The influence of dissolved metal ions on the photocatalytic degradation of phenol in aqueous TiO_2 suspensions

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Abstract

The photocatalytic degradation of phenol was investigated in the oxygen-saturated titanium dioxide suspensions in the presence of dissolved metal ions Ca^{2+}, Mg^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+}, Cu^{2+}, Cr^{3+} and Fe^{3+} in the concentration range 0.28–1.1 mM. The most photoactive systems for phenol degradation were found in the presence of ferric ions, while the addition of Cr^{3+} strongly inhibited the photocatalytic decomposition of phenol. The role of dissolved metal ions in the photocatalytic processes on TiO_2 surface is discussed.

1. Introduction

The increased pollution of water and air by industrial wastes demands the application of modern purification technologies [1]. The photocatalytic reactions on semiconductor powders (TiO_2, ZnO, CdS) are very hopeful in the removal of organic and inorganic harmful substrates from water [2,3]. The photocatalytic water purification on the irradiated titanium dioxide surface in the presence of oxygen is a very effective process resulting in the complete mineralization of organic substrates [4]. The efficiency of the photocatalytic mineralization on TiO_2 is strongly dependent on the experimental conditions, e.g., presence or absence of oxygen, temperature, TiO_2 and substrate concentrations, pH, light intensity, presence of electron donors and acceptors [4–6]. Also the dissolved metal ions present in the natural and waste waters can significantly modify the purification process [7,8]. Considerable interest is now being focused on the degradation of phenols and phenol derivatives by irradiation of aqueous TiO_2 suspensions [9–19]. The dependence of type, species distribution, standard reduction potential, and concentration of transition metals on the rate of photocatalytic oxidation of toluene was studied in the presence of 10^{-5} M Cu^{2+}, Fe^{3+}, and Mn^{2+} at pH = 3 [7].

The photoexcitation of TiO_2 semiconductor particles with the light of energy higher than the band gap energy E_{bg} (E_{bg} = 3.2 eV for TiO_2 anatase) results in the formation of electrons (e^-) in the conduction band (band edge potential of -0.4 V vs. NHE at pH = 7 [20]), and positive holes (h^+) in the valence band (band edge potential of 2.8 V vs. NHE at pH = 7 [20]) as is depicted in Fig. 1.

Corresponding photogenerated charge carriers are involved in the reduction and oxidation proc-
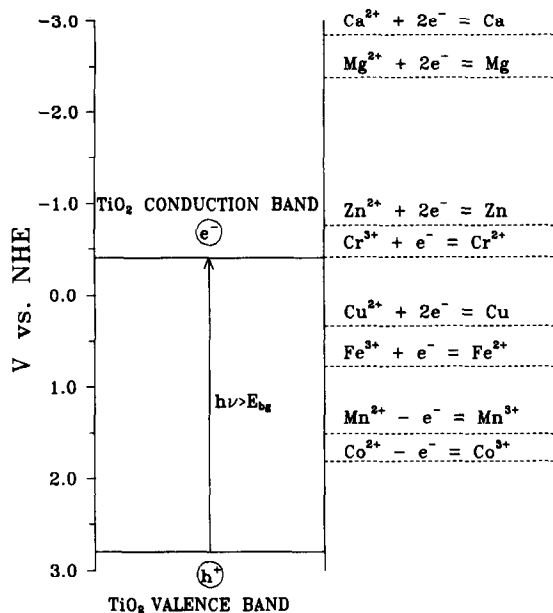
Fig. 1. Schematic illustration of valence and conduction band potentials in TiO_2 (anatase) at pH = 7 with the corresponding photochemical generation of reduction sites (e^-) and oxidation sites (h^+) [20] along with the standard reduction potentials [32] of metal ions used in study.

esses on the TiO_2 surface [3]. The most important reactions in the oxygenated aqueous suspensions are the oxidation of surface water and hydroxyl groups generating reactive hydroxyl radicals, and the electron capture by oxygen generating superoxide anion-radical O_2^- [21].

The reactive radical species generated ($^\cdot OH$, $O_2^-{}^\cdot$, H_2O_2) attack the phenol molecules present in the suspensions and cause its hydroxylation, oxidation, and finally mineralization to carbon dioxide and water [14,15,17,18].

In the present work we investigate the influence of dissolved metal ions Ca^{2+}, Mg^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Cu^{2+}, Cr^{3+}, and Fe^{3+} in the concentration range 0.28–1.1 mM, on the rate of phenol degradation in the irradiated TiO_2 suspensions.

2. Experimental

Phenol, purchased from Reactivul (Romania), was used without further purification. Metal chlorides, NaCl, $MgCl_2 \cdot 5H_2O$, $ZnCl_2$, $MnCl_2 \cdot 4H_2O$, $NiCl_2 \cdot 6H_2O$, $CrCl_3 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$ (Lachema, Czech Republic), $FeCl_3 \cdot 6H_2O$ (Reachim, Russia), $CaCl_2 \cdot 2H_2O$ (Avondale, England), and $CuCl_2 \cdot 2H_2O$ (Reactivul, Romania), were applied to the metal solutions preparation. All the chemicals employed were of analytical grade. Titanium dioxide P25 (Degussa, Germany), which is predominantly anatase (80% anatase, 20% rutile) with surface area of 55 m^2 g^{-1}, was used in all photocatalytic experiments. The prepared aqueous suspensions of phenol, dissolved metal chloride and TiO_2 were stirred 10 min in ultrasound before irradiation. The initial phenol concentration (1 mM) and titanium dioxide concentration (0.8 g dm^{-3}) were constant in all experiments. The concentration of the metal ions varies in the range of 0.28–1.1 mM. The photoreactions (sample volume, 130 ml) were carried out at $25 \pm 0.1°C$ in a photochemical immersion well (Applied Photophysics, UK) using a Pyrex sleeve for cutting out radiation below 300 nm. A 125 W medium-pressure mercury lamp (Applied Photophysics, UK) was employed as irradiation source. During exposure the reaction mixtures were bubbled by oxygen (flow rate, 200 ml min^{-1}) and stirred by magnetic stirrer. After irradiation, the samples were immediately centrifuged at 5000g for 20 min on a centrifuge (MLW T62.2, Germany) and before analysis were filtered on Millipore (0.2 μm) filters. The phenol and intermediates concentrations in the samples were determined by high performance liquid chromatography (HPLC) (FPLC Pharmacia, Sweden) using a Separon SIX C-18 column (Tessek, Czech Republic) and UV detector ($\lambda = 280$ nm). The mixture of methanol:water:H_3PO_4 (35:65:0.1) was applied as the mobile phase. The reflectance spectra of titanium dioxide samples were measured on an UV–visible spectrophotometer M40 (Zeiss, Germany) equipped with a reflectance accessory with an integration sphere. The concentration of ferrous ions in the samples was determined spectrophotometrically using 1,10-phenanthroline as a colour former.
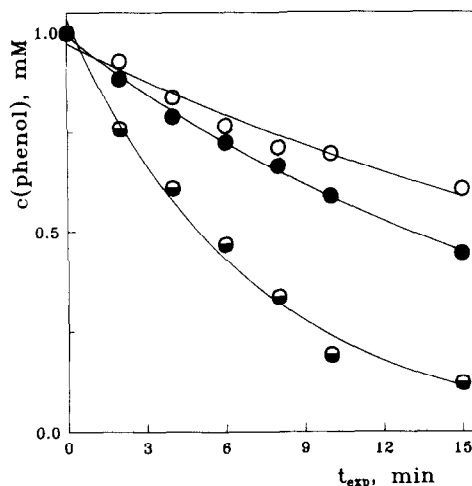
Fig. 2. The dependence of phenol concentration on the irradiation time in the aqueous oxygen-saturated TiO_2 suspensions: ● pure TiO_2 suspension; ○ 0.06 mM Cu^{2+}; ◐ 0.06 mM Fe^{3+} added. (The initial phenol concentration 1 mM, titanium dioxide concentration 0.8 g dm^{-3}.)

The pH values were measured at 25°C by the digital pH-meter OP-211/1 (Radelkis, Budapest); a combined glass electrode was used.

The infrared spectra of TiO_2/Cu powder and reference samples were performed on IR spectrophotometer Perkin Elmer 599.

3. Results and discussion

3.1. Photocatalytic degradation of phenol

The detailed mechanism of TiO_2 sensitized oxidation of phenol was recently studied in refs. [9–19]. We performed the photocatalytic degradation of phenol in aqueous oxygen-saturated TiO_2 suspensions without addition of metal ions in order to obtain the basic degree of phenol decomposition during 15 min exposure under given experimental conditions. (The influence of chloride anions was investigated in the suspensions with NaCl added, and no effect of chloride concentration on the phenol degradation rate was observed under experimental conditions.) Fig. 2 illustrates the phenol concentration decrease in irradiated TiO_2 suspensions without metal ions, along with systems irradiated in the presence of dissolved $CuCl_2$ and $FeCl_3$.

By the reduction of Fe^{3+} ions, the dissolved ferrous cations are formed, (as will be confirmed below), which can additionally produce hydroxyl radicals via the Fenton reaction with hydrogen peroxide generated in photocatalytic system (Eq. 1).

$$M^{(n-1)+} + H_2O_2 + H^+ \rightarrow M^{n+} + {}^\cdot OH + H_2O$$

(1)
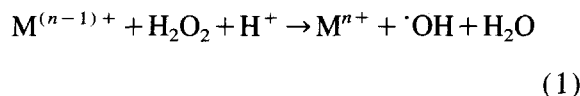
So in the irradiated aqueous TiO_2 suspension in the presence of Fe^{3+} ions, two sources of hydroxyl radical generation are present.

The situation in the presence of Cu^{2+} ions in the aqueous TiO_2 suspension is quite different. Cupric ions are reduced to the unreactive form Cu^0 under given experimental conditions and the deposition of metal copper can be observed on the surface of TiO_2. The deposition of elemental copper can significantly change the surface properties of TiO_2 (separation of charge carriers, adsorption of phenol), and the observed phenol degradation rate was lower.

The dependence of phenol concentration on the irradiation time was successfully fitted (by the non-linear minimization procedure of least squares) to an exponential function using program SCIENTIST (MicroMath). Formal first-order kinetics were proposed for phenol decomposition, the formal first-order rate constants were evaluated and from these the phenol half-times, $\tau_{0.5}$, in the experimental systems were calculated. The calculated values of phenol half-time were used for the comparison of the efficiency of the photocatalytic process under different reaction conditions.

The half-time of phenol obtained in the irradiated oxygen-saturated aqueous TiO_2 suspensions was 14.0 ± 0.5 min under given experimental conditions.

The formation of primary reaction products, i.e., hydroquinone and catechol [14] during 15 min exposure in oxygen-saturated suspension without added metal ions, is depicted in Fig. 3. The initial selectivities in catechol and hydroquinone were not influenced by the presence of metal
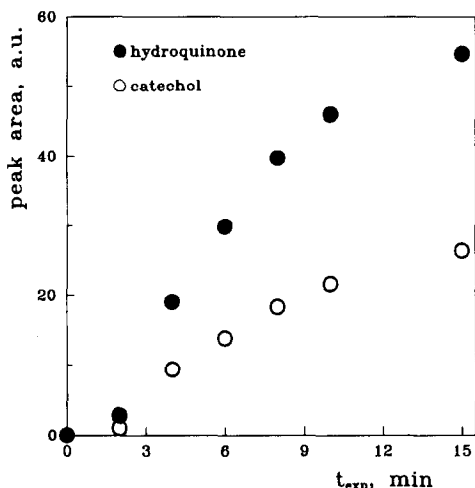
Fig. 3. The formation of hydroquinone and catechol during irradiation of phenol in the pure oxygen-saturated TiO_2 suspension. (Initial phenol concentration 1 mM, titanium dioxide concentration 0.8 g dm^{-3}.)

ions in the irradiated TiO_2 suspensions under given experimental conditions.

3.2. Influence of Ca^{2+}, Mg^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+} and Co^{2+}

In the presence of metal ions M^{n+} the photogenerated electrons and holes may be involved in the surface reduction and oxidation processes [7].

$$M^{n+} + e^- \rightarrow M^{(n-1)+} \tag{2}$$

$$M^{(n-1)+} + h^+ \rightarrow M^{n+} \tag{3}$$

The influence of dissolved metal ions on the rate of photocatalytic degradation may be approximately estimated by comparing the standard reduction potential of metal ions to the band edge potentials of TiO_2 [20] as schematically depicted in Fig. 1. The reduction of metal cations can result in the photodeposition of metal on TiO_2 surface, which can significantly change the surface properties [8]. This method can also be applied to prepare metal supported photocatalysts [8]. Both cation species M^{n+} and $M^{(n-1)+}$ may be also dissolved in water (e.g. Fe^{3+}/Fe^{2+}, Co^{3+}/Co^{2+}, Mn^{3+}/Mn^{2+}), and their reaction with generated hydrogen peroxide [7,13] and surface peroxidic groups via the Fenton reaction [22], represents

the additional source of hydroxyl radicals (Eq. 1).

The phenol half-time in the irradiated TiO_2 suspensions with Ca^{2+}, Mg^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+} and Co^{2+} addition is strongly dependent on the standard reduction potential of metal, E^0, as illustrated in Table 1. It is interesting that the dependence of phenol half-time on concentration of these metals in the applied concentration range (0.28–1.1 mM) is only negligible. The phenol half-times in the irradiated TiO_2 systems with dissolved Ca^{2+}, Mg^{2+}, Zn^{2+} and Ni^{2+} were 14 ± 1 min under given experimental conditions.

The detrimental effect of Mn^{2+} and Co^{2+} on the phenol degradation rate in irradiated TiO_2 suspensions may be well explained by the electron transfer from metal ions [23,24] to the photogenerated holes (Eq. 3) in the valence band (Fig. 1). This process probably decreases the yield of hydroxyl radicals production resulting in the lower phenol degradation rate in these systems.

3.3. Influence of Cu^{2+}

The dissolved Cu^{2+} ions (concentration of 0.28–1.1 mM) significantly hindered the phenol degradation in the irradiated TiO_2 suspensions as shown in Fig. 4. The inhibition effect of Cu^{2+} on phenol decomposition is important for Cu^{2+} concentrations higher than 1 mM, where the photodeposition of copper species on TiO_2 surface is

Table 1

The correlation between the standard reduction potential of metal ions [32] and the experimentally obtained half-times of phenol in photocatalytic degradation

Redox system	E^0 (V)	$\tau_{0.5}$ (min)
$Ca^{2+} + 2e^- \rightleftharpoons Ca$	-2.84	14
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	-2.38	14
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	-0.763	14
$Ni^{2+} + 2e^- \rightleftharpoons Ni$	-0.23	14
$Mn^{3+} + e^- \rightleftharpoons Mn^{2+}$	1.51	17
$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	1.82	22

Initial phenol concentration 1 mM, titanium dioxide concentration 0.8 g dm^{-3}, metal ion concentration in the range 0.28–1.1 mM. The influence of metal ion concentrations on the phenol half-time in these systems was negligible.
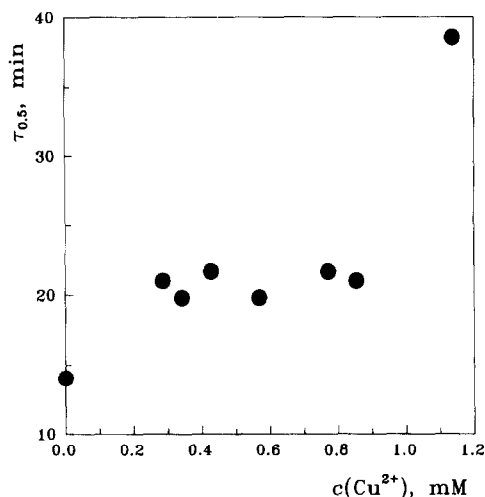
Fig. 4. The dependence of phenol half-time on the Cu^{2+} concentration in the irradiated oxygen-saturated TiO_2 suspension. (Initial phenol concentration 1 mM, titanium dioxide concentration 0.8 g dm^{-3}.)

evident. The reflectance spectra of original TiO_2 and TiO_2/Cu powder obtained from the irradiated phenol suspension ($Cu^{2+} = 1.1$ mM) are depicted in Fig. 5. The attempts to obtain the distributions of copper species on titanium dioxide surface using X-ray microanalysis were unsuccessful, probably due to the low concentration of deposited copper compound.

The IR spectra ($4000-400$ cm^{-1}) of TiO_2/Cu powder were compared with IR spectra of Cu_2O and Cu^0 reference samples. The presence of the absorption peak at 630 cm^{-1} [25] indicated the presence of Cu_2O in the TiO_2/Cu sample. However the absorption characteristic for elemental copper was also measured. In accordance with the obtained IR spectra we may confirm that copper is present on the TiO_2 surface as the mixture of Cu^0 and Cu_2O. Copper deposited on the TiO_2 surface may modify the processes of generation and recombination of the charge carriers and radical intermediates [2,26]. The reduction of Cu^{2+} by photogenerated electrons (Eq. 2) may compete with the formation of superoxide anion-radicals and consequently may reduce the formation of peroxidic species, destroying phenol molecules, in the irradiated systems. In the literature there are also reports of the formation of surface complex structures of Cu^{2+} ions with organic compounds

present in the suspensions, which can act as surface poison [27].

3.4. Influence of Cr^{3+}

The addition of 0.28 mM Cr^{3+} in the TiO_2 suspension resulted in the strong decrease of phenol degradation rate in TiO_2 suspensions ($\tau_{0.5} = 90$ min). The process of phenol decomposition was fully stopped after further increase of Cr^{3+} concentrations.

We were intensively looking for a reason of the observed photocatalytic activity decrease in systems with $CrCl_3$ added. The formation of Cr^{6+} or Cr^0 was not observed during exposure. Possible inhibition effect of Cr^{3+} ions on the phenol degradation rate can also be explained by the competitive adsorption between cations and phenol; Cr^{3+} ions may also create acceptor and donor surface centres that behave as recombination centres for the photogenerated charge carriers [2,28].

The adsorption of Cr^{3+} ions on the surface was investigated by monitoring the decrease of pH values of TiO_2 suspensions containing phenol, after addition of various concentrations of Cr^{3+}. The decrease in pH values of the TiO_2 suspensions after the addition of metal ions is indicative of the replacement of surface protons by the adsorbed cations (Eq. 4) [29].
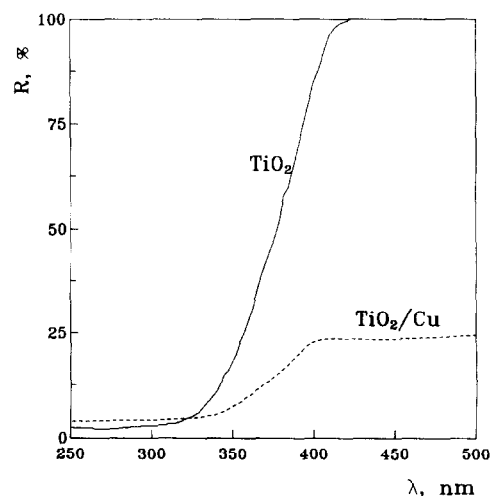

Fig. 5. The reflectance spectra of original powder TiO_2 P25 (Degussa) and TiO_2/Cu powder obtained from the irradiated phenol suspension (addition of 1.1 mM Cu^{2+}).
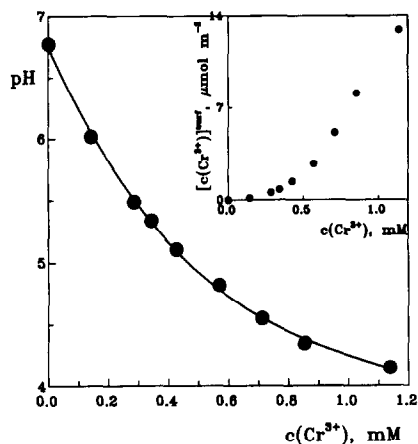
Fig. 6. The pH values decrease in TiO_2 suspensions containing phenol, after addition of various concentrations of Cr^{3+} ions. Inset: dependence of surface concentration of Cr^{3+} on the concentration of Cr^{3+} dissolved in suspension.
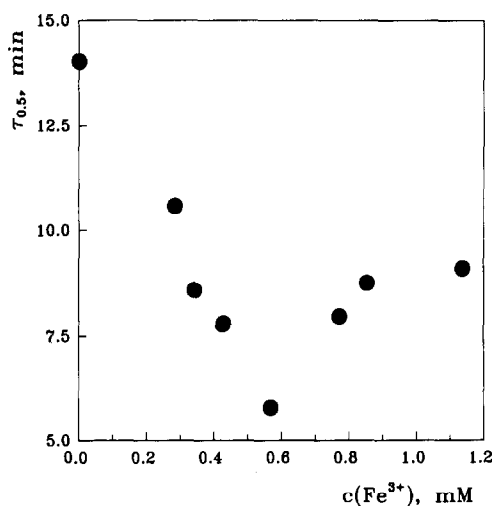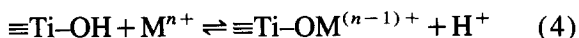

Fig. 7. The dependence of phenol half-time on the Fe^{3+} concentration in the irradiated oxygen-saturated TiO_2 suspension. (Initial phenol concentration 1 mM, titanium dioxide concentration 0.8 g dm^{-3}.)

$$\equiv Ti\text{–}OH + M^{n+} \rightleftharpoons \equiv Ti\text{–}OM^{(n-1)+} + H^+ \qquad (4)$$

The measured pH values decrease in TiO_2 suspension containing phenol after addition of Cr^{3+} ions, is depicted in Fig. 6. The evaluated dependence of the surface concentration of Cr^{3+} ions on the concentration of dissolved Cr^{3+} in suspension, is shown in the inset of Fig. 6. The obtained results confirm the strong interaction of titanium dioxide surface with Cr^{3+} ions, which probably causes the decrease of photocatalytic phenol degradation.

3.5. Influence of Fe^{3+}

The addition of Fe^{3+} ions in the oxygen-saturated TiO_2 suspensions caused the significant decrease of phenol half-times as is shown in Fig. 7. The lowest half-time (5.8 min) was achieved for Fe^{3+} concentration of 0.57 mM. Further increase of dissolved Fe^{3+} did not improve the rate of phenol degradation (Fig. 7). During irradiation of photocatalytic TiO_2 systems with added ferric ions the formation of Fe^{2+} ions was confirmed [13,30]. The dependence of ferrous ions concentration on irradiation time is depicted in Fig. 8.

The presence of redox couple Fe^{3+}/Fe^{2+} in TiO_2 suspension strongly influences the reaction of the generated hydrogen peroxide and surface peroxidic groups [13,26,30]. The reaction of Fe^{2+} with hydrogen peroxide (Eq. 1) represents a supplementary source of hydroxyl radicals [7,26] resulting in the increase of the phenol decomposition rate in the irradiated systems. Higher concentrations of Fe^{3+} probably inhibit the formation of superoxide anion-radicals, radical intermediates and peroxo titanium species by the competitive reaction of photogenerated electrons with Fe^{3+} ions, thus the phenol half-times became higher (Fig. 7).
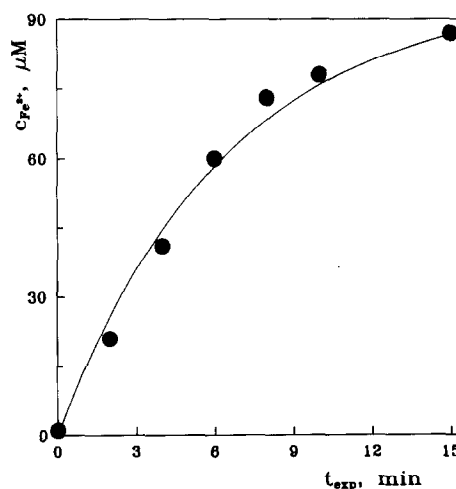

Fig. 8. The formation of ferrous ions during irradiation of aqueous oxygen-saturated TiO_2 phenol suspension with addition of 1.1 mM Fe^{3+}. (Initial phenol concentration 1 mM, titanium dioxide concentration 0.8 g dm^{-3}.)

3.6. Homogeneous photochemical reactions

The results of blank experiments showed that the simultaneous presence of titanium dioxide, light and oxygen is necessary for the effective photocatalytic decomposition of phenol in aqueous solutions.

The direct photochemical degradation of phenol by the irradiation of its aqueous solutions in the presence of dissolved metal ions cannot be excluded from the degradation mechanism. In order to investigate this direct photochemical process, the irradiation of phenol in homogeneous oxygen-saturated aqueous solutions with dissolved metal ions (in the same concentrations as in photocatalytic experiments) was performed in order to investigate the contribution of homogeneous photochemical degradation sensitized by metal ions. The decrease in phenol concentration under these experimental conditions was observed only by irradiation in the presence of ferric ions.

In the irradiated homogeneous aqueous solution of Fe^{3+} ions, the hydroxyl radicals are formed according to the mechanism ascribed by Eqs. 1 and 5

$$Fe^{3+} + H_2O \xrightarrow{h\nu} {}^{\cdot}OH + H^+ + Fe^{2+} \qquad (5)$$
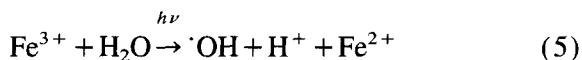
and the generated hydroxyl radicals cause the degradation of phenol molecule [31].

The phenol half-times calculated for the homogeneous systems with various Fe^{3+} concentrations are considerably higher than in TiO_2 photocatalytic systems (Fig. 9) and the contribution of homogeneous photochemical reactions is not significant.

4. Conclusions

The effect of dissolved metal ions in the concentration range 0.28–1.1 mM on the photocatalytic degradation rate in the irradiated oxygen-saturated TiO_2 suspensions was investigated. The obtained results may be summarized as follows:
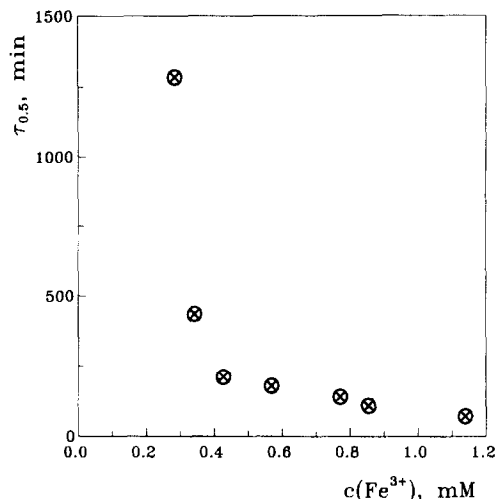

Fig. 9. The dependence of phenol half-time on the Fe^{3+} concentration in the irradiated oxygen-saturated homogeneous aqueous solution. (Initial phenol concentration 1 mM.)

- The presence of Ca^{2+}, Mg^{2+}, Zn^{2+}, Ni^{2+} had no influence on the phenol degradation rate.
- The dissolved ions Mn^{2+}, Co^{2+} and Cu^{2+} inhibited phenol degradation; the photodeposition of Cu^0 and Cu_2O on TiO_2 was observed under given experimental conditions.
- The addition of Cr^{3+} in the TiO_2 suspensions stopped the photocatalytic phenol degradation.
- The highest phenol degradation rates were obtained in the presence of ferric ions; the phenol half-time 5.8 min was achieved for Fe^{3+} ions concentration 0.57 mM under given experimental conditions.

For the technical applications of the photocatalytic systems in the purification of water no dissolved cations can be added in water. However, the dissolved metal ions may be present in the underground, ground and waste waters already before the purification process and is necessary to know what influence the metal ions have on the degradation of pollutants.

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