations using one of the substrates is described by Michealis–Menten equation

$$v_0 = \frac{V[S]}{K_m + [S]} \quad (1)$$

where  $[S]$  is the concentration of substrate,  $K_m$  the Michaelis constant,  $V$  the maximum reaction rate.

For the purpose of studying the dependence between initial oxidation rate of  $H_2Q$  and  $H_2O_2$  concentrations series of experiments were done.  $H_2Q$  conversion in first reaction stage (10 min) was measured for

Oxidation reaction parameters					
t (min)	H <sub>2</sub> Q (mol /dm <sup>3</sup> )	H <sub>2</sub> O <sub>2</sub> (mol /dm <sup>3</sup> )	[H <sub>2</sub> O <sub>2</sub> ]:[H <sub>2</sub> Q] molar ratio	Catalyst	[H <sub>2</sub> Q]:[Cu(II)] molar ratio
0-80	4,0*10 <sup>-3</sup>	5,56*10 <sup>-3</sup>	1,4	KA-62a S = 0,90 mmol/g	(356 - 2):1

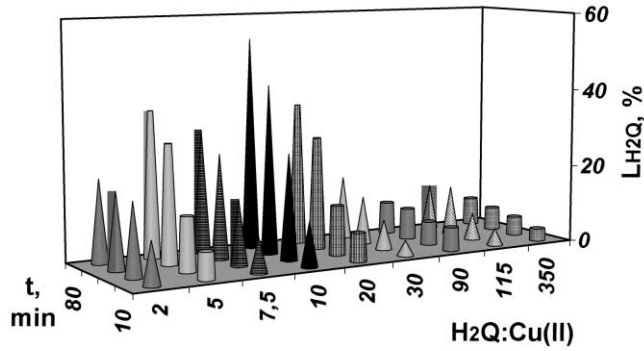


Fig. 5. The influence of hydroquinone to Cu(II) ([H<sub>2</sub>Q]:[Cu(II)]) ratio on the loss of hydroquinone ( $L_{H_2Q}$ ) as function of reaction time.

Oxidation reaction parameters					
t (min)	[H <sub>2</sub> Q] (mol /dm <sup>3</sup> )	[H <sub>2</sub> O <sub>2</sub> ] (mol /dm <sup>3</sup> )	[H <sub>2</sub> Q]:[H <sub>2</sub> O <sub>2</sub> ] vol. ratio	Catalyst	[H <sub>2</sub> Q]:[Cu(II)] molar ratio
60	4,0*10 <sup>-3</sup>	2,02*10 <sup>-5</sup> +1,3*10 <sup>-2</sup>	1:1	KA-61	10:1

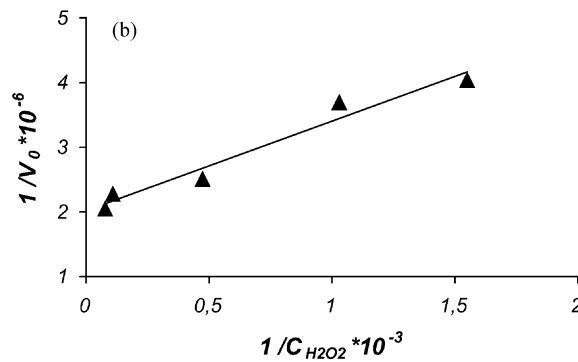
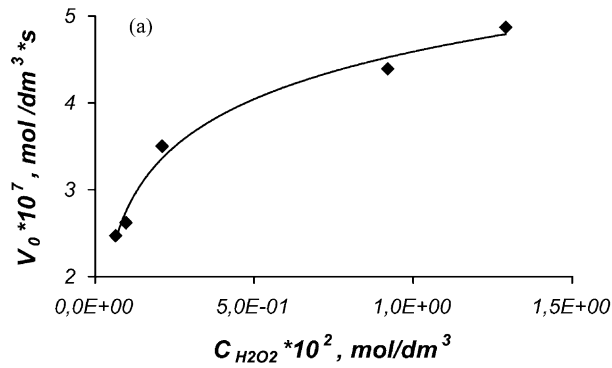


Fig. 6. (a) Influence of H<sub>2</sub>O<sub>2</sub> concentration on the initial reaction rate  $v_0$ ; (b) Graph relationship:  $1/v_0 = f(1/C_{H_2O_2})$ .

Oxidation reaction parameters						
t (min)	pH	[H <sub>2</sub> Q] (mol/dm <sup>3</sup> )	[H <sub>2</sub> O <sub>2</sub> ] (mol/dm <sup>3</sup> )	[H <sub>2</sub> O <sub>2</sub> ]:[H <sub>2</sub> Q] molar ratio	Catalys t	[H <sub>2</sub> Q]:[Cu(II)] molar ratio
10-80	4,3-5,5	4,0·10 <sup>-3</sup>	4,0·10 <sup>-2</sup>	10	KA-62b	10:1

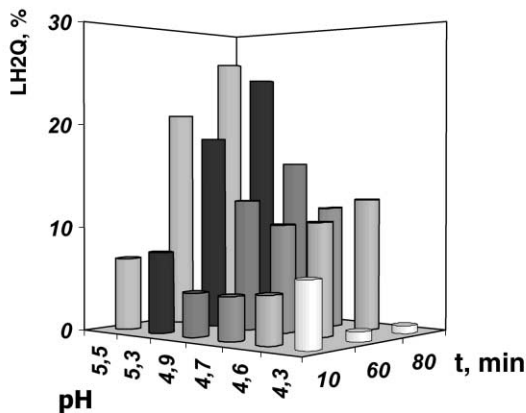


Fig. 7. Influence of solution pH on the loss of hydroquinone ( $L_{H_2Q}$ ).

different concentrations of hydrogen peroxide. Based on obtained data the relationship of the initial reaction rate ( $v_0$ ) versus  $H_2O_2$  concentration ( $C_{H_2O_2}$ ) was drawn (Fig. 6a). The curve in Fig. 6a shows saturation kinetic typical for enzymes. The concentration of transition substrate–enzyme complex comes closer to constant value when the concentration of substrate increases. It confirms assumption about formation of catalyst– $H_2O_2$  complex during reaction.

Transformation of Eq. (1) leads to Lineweaver–Bruk relationship

$$\frac{1}{v_0} = \frac{K_m}{V} \left( \frac{1}{[S]} + \frac{1}{V} \right). \quad (2)$$

The points of the relationship  $1/v_0 = f(1/C_{H_2O_2})$  in Fig. 6b give approximately straight line. From coefficients of a linear equation the maximum oxidation rate was calculated. The maximum oxidation rate ( $V$ ) of  $H_2Q$  solution (concentration of  $H_2Q$  solution was  $4 \times 10^{-3}$  mol/l) was equal to  $3.33 \times 10^{-7}$  (mol/l).

### 3.6. Influence of reaction pH on loss of $H_2Q$ and on initial reaction rate

In order to optimize next parameter of  $H_2Q \rightarrow Q$  oxidation, which was a reaction solution pH, a series

of experiments was carried out (Fig. 7). It was shown that reaction degree of  $H_2Q$  (loss of  $H_2Q$ ) increases with increase of pH. For pH = 4.3, the highest loss of  $H_2Q$  was observed after 10 min of reaction. After 60 and 80 min, the loss of  $H_2Q$  was lower. This could be the effect of formation of by-product— $Q(OH)_2$ . The overlapping of peaks of  $H_2Q$  and  $Q(OH)_2$  and formation of one peak at about 289 nm were observed. It can be seen, that at low pH reaction proceeds towards by-product  $Q(OH)_2$  and higher pH leads to product  $Q$ . It can be supposed that the optimal pH of reaction is 4.9. It causes an increase of oxidation yield but also an increase of the selectivity of used catalyst (Table 2).

## 4. Conclusion

A number of parameters, which can not be changed independently, have an influence on the activity of catalyst obtained by Cu(II) ions immobilization on acrylonitrile, vinyl acetate and divinylbenzene matrix with aminoguanidyl ligands. In the optimal model reaction—oxidation of  $H_2Q$  to  $Q$ —only main product can be considered as the reaction product. The catalytic activity and selectivity in the Cu(II)–resin system increases in comparison with the yield of reaction without catalyst and with native Cu(II) ions



and achieves 98%. Initial oxidation rate for the best catalyst increased 57 times compared to the same reaction without catalyst and 16 times in comparison with native Cu(II) ions. The oxidation reaction of H<sub>2</sub>Q showed a kinetic behaviour typical for a Michaelis–Menten mechanism. The optimal oxidation parameters in the reaction H<sub>2</sub>Q → Q are

- H<sub>2</sub>Q:Cu(II) ratio—10:1,
- H<sub>2</sub>O<sub>2</sub> concentration— $5 \times 10^{-2}$  (mol/l),
- pH above 5,
- Cu(II) loading of catalyst must be small.

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### References

- [1] E.A. Becturov, S.E. Kudaibergov, *Catalysis by Polymers*, Zug, Heidelberg, Oxford, 1996.
- [2] K. Eckeschlager, J. Veprzak-Sziszka, *Coll. Czech. Chem. Commun.* 38 (1972) 1623.
- [3] E.M. Stricelowa, W.I. Pietraszen, *Żur. Analit. Chimmii.* 20 (1965) 1169.
- [4] I.F. Domalowa, W.M. Pieszkowa, *Żur. Analit. Chimmii.* 19 (1964) 297.
- [5] M. Sato, Y. Inaki, K. Kondo, *J. Polym. Sci. Polym. Chem. Ed.* 15 (1977) 2059.
- [6] M. Sato, H. Shindo, *J. Polym. Sci. Polym. Chem. Ed.* 18 (1980) 101.
- [7] N. Egawa, T. Nonaka, N. Kazakura, *Bull. Chem. Soc. Jpn.* 55 (1982) 3536.
- [8] N.P. Butina, V.S. Pshezhetskii, D.I. Stom, *Vysokomol. Soedin. Ser. B* 26 (1984) 812.
- [9] J.W. Fray, J. Klein, E. Klesper, *Makromol. Chem.* 188 (1987) 821.
- [10] K. Yamashita, I. Okada, *Makromol. Chem. Rapid Commun.* 9 (1988) 705.
- [11] K. Yamashita, T. Kanamori, M. Nango, K. Tsuda, *Polymer* 34 (1993) 2638.
- [12] N. Nemoto, H. Ishii, M. Ihara, K. Ikeda, N. Takamiya, *J. Polym. Sci. Polym. Chem.* 32 (1994) 2457.
- [13] B.N. Kolarz, A. Trochimczuk, M. Wojaczyńska, J. Liesiene, J. Łobarzewski, A. Gorbunov, M. Bryjak, *React. Polym.* 17 (1992) 51.
- [14] B.N. Kolarz, J. Jezierska, D. Bartkowiak, A. Gontarczyk, *React. Polym.* 23 (1994) 53.