Photooxidation of phenols in aqueous solution, catalyzed by mononuclear and polynuclear metal phthalocyanine complexes

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Abstract

The photocatalytic oxidation of phenols by oxygen has been studied in alkaline aqueous medium upon irradiation with visible light. Metal Zn(II) and Al(III) mono- and polynuclear phthalocyanine complexes, soluble in water, have been used as photocatalysts. The studied polynuclear complexes represent two-dimensional polymers, formed of condensed phthalocyanine macrocycles. The number of the phthalocyanine units in them is 3 or 4. No visible batochromic shifting is observed in the Q-band electron transition ($\lambda = 665–680\,nm$) of the polynuclear complexes with respect to their mononuclear analogues. This fact is an indication of a low π–π electron delocalization between the phthalocyanine units of the polynuclear complexes in the excited state. The photocatalytic activity per mole of the polynuclear complexes at pH = 7 or 13 is much higher than that of the respective mononuclear phthalocyanine complexes. The high photocatalytic activity of the polymers might be explained by the proceeding of an intra-molecular triplet–triplet energy transfer between the phthalocyanine macrocycles in accordance with the mechanism of Dexter. The singlet oxygen, obtained by photon-induced energy transfer from the excited mono- and polynuclear photosensitizers, dominates the initial steps of photooxidation.

The rate of photocatalytic oxidation of phenols depends on the pH of the medium and on the phthalocyanine complex aggregation degree. The products of the oxidation of phenols in alkaline medium are the same in the both cases of using mono- and polynuclear phthalocyanine complexes as catalysts. The formation of quinones is an intermediate step during the photocatalytic oxidation of phenols at pH = 13 within the process of destruction of the substrate. Maleic and fumaric acids as well as carbon dioxide have been registered as final products of the photooxidation. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Photocatalysis; Oxidation; Polynuclear phthalocyanine complexes; Phenols; Quinones

1. Introduction

The basic sources of natural waterways pollution and atmospheric pollution with organic compounds are the oil-processing plants, cellulose industry, the use of oil fractions, natural gas and coal as fuels, fine c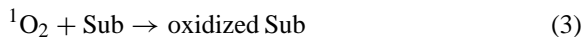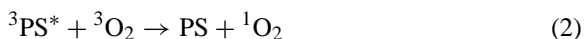hemicals and dye manufacturing industries. The phenols and the sulfur-containing compounds are among the basic soluble pollutants of communal and industrial waste waters. Oxidative decomposition and transformation of organic and inorganic substrates by oxygen using photocatalysts is one of the most frequently used methods for purification of waste waters. So far, two main techniques have been utilized for removing the sulfur and phenol-containing pollutants from waste waters before discharging them into waterways. According to the first method the pollutants are photocatalytically oxidized by oxygen

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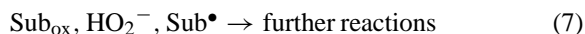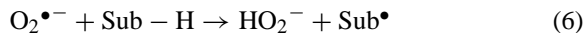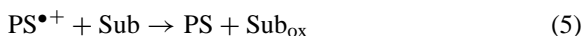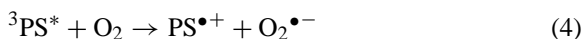*E-mail address:* iliev@ic.bas.bg (V. Iliev).

with the use of semiconductors [1–3], whereas in the second one the photocatalytic redox process occur in the presence of molecular catalysts during irradiation with visible light [4–13].

Photocatalytic reactions on semiconductor powders are of great interest because of their applicability to the treatment of a large variety of pollutants [1–3]. One of the semiconductors, most widely used as photocatalysts, triggering the oxidative destruction and mineralization of organic substrates is TiO_2. Due to the band gap of TiO_2 (3.2 eV), the processes of catalytic oxidative destruction are accomplished upon irradiation with light of the UV region, where only approximately 4% of the solar radiation is effective. In order to overcome this disadvantage, photosensitizers adsorbing in the visible region are used [14].

Oxidative decomposition of organic and inorganic substrates by oxygen using visible light activation of photosensitizers is of increasing interest. The most frequently used molecular catalysts, applied to photooxidation of organic and inorganic substrates, are dyes, porphyrines and phthalocyanines, as well as some other organometallic complexes. Photochemical homogeneous and heterogeneous catalytic oxidation processes with porphyrin analogues, such as 5,10,15,20-tetraphenylporhyrins and phthalocyanines, have been carried out in oxygen saturated aqueous solutions of thiols, sulfides and phenols [4–13]. After excitation of the photosensitizer (PS), triplet–triplet energy transfer to triplet oxygen is the dominating initial elementary step. A chemically more reactive $^1O_2(^1\Delta_g)$ is being formed, followed by oxidation of the substrate (Sub) (so-called type II reaction) [8,15]

$$PS \rightarrow {}^1PS^* \rightarrow {}^3PS^* \qquad (1)$$

$$^3PS^* + {}^3O_2 \rightarrow PS + {}^1O_2 \qquad (2)$$

$$^1O_2 + Sub \rightarrow oxidized\ Sub \qquad (3)$$

An additional photon-induced electron transfer between oxygen and the excited triplet state of the sensitizers can be realized. The formation of the superoxide anion radical by photon-induced electron transfer cannot be ruled out as a side reaction (so-called type I reaction) [15,16]

$$^3PS^* + O_2 \rightarrow PS^{\bullet+} + O_2^{\bullet-} \qquad (4)$$

$$PS^{\bullet+} + Sub \rightarrow PS + Sub_{ox} \qquad (5)$$

$$O_2^{\bullet-} + Sub - H \rightarrow HO_2^- + Sub^\bullet \qquad (6)$$

$$Sub_{ox},\ HO_2^-,\ Sub^\bullet \rightarrow further\ reactions \qquad (7)$$

The photocatalytic oxidation of the substrates according to Eqs. (3), (5)-(7) proceeds only in the cases when the photosensitizers possess a long-living triplet state.

The photooxidation of sterically hindered phenols has been studied aiming at the elucidation of the mechanism of action and photodestruction of this type of compounds, used as elastomer stabilizers [4–6]. During the recent years the investigations are associated mainly with selective photooxidation of phenols into *p*-benzoquinones, as well as their removal from waste waters by oxidative destruction upon irradiation with visible light [9,13,17–21]. Some dyes have been used as photosensitizers (eosin, rose bengal, methylene blue, riboflavin), as well as zinc, aluminum and gallium mononuclear phthalocyanine complexes. The oxidation of substituted phenols is considered to be the result of their interaction with singlet oxygen, generated by the sensitizers [4–6,9,13,17–21]. The mechanistic and kinetic aspects of the photocatalytic oxidation of substituted phenols in organic solvents or aqueous solutions have been studied [9,17,18]. It has been established that the basic products during photooxidation of phenols in organic solvents are *p*-benzoquinone derivatives [4–6,17–20]. The photooxidation of phenols in alkaline aqueous medium, catalyzed by mononuclear phthalocyanine complexes, is accompanied by destruction of quinones and obtaining unsaturated mono- and dicarboxylic acids and carbon dioxide as final products [9].

The catalytic photooxidation of phenols and *p*-benzoquinone in aqueous medium upon irradiation with visible light has been studied in this work. The *p*-benzoquinones are the possible intermediate products in the case of phenols catalytic oxidation in the presence of phthalocyanine complexes. Mono- and polynuclear phthalocyanine complexes have been used as photocatalysts in the oxidation of phenols. The photocatalytic oxidation of phenols, catalyzed by mononuclear phthalocyanine complexes has already been studied earlier [9]. The aim of the present work is to study the photocatalytic properties of the polynuclear phthalocyanine complexes and the effect of polymerization on their activity.

2. Experimental

Merck phenol was used after distillation in an inert atmosphere. The Merck *p*-benzoquinone was recrystallized consecutively in ethanol and tetrachloromethane before use. Zn(II) 2,9,16,23-phthalocyanine tetracarboxylic acid [ZnPc(COOH)$_4$] and Al(III) 2,9,16,23-phthalocyanine tetracarboxylic acid [AlClPc(COOH)$_4$] were prepared by the interaction of trimellitic anhydride with urea and purified according to the methods described in the literature [22,23]. The polynuclear phthalocyanine complexes [AlPc(COOH)$_n$]$_{poly}$, [ZnPc(COOH)$_n$]$_{poly}$ and [CoPc(COOH)$_n$]$_{poly}$ were synthesized by condensation of pyromellitic acid in the presence of urea and the respective metal salt [24,25]. The purification and separation of the polynuclear phthalocyanine complexes from the mononuclear ones was carried out in accordance with the methods, described in the current literature [24–26]. The average number of phthalocyanine structural units in the polynuclear complexes was estimated on the basis of the data from the elemental analysis, titration of the carboxylic groups in peripheral position and determination of the viscosity of the complexes in a dimethylformamide (DMF) solution. The viscosity of solutions containing 0.0108 g of phthalocyanine in 100 ml of DMF was determined at 298 K by means of an Ostwald viscosimeter. Moreover, the relative viscosity, η_{rel}, was estimated on the basis of the ratio between the time interval of flowing out of the solution and that of the solvent. The absorption spectra of the phthalocyanine complexes were registered on a Hewlett-Packard 89500 UV–Vis spectrophotometer.

The rates of phenol or *p*-benzoquinone catalytic and photocatalytic oxidation were evaluated by the consumption of dioxygen, which was measured by a gas burette. The oxidation and photooxidation processes were performed at 293 K, pH = 7 and 13 and atmospheric pressure in a static reactor by exposure to a halogen lamp light (12 V, 50 W), the illumination being 38 mW/cm^2.

The products of the photocatalytic phenol and quinone oxidation reactions have been analyzed after the termination of oxygen consumption. The oxidation products have been detected by elemental analysis, UV–Vis (Hewlett-Packard 89500) and IR (Bruker IRS-113V) spectroscopy.

3. Results

The studied polynuclear phthalocyanine complexes represent two-dimensional polymers, formed of condensed phthalocyanine macrocycles (Fig. 1). The delocalization of the π-electrons over the entire macromolecule is hampered in them by the units, connecting the phthalocyanine nuclei [25,27,28]. The Q-band electron transitions in the studied mono- and polynuclear phthalocyanine complexes are almost identical (Fig. 2). This fact, however, does not exclude the possibility that weak π–π exchange interactions are occurring between the neighboring phthalocyanine units [25,27,28]. Some changes are observed in the molar extinction coefficients. They have quite lower values for the polynuclear phthalocyanine complexes in comparison to those for the mononuclear ones. It is considered [25,27,28] that the absorbance of light is associated with a single electron transition $S^0 \rightarrow S^*$ whereupon it is only one phthalocyanine unit of the polynuclear complex that is participating in the elementary act.

The separation of the polynuclear phthalocyanine complexes from their mononuclear analogues MPc(COOH)$_8$ has been carried out by their extraction with DMF [25]. The average number of phthalocyanine units in the polynuclear complexes may be estimated on the basis of their elemental analysis, the acid–base titration of the carboxylic groups in peripheral position and the determination of the complex solution viscosity.

The C/N ratios of the elemental analysis of the complexes, which are the most sensitive to changes in the number of phthalocyanine units in the polynuclear complex [25] are respectively: [AlPc(COOH)$_n$]$_{poly}$ = 3.65, [ZnPc(COOH)$_n$]$_{poly}$ = 3.52 and [CoPc(COOH)$_n$]$_{poly}$ = 3.54. The ratio in all the four mononuclear analogues (MPc(COOH)$_8$) of the polymers is ≈4.5. Having in mind the previous detailed studies focused on the analysis of the polynuclear phthalocyanine complexes [25–28], the obtained results may be interpreted to the effect that the average number of phthalocyanine units in the studied polymers is the following: [AlPc(COOH)$_n$]$_{poly}$ ≈ 3, [ZnPc(COOH)$_n$]$_{poly}$ ≈ 4 and [CoPc(COOH)$_n$]$_{poly}$ ≈ 4. This result is confirmed also by the data from the titration of carboxylic groups in peripheral position in the polymers, which
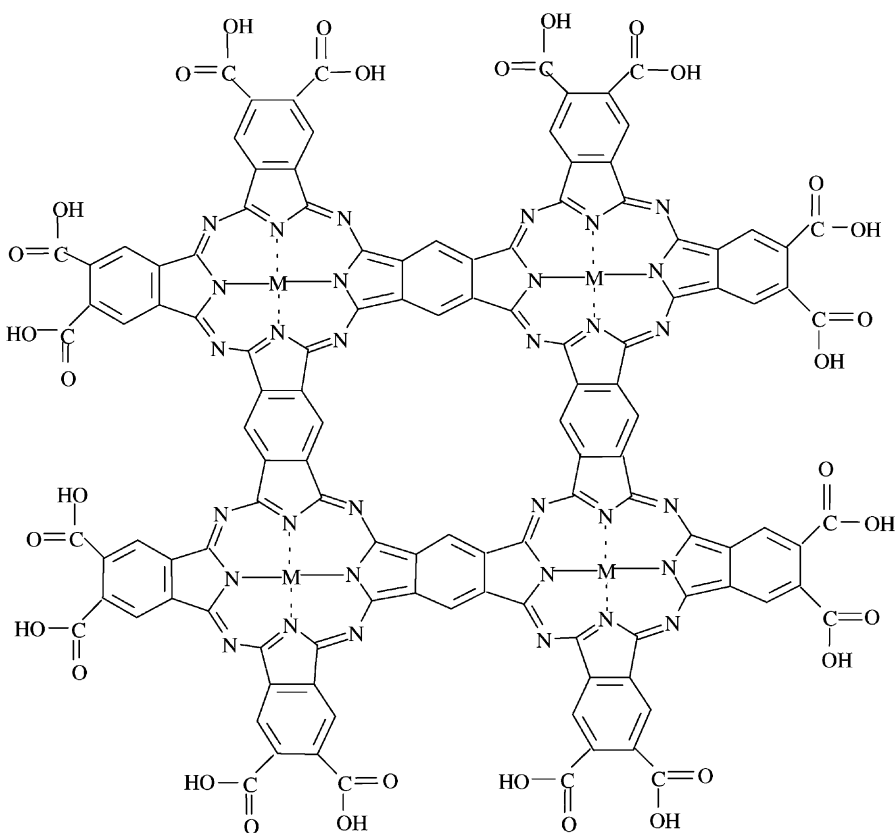
Fig. 1. Two-dimensional polynuclear phthalocyanine complex.

lie within the interval 7.0–7.6 mmol COOH per gram of the respective complex. In the case of the mononuclear analogues (MPc(COOH)$_8$) the number of the carboxylic groups in peripheral position amounts to 8.4 mmol/g. The relative viscosities η_{rel} of MPc and (MPc)$_{poly}$ are respectively 1.02 and 1.13–1.17, which is evidence for the formation of polynuclear complexes of different molecular weight.

The effectiveness of phthalocyanine complexes as photocatalysts for oxidation of organic compounds is decreased in the case of self-association [7–11,29,30]. In photoinitiated processes, upon formation of dimers, the excited triplet electron state of the complexes is quenched as a result of bimolecular triplet annihilation and thus the quantum yield of $^1O_2(^1\Delta_g)$ is being decreased [7–13]. The existence of monomer–dimer equilibrium of the phthalocyanine complexes in
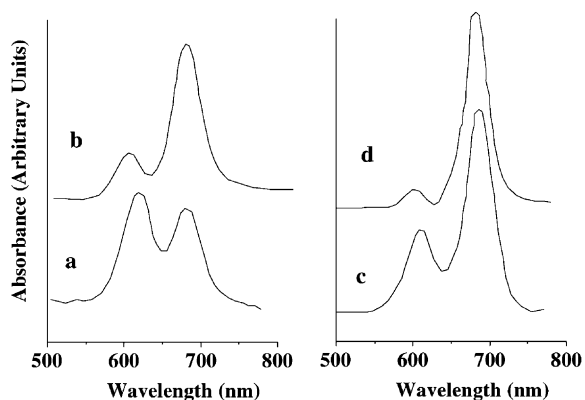

Fig. 2. UV–Vis spectra of: (a) ZnPc(COOH)$_4$; (c) [ZnPc-(COOH)$_n$]$_{poly}$ dissolved in H$_2$O–C$_2$H$_5$OH and (b) ZnPc(COOH)$_4$; (d) [ZnPc(COOH)$_n$]$_{poly}$ dissolved in H$_2$O–TBAC.

solution is confirmed by the specific electron transitions in the Q-band at 670–680 and 630 nm (Fig. 2) which are attributed to the presence of monomeric and dimeric species, respectively [7,8,31,32]. The aggregation of polynuclear phthalocyanine complexes in water–ethanol medium (Fig. 2) is to a smaller extent than that of the mononuclear complexes.

The photooxidation of phenols and quinones, catalyzed by the studied mono- and polynuclear phthalocyanine complexes, has been carried out at pH = 7 and 13 in aqueous solutions. During oxidation of phenols, catalyzed by mononuclear phthalocyanine complexes, *p*-benzoquinone is one of the basic intermediate products of the substrate photodestruction [9]. The results from phenol and *p*-benzoquinone photooxidation, catalyzed by mono- and polynuclear phthalocyanine complexes, are represented in Table 1. The activities of the investigated catalyst samples (Table 1) in the oxidation of phenol or *p*-benzoquinone are expressed by the rate r (mol O_2/min/mol of catalyst). Standard calculation methods have been applied to determine the initial rates of the substrate transformation.

The initial rates of the photocatalytic oxidation of phenols at pH = 13 and the amount of the consumed oxygen at the end of the process are higher than those at pH = 7 (Figs. 3 and 4). The photocatalytic activity per mole of the polynuclear phthalocyanine complex is much higher in both cases in comparison to that of the mononuclear complexes (Table 1). After the termination of the catalytic process at pH = 13 it was established that 3.4–3.7 mol of oxygen had been consumed per mole of phenol (Table 1). The consumption of oxygen is one and the same in the presence of mono- and polynuclear complexes. An amount of 1.9 mol of oxygen is consumed per mole of phenol at pH = 7 in the presence of both types of phthalocyanine complexes (Table 1). The growth of the rate of photocatalytic oxidation of phenol at pH = 13 in the presence of bulky cations like tetrabutylammonium chloride (TBAC) (Table 1) is due to a decrease in the aggregation degree of the mono- and polynuclear complexes (Fig. 2) and the increase of the quantum yield of $^1O_2^*$ generation [7–13].

Table 1
Photooxidation of phenol (0.64 mmol) and quinone (0.64 mmol) in aqueous solution at pH = 13 and 7 catalyzed by water-soluble mono- and polynuclear phthalocyanine complexes

No.	Complex	Substrate	pH	Medium	MPc (μmol)	r (μmol O_2/min)	r (min^{-1})	O_2/substrates[a]
1	No	Phenol	13	H_2O–C_2H_5OH	–	0.2	–	–
2	[CoPc(COOH)$_n$]$_{poly}$	Phenol	13	H_2O–C_2H_5OH	1.64	0.2	0.12	–
3	ZnPc(COOH)$_4$	Phenol	13	H_2O–C_2H_5OH	1.64	18.4	11.20	3.51
		Phenol	13	TBAC[b]	1.64	44.3	27.00	3.59
4	AlOHPc(COOH)$_4$	Phenol	13	H_2O–C_2H_5OH	1.64	24.5	14.94	3.62
		Phenol	13	TBAC[b]	1.64	28.1	17.13	3.56
5	[ZnPc(COOH)$_n$]$_{poly}$	Phenol	13	H_2O–C_2H_5OH	1.64	160.7	98.00	3.52
		Phenol	13	D_2O	1.64	211.2	128.80	3.75
		Phenol	13	H_2O–NaN$_3$[c]	1.64	102.5	62.50	3.36
		Phenol	13	TBAC[b]	1.64	250.0	152.44	3.68
6	[AlOHPc(COOH)$_n$]$_{poly}$	Phenol	13	H_2O–C_2H_5OH	1.64	50.9	31.00	3.55
		Phenol	13	TBAC[b]	1.64	64.3	39.21	3.57
7	ZnPc(COOH)$_4$	Phenol	7	TBAC[b]	1.64	2.6	1.58	–
8	AlOHPc(COOH)$_4$	Phenol	7	TBAC[b]	1.64	1.1	0.67	–
9	[ZnPc(COOH)$_n$]$_{poly}$	Phenol	7	TBAC[b]	1.64	6.7	4.10	1.97
10	[AlOHPc(COOH)$_n$]$_{poly}$	Phenol	7	TBAC[b]	1.64	4.0	2.44	1.95
11	No	Quinone	13	H_2O–C_2H_5OH	–	97.1	–	1.40
12	ZnPc(COOH)$_4$	Quinone	13	H_2O–C_2H_5OH	0.164	100.3	610.7	2.26
13	[ZnPc(COOH)$_n$]$_{poly}$	Quinone	13	H_2O–C_2H_5OH	0.164	217.2	1324.3	2.36
14	ZnPc(COOH)$_4$	Quinone	7	TBAC[b]	1.64	6.6	4.01	0.75
15	[ZnPc(COOH)$_n$]$_{poly}$	Quinone	7	TBAC[b]	1.64	43.0	26.20	0.84

[a] After termination of the photocatalytic process.

[b] 1.2 mmol TBAC dissolved in H_2O–C_2H_5OH.

[c] 0.30 mmol NaN$_3$.

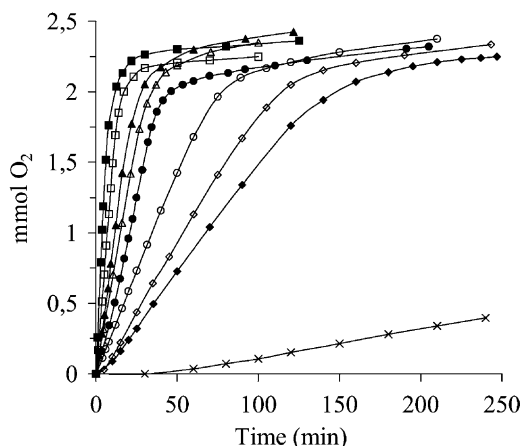Fig. 3. Photooxidation of phenol (0.64 mmol) at pH = 13 catalyzed by 1.64 μmol phthalocyanine complexes: catalysts dissolved in $H_2O–C_2H_5OH$: ($\square$) $[ZnPc(COOH)_n]_{poly}$; ($\triangle$) $[AlOHPc(COOH)_n]_{poly}$; ($\diamondsuit$) $AlOHPc(COOH)_4$; ($\blacklozenge$) $ZnPc(COOH)_4$; ($\times$) in the absence of catalysts. Catalysts dissolved in $H_2O–TBAC$: ($\blacksquare$) $[ZnPc(COOH)_n]_{poly}$; ($\blacktriangle$) $[AlOHPc(COOH)_n]_{poly}$; ($\bullet$) $ZnPc(COOH)_4$; ($\bigcirc$) $AlOHPc(COOH)_4$.

P-benzoquinone is oxidized by oxygen in alkaline aqueous solution even in the absence of catalysts [5,33,35]. The rate of photooxidation of *p*-benzoquinone at pH = 13 and the amount of consumed oxygen are increased in the presence of $ZnPc(COOH)_4$
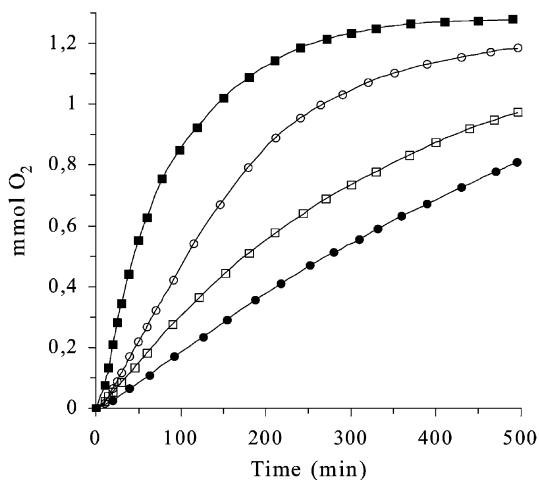

Fig. 4. Photooxidation of phenol (0.64 mmol) at pH = 7 catalyzed by 1.64 μmol phthalocyanine complexes. Catalysts dissolved in $H_2O–TBAC$: ($\blacksquare$) $[ZnPc(COOH)_n]_{poly}$; ($\bigcirc$) $[AlOHPc(COOH)_n]_{poly}$; ($\square$) $ZnPc(COOH)_4$; ($\bullet$) $AlOHPc(COOH)_4$.
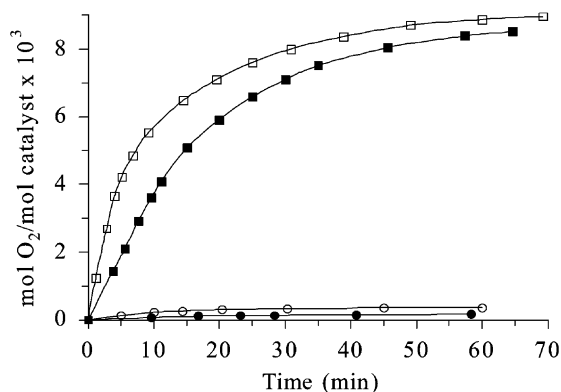

Fig. 5. Influence of pH of the medium on the photocatalytic oxidation of quinone (0.64 mmol). Catalysts (0, 164 μmol) at pH = 13 dissolved in $H_2O–C_2H_5OH$: ($\square$) $[ZnPc(COOH)_n]_{poly}$; ($\blacksquare$) $ZnPc(COOH)_4$. Catalysts (1, 64 μmol) at pH = 7 dissolved in $H_2O–TBAC$: ($\bigcirc$) $[ZnPc(COOH)_n]_{poly}$; ($\bullet$) $ZnPc(COOH)_4$.

and $[ZnPc(COOH)_n]_{poly}$ (Table 1). The initial rates of photocatalytic oxidation of *p*-benzoquinone at pH = 13 are higher than those of the phenol (Table 1). The photocatalytic activity of $[ZnPc(COOH)_n]_{poly}$ per mole of catalyst is higher than that of $ZnPc(COOH)_4$ (Fig. 5). The quantity of consumed O_2 at pH = 13 at the end of the redox process in the presence of both types of phthalocyanine complexes is approximately 2.4 mol of oxygen per mole of quinone. The quinones are not oxidized practically at pH = 7.

There are several possibilities for the qualitative demonstration whether singlet oxygen is involved or not in the photooxidation. First, it is possible to quench singlet oxygen in the presence of physical quencher sodium azide and, second, singlet oxygen has a longer lifetime in D_2O [8,9,30]. During photooxidation of phenols, catalyzed by mononuclear phthalocyanine complexes it was established, that the singlet oxygen obtained via photon-induced energy transfer from the excited photosensitizer, is involved in the photooxidation process of phenol [9]. In order to gain insight if singlet oxygen is involved in the photooxidative process catalyzed by polynuclear phthalocyanine complexes, different experiments have been carried out. The photooxidation of phenol in the presence of $ZnPc(COOH)_{poly}$ has been carried out in H_2O, D_2O and in water containing sodium azide. The initial rates, r (min^{-1}) are increased in
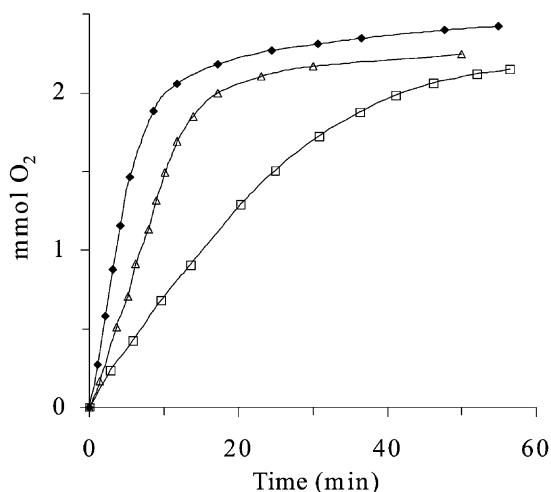
Fig. 6. Photooxidation of phenol at pH = 13 catalyzed by $[ZnPc(COOH)_n]_{poly}$. Medium: ($\blacklozenge$) D_2O; ($\triangle$) H_2O; ($\square$) 0.30 mmol NaN_3 dissolved in H_2O.

D_2O, but decreased in NaN_3 solution (Table 1), which fact confirms the participation of singlet oxygen in the redox process. The effect of D_2O and NaN_3 on the rate of photocatalytic oxidation of phenols, catalyzed by $[ZnPc(COOH)_n]_{poly}$ is represented in Fig. 6.

The reaction products of the photocatalytic phenol oxidation have been analyzed after the termination of oxygen consumption. The final oxygen consumption as a result of phenol photooxidation at pH = 13, catalyzed by mono- and polynuclear phthalocyanine complexes lies within the range 3.4–3.7 mol O_2 per mole of phenol (Table 1). The same quantity of consumed O_2 during photooxidation of phenols catalyzed by mono- and polynuclear phthalocyanine complexes (Fig. 3) show that the products of photocatalytic oxidation do not differ with the two types of complexes. This fact is confirmed by the analysis of the phenol oxidation products, catalyzed by $ZnPc(COOH)_{poly}$. After termination of the photocatalytic process the solution was acidified down to pH = 2 and then extracted with ether. The solution is vaporized and the residual is recrystallized from water to ethanol (1:1) medium. The crystalline product is characterized by elemental analysis and IR spectroscopy and it represents a mixture of fumaric and maleic acid. The elemental analysis gives: calculated H, 3.45; C, 41.38;

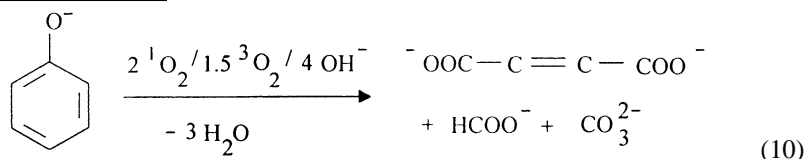found H, 3.52; C, 40.95. IR (CsI): 1711, 1676 cm^{-1} (ν C=O); 1430 cm^{-1} (ν C–O); 1632 cm^{-1} (ν C=C).

According to the method described in [9] it was established that CO_2 is being formed as a result of the mineralization of phenols at pH = 13. After the termination of the catalytic process the reaction mixture is treated with acidic agent and the quantity of carbon dioxide is determined as $BaCO_3$ gravimetrically. The amount of CO_2 is one and the same (within the limits of the experimental error) in both cases of photocatalysis in the presence of mono- and polynuclear complexes, namely it is approximately 1 mol of CO_2 formed by the oxidation of 1 mol of phenol.

The reaction products of phenol oxidation at pH = 7 were detected after a reaction time interval of 500 min. It was established that the basic product of photooxidation, catalyzed by mono- and polynuclear phthalocyanine complexes is the p-benzoquinone formed. In comparison to the oxidation of quinones at pH = 13 and at pH = 7 the number of moles of consumed oxygen per mole of quinone is much smaller (Fig. 5). A specific band at 245 nm, characteristic for p-benzoquinone absorption, was registered by UV–Vis spectroscopy in the reaction mixture. The vibrations of the conjugated carbonyl group ($\nu = 1682$ cm^{-1}) were registered by IR spectroscopy as well as the vibrations of the carbon–carbon double bond ($\nu = 1659$ cm^{-1}), characteristic for p-benzoquinone.

4. Discussion

The oxidation of phenols proceeds very slowly in alkaline medium and in the absence of catalyst (Fig. 3). The studied phthalocyanine complexes do not catalyze the oxidation of phenols in the dark. The activity of the catalysts increases several times during irradiation with visible light (Table 1). The reactions of D_2O and in the presence of sodium azide clearly show that the singlet oxygen $^1O_2^*$, obtained via photon-induced energy transfer from the excited photosensitizer, is involved in the photooxidation process of phenol (Eqs. (1)–(3)). The cobalt phthalocyanine complexes do not catalyze the oxidation of phenols, which is an indication that during the first step the redox process does not follow a mechanism, involving an electron transfer from the phenol molecule to that of the oxygen. The redox processes catalyzed by

cobalt phthalocyanine complexes are known to occur through an electron transfer from the substrate to the oxygen molecule, involving the formation of a superoxide ion from the latter [26,34–36]. Therefore the

$$\text{(phenolate)} \xrightarrow[-3\,H_2O]{2\ ^1O_2 / 1.5\ ^3O_2 / 4\ OH^-} {}^-OOC\!-\!C\!=\!C\!-\!COO^- + HCOO^- + CO_3^{2-} \tag{10}$$

photocatalytic oxidation of phenols to quinones proceeds mainly with the participation of singlet oxygen whereupon hydroperoxycyclohexadienone [4–6,9] is formed intermediately via the following general scheme:

$$\text{(OH phenol)} \xrightarrow{^1O_2} \left[\text{(OOH intermediate)} \right] \xrightarrow{-H_2O} \text{(benzoquinone)} \tag{8}$$
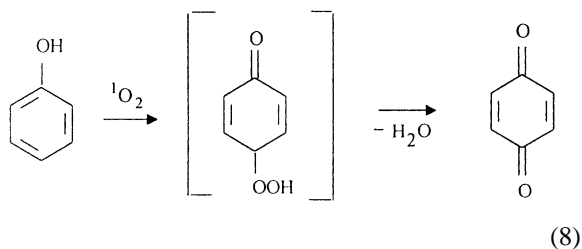
The moles of consumed oxygen per mole of phenol in alkaline medium lie in the range 3.4–3.7 (Table 1), which shows that the photocatalytic oxidation of phenols does not end with the formation of *p*-benzoquinone. This fact is confirmed also by the analysis of the reaction products after the termination of the redox process. The quinones are oxidized in alkaline medium both by the triplet oxygen [33], as well as by the singlet oxygen, generated by the photocatalysts [9]. The moles of consumed oxygen per mole of quinone at the end of the catalytic process at pH = 13 are approximately 2.2–2.4, whereupon 1.4 mol out of them are triplet oxygen (Table 1, No. 11–13). A conclusion can be drawn on the basis of the reaction products and the amount of consumed oxygen that the photocatalytic oxidation of quinones in alkaline medium proceeds in accordance with the following equation:
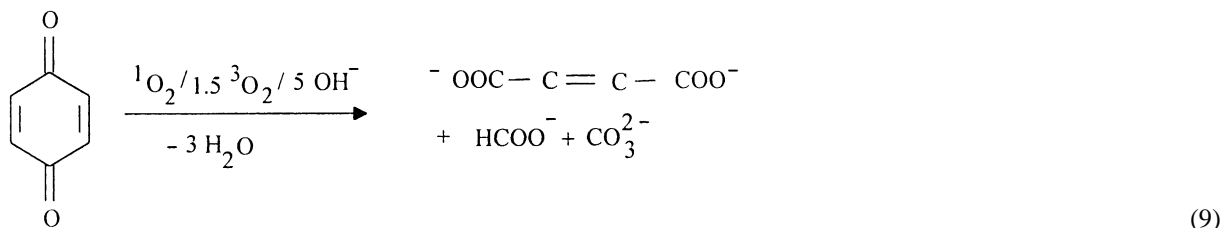
Therefore, the photocatalytic oxidation of phenols in alkaline medium, catalyzed by mono- and polynuclear phthalocyanine complexes, can be described by the following general equation:

During photocatalytic oxidation of phenols and quinones the activity per mole of the polynuclear phthalocyanine complexes, r (min^{-1}) is several times higher than that of the respective mononuclear phthalocyanine complexes (Table 1). Their high photocatalytic activity is to be explained with the option of intercomponent energy transfer realized by means of exchange interactions between the phthalocyanine units in the polynuclear complexes via the mechanism of Dexter [37]. The necessary conditions are available to realize the intercomponent energy transfer [37–39] in the studied supramolecular complexes, and namely: the absence of effective conjugation in the polynuclear phthalocyanine complexes [25,27,28], whereupon the electron transition $S^0 \rightarrow S^*$ is registered due to excitation of a structural unit in the polymer and the small distance 0.5–0.7 nm (Fig. 1) between the π-electron systems of the neighboring phthalocyanine units. The supposition of weak charge-transfer interactions between the π-electron systems of the phthalocyanine units has been put forward in earlier studies [25,27,28]. In addition metal-free phthalocyanine complexes and those containing a central metal ion with filled electron shells or d-orbitals manifest long lifetimes of the excited triplet electron state, which is due to absence of exchange interactions arising from mixing the π- and d-electronic states of the ligand and the metal [40]. The intercomponent triplet–triplet energy transfer in polynuclear phthalocyanine complexes, described by

$$\text{(benzoquinone)} \xrightarrow[-3\,H_2O]{^1O_2 / 1.5\ ^3O_2 / 5\ OH^-} {}^-OOC\!-\!C\!=\!C\!-\!COO^- + HCOO^- + CO_3^{2-} \tag{9}$$
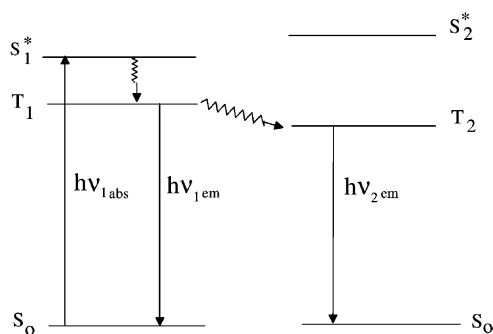
Fig. 7. A schematic representation of intercomponent energy transfer in polynuclear phthalocyanine complexes.

the mechanism of Dexter is represented schematically in Fig. 7. The probability of realizing an energy transfer from the triplet state of one of the excited phthalocyanine units, T_1, to the triplet state of neighboring phthalocyanine units of the polymer, T_2 is higher, taking into account the structure of polynuclear phthalocyanine complexes and the small distance between the structural units in them. The oxygen $^3O_2$, may interact with the triplet T_1 and T_2 states of the polynuclear molecule in accordance with Eq. (2), as a result of which the quantum yield of singlet oxygen $^1O_2^*$, is increased. The higher rate of oxidation of the substrates according to Eq. (3) is connected with the increased concentration of the singlet oxygen, generated by the polynuclear complexes. The complete oxidation of the substrates gives the reason to conclude that the photocatalytic redox process occurs with the participation of singlet oxygen according to Eqs. (2) and (3).

The increased probability of interaction of $^1O_2^*$ with the substrates in the solvent cage may also influence the higher photocatalytic activity of metal polynuclear phthalocyanine complexes. It is known that $^1O_2^*$ is a short-living species with a lifetime of $4.4\,\mu s$ in aqueous medium [41] and a diffusion pathway of around $780\,nm$ [42,43]. In case of adduct formation as a result of reversible coordination of the substrates to the central metal atom of the phthalocyanine complexes their local concentration around the photosensitizer is growing up. In comparison to the mononuclear metal phthalocyanine complexes [11,32] the possibility of axial adduct formation in the case of polynuclear complexes is higher due to the larger number of phthalocyanine macrocycles (Fig. 1). This results in increase

of the quantum yield of the photocatalytic processes, occurring in the presence of polynuclear phthalocyanine complexes.

The different rates of phenol oxidation at pH = 7 and 13 are due to the transformation of phenol in aqueous alkaline medium into a phenolate ion, the redox potential of which changes from -9.81 to $-2.69\,eV$ respectively [9]. The phenolate ion forms axial adducts with the metal phthalocyanine complexes more easily, whereupon the local concentration of the substrate in the first coordination sphere of the phthalocyanine complexes increases. The change in the redox potential and the increased local concentration of the phenol enable its more effective interaction with the $^1O_2^*$ generated by the photocatalysts.

The oxidative transformation of the phenols in alkaline aqueous solutions proceeds completely in comparison to the photocatalytic processes at pH = 7. This fact is evidenced by the number of moles of oxygen consumed per mole of phenol after the termination of the photocatalytic process (Table 1). The finally isolated products of phenol photooxidation at pH = 13 are a mixture of fumaric and maleic acid and CO_2. P-benzoquinone, which is missing among the reaction products, has an oxidation rate 3–4 times higher than that of phenol (Table 1), besides the quinones are quickly oxidized in alkaline medium in the presence of oxygen even non catalytically. The final products of the photocatalytic oxidation of quinones in aqueous medium at pH = 13 are the same as in the case of phenol oxidation. The quinones are known to react with triplet oxygen in aqueous alkaline medium, whereupon the respective unsaturated carboxylic acids are obtained [9].

5. Conclusions

Mineralization of phenol in alkaline medium is being registered during their photooxidation in the presence of mono- and polynuclear phthalocyanine complexes, irradiated with visible light. The photocatalytic activity per mole of the polynuclear phthalocyanine complexes, [ZnPc(COOH)$_n$]$_{poly}$ and [AlPc(COOH)$_n$]$_{poly}$, in the oxidation of phenol is much higher than that of the respective mononuclear complexes. There are two factors influencing the activity of the polynuclear complexes: the first

one is the increase of the quantum yield of singlet oxygen as a result of exchange interactions between phthalocyanine units, proceeding in accordance with the mechanism of Dexter. The second one is the higher probability for interaction of $^1O_2^*$ with the substrates in the solvent cage, due to their increased local concentration, caused by the adduct formation.

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