THE INFLUENCE OF FERROUS/FERRIC IONS ON THE Efficacy of PHOTOCatalytic OXIDATION of POLLUTANTS IN GROUNDWATER

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ABSTRACT

The complex influence of ferrous/ferric ions on the efficacy of aqueous photocatalytic oxidation (PCO) of 2-ethoxyethanol (2-EE), methyl tert-butyl ether (MTBE) and humic substance (HS) was studied. A kinetic efficiency increase at lower concentrations of ferrous ions was observed to change to a steep decrease at higher concentrations for 2-EE and MTBE; whereas for HS only an inhibitory effect of Fe2+ on the PCO efficiency was noticed. The authors proposed an explanation for the observed phenomena based on the different sensitivities of pollutants towards radical-oxidation reactions and the competition-absorption of metallic ions and pollutants on the TiO2 surface.

Keywords: 2-ethoxyethanol (2-EE), methyl tert-butyl ether (MTBE), humic substances (HS)

INTRODUCTION

The present research is devoted to analysing the influence of ferrous/ferric ion additives on the photocatalytic oxidation (PCO) of different organic substances in acidic media: humic substances (HS), deicing agents and motor fuel oxygenates. Humic substances are largely found in natural water as an ultimate decomposition product of living matter. 2-Ethoxyethanol (2-EE, CH3-O-CH2-CH2-OH) is used as a solvent, a de-icing agent for runways and airports, and an antifreeze motor and jet fuel additive. Methyl tert-butyl ether (MTBE, CH3-O-C(CH3)2) is widely used as an anti-detonating oxygenated component of motor fuels. Despite being different in their chemical nature, these substances are often present simultaneously in groundwater: de-icing agents and motor fuel oxygenates can be leached in natural water as a result of leakage, accidental spillage and uncontrolled disposal. Humic substances may be objectionable due to the colour and turbidity they add to water. More importantly, they represent a health hazard through chelation of heavy metal ions and also binding with toxic such as pesticides, making the removal of the heavy metals and pesticides problematic. Humic substances also serve as precursors of carcinogenic polycyclic aromatics in water chlorination [1]. 2-Ethoxyethanol has negative effects on the kidneys, respiratory, and reproductive systems, and also acts as a depressant of the central nervous system. The suspected carcinogen MTBE represents a hazard to the environment [2].

These substances have been proven by earlier studies to be refractory against biodegradation and thus they accumulate and remain intact in groundwater for long times [3, 4]. The photocatalytic oxidation of organic pollutants is based on the action of positively charged holes on the semiconductor surface [5]. When subjected to UV-irradiation, the semiconductor’s valence band electrons are displaced from the valence band to the conduction band, creating positively charged holes. The positively charged holes oxidize the organic pollutant molecules adsorbed on the photocatalyst surface. The decomposition of water molecules into hydroxyl radicals also takes place on the holes. However, the holes may recombine rapidly with conduction band electrons, decreasing the PCO efficiency. Prolongation of the holes’ lifetime should, therefore, increase the efficiency of PCO. For this purpose, multivalent metal ions may be added to the treated solutions, or, more precisely, to the photo-catalyst surface, to scavenge electrons at the surface of the titanium dioxide, thus preventing electron-hole recombination and improving the oxidation performance.

Several previous studies [6-8] have reported higher PCO rates following the addition of small amounts of ferrous ions. Succinic, carboxylic acids and textile dye dyes were the organic pollutants in those studies. However, higher concentrations of ferrous ion reduced the decomposition rate significantly. A similar trend was observed with other multivalent metals influencing PCO of phenol and sucrose [9, 10]. Our previous studies showed the positive role of ferrous ions.
ions at low concentrations in the efficiency of PCO of MTBE, although the PCO experiments with 2-EE, carried out in the same range of concentrations of Fe(III), indicated only a negative effect of iron ions. The results of more detailed investigation given here broaden the knowledge of the influence of iron ions on pollutants of various types and show the complex character of the dependence of the PCO efficiency on the concentration of iron ions.

**EXPERIMENTAL SECTION**

Two 200-mI simple batch reactors with inner diameter 100 mm (evaporation dishes), aperture 40 m², n², thermostated at 20±1°C and mechanically agitated with magnetic stirrers were used in the PCO experiments; the one used for the PCO was called "active" and the other containing no photocatalyst was called "reference". Both reactors were exposed to identical experimental conditions. The samples from the active reactor were compared to the reference samples to avoid complications caused by water evaporation. A UV-light-source, Phillips 365-nm low pressure luminescent mercury UV-lamp (35 W), was positioned horizontally over the reactor (see Fig. 1), providing irradiance of about 0.7 mW cm² measured at a distance corresponding to the level of the free surface of the reactor by the optical radiometer Mistras MPS100 (Mistras Technology, UK).

The experiments were carried out using aqueous solutions of 2-EE, MTBE and HSO₄ (sodium salt of humic acid) supplied by Aldrich. The experiments were conducted with synthetic solutions at concentrations of 300, 100 and 10 mg I⁻¹ for 2-EE, MTBE and HSO₄ respectively. The concentrations of pollutants were chosen to be consistent with their presence in polluted groundwater and experimental conditions applied previously [11]. All experiments were carried out at pH 5.0, adjusted with 6-N solution of sulphuric acid. With 2-EE, the treatment time was 24 h, with MTBE - 1 h and with HS - 6 h. The treatment time was chosen to reduce the concentration of pollutants below 95% of the residual concentration and was used in calculations of the process efficiency E (see eq. 3). All the experiments were carried out at least three times under identical experimental conditions to derive the average value of the process efficiency. The average deviation of data in parallel experiments did not exceed 5%.

The experiments were performed using titanium dioxide Degussa P25 in the following mode, slurry of TiO₂ at 1 g I⁻¹ was used in the PCO experiments with 2-EE and MTBE, since HS formed hard-to-separate stable suspensions with TiO₂. Slurry of TiO₂, attached to buoyant hollow glass microspheres was used for oxidation of HS to avoid this problem. The buoyant catalyst was also tested for its activity with 2-EE. The hollow glass microspheres used in this study had an average diameter of 60 to 70 pm and a density 0.27 g cm⁻³ (the product of LP Impex, Tokyo). Titanium dioxide was attached to the surface of the microspheres by the thermal

![Figure 1. PCO reactor.](image)
method [12]: equal volumes of dry micro-spheres and the aqueous suspension of titanium dioxide with concentration of 1 g/L were thoroughly mixed by stirring and sonication in an ultrasonic bath for 30 min. The micro-spheres were then separated from the mixture by filtration with a membrane filter, heated to dryness at 120°C and calcined in air at a temperature of 1,000°C for 2 h. This procedure was repeated six times, which was found to be the optimum number of the attachment operations for the best performance of the photocatalyst attached to the borosilicate glass micro-beads [13]. Analogously, TiO₂ was attached to the surface of the glass plates (one side) in approximately equal amounts either by multiple submerging of the plates in the TiO₂ suspension with subsequent drying after each submersion, or by spraying the TiO₂ suspension over the surface of the plates and drying. TiO₂ attached to glass plates, submerging horizontally in the solution to be treated at a depth from 3 to 10 mm, was used in POC of 2-EE. Since 2-EE does not absorb UV light at 365 nm, the depth of the submersion was not important within the indicated limits. This was confirmed by specially conducted experiments.

The decrease in the pollutant concentration was determined for 2-EE and MTBE from the decrease in chemical oxygen demand (COD), measured by a standard method [14]. For the COD, colour was determined with the photocolorimeter MACH DR/2010 at 436 nm. Absorbance at 254 nm was measured by Spectronic Unicam spectrophotometer (Hicks, UK). Both indices were correlated with the content of HS by preliminary calibration.

Adsorption experiments for ferrous/ferric ions, introduced as sulphates, 2-EE, MTBE and HS on the TiO₂ surface were conducted in closed flasks, equipped with magnetic stirrers, thermostated at 26.1°C and adjusted to pH 3.0. The amount of substances adsorbed was derived from the batch mass balance: the concentration of the dissolved substance was determined before and after adsorption. The points of isotherms are the average out of three experimental sets. The concentrations of iron ions were determined by a photoelectrometric method described in standard methods [14]. The PCO by-products of 2-EE, mainly carbonic acids, were qualitatively determined by the methods described in Pohoudeck-Fabry and Biechler [15]. Oxalic, glycolic and formic acid were determined by their reaction with tritylazic acid -- through the formation of iron (III) azate.

RESULTS AND DISCUSSION

The performance of PCO with artificial radiation sources was characterized by the process efficiency E. The efficiency E is defined as the decrease in the amount of pollutant divided by the amount of energy reaching the surface of the treated sample (eq. 1).

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E = \frac{\Delta C - V \cdot \frac{\text{m}}{3600}}{I \cdot \frac{s}{3600}}
\]

where \( E \) -- PCO efficiency, mg W⁻¹ h⁻¹; \( \Delta C \) -- the decrease in the concentration of the pollutant, mgL⁻¹ or mg L⁻¹ for COD of 2-EE and MTBE solutions, and mg L⁻¹ for HS; \( V \) -- the volume of the sample to be treated, L; \( I \) -- irradiance, mW cm⁻²; \( s \) -- irradiation area, cm²; \( t \) -- treatment time, h.

Both ferrous and ferric ions were tested in the experiments with 2-EE. Sulphate was chosen as the counter-ion due to its low inhibitory effect on PCO efficiency observed with 2-EE in Khrushevskaya et al. [11]. The results of the experiments are shown in Fig. 2. One can see a similar trend in the dependence of PCO performance on the concentrations of both ionic species. Ferric ions were therefore seen to have the same effect as ferrous ions, which may be explained with an equilibrium established between ferrous and ferric ions in aqueous solutions in the presence of dissolved oxygen at pH 3 in TiO₂ slurry, i.e. a strongly oxidative media, as described in Catteneo et al. [16].

Ferrous ions appeared to play a significant role in PCO of 2-EE. The addition of small amounts of ferrous ion, up to 0.09 mM, resulted in a drastic, up to 60 %, increase in the process efficiency (Fig. 2). With further increase in the concentration of Fe²⁺, the PCO efficiency decreased dramatically.

A similar dependency pattern, in which the PCO efficiency of 2-EE had its maximum with a Fe²⁺ concentration of 0.09 mM, was observed for TiO₂ attached to the glass plates, although the absolute values of the PCO efficiency were about 40 to 70 % lower than with the TiO₂ slurry. Borosilicate micro-beads with attached TiO₂ were the least effective. The maximum PCO efficiency was, however, observed also at 0.09 mM of ferrous/ferric ions (Fig. 3).

Figure 3 shows that the difference in the procedure of TiO₂ attachment to the glass plates makes a difference in the PCO efficiency: attachment by spraying appeared to be more effective. This may not be explained by the difference in the mass of TiO₂, since the attached mass was virtually the same, but is most probably due to uneven relief and porosity of the catalyst surface and, thus, a larger contact surface resulting from non-ambient spray attachment.

Methyl tert-butyl ether showed a trend somewhat similar to 2-EE (Fig. 4) for drastic increase in PCO efficiency at smaller concentrations of Fe²⁺ ions was followed by a decrease with further addition of ferrous/ferric ions [11]. However, one can see a significant difference in the behaviour between MTBE and 2-EE: the maximum efficiency for MTBE was observed at the Fe²⁺ concentration of 1 mM, which is about ten times bigger than that for 2-EE. Furthermore, a further increase in the concentration of Fe²⁺ ions resulted in a gradual increase of PCO efficiency, which was not observed with 2-EE. This may be explained by the difference in the PCO mechanism of these two substances and their different
Figure 2. The efficiency of PCO of 2-ethoxyethanol in TiO₂ slurry vs. concentration of Fe²⁺ (Δ) and Fe³⁺ (●) ions at pH 3.0.

Figure 3. Efficiency of PCO of 2-ethoxyethanol at 0.09 mM of Fe²⁺⁺ with TiO₂ application modes: 1 - TiO₂ Degussa P25 suspension (1 g l⁻¹); 2 - TiO₂ sprayed to the glass plate, 0.6 mg cm⁻²; 3 - TiO₂ settled at the glass plate, 0.7 mg cm⁻²; 4 - TiO₂ attached to hollow glass micro-spheres, the amount of buoyant catalyst in the reactor 50 g m⁻³; 5 - same as 4 at 25 g m⁻³.
adsorption properties at the surface of the titanium dioxide. Ferrous/ferric ions unambiguously demonstrated an inhibitory effect in the PCO of HS at all detectable concentrations (Fig. 5).

The difference in the behaviour of 2-EE, MBTE and HS can be explained by a dual mechanism of PCO [9]: 1) the adsorption of the pollutant by the surface of the titanium dioxide is followed by a direct abstraction of the pollutant's electrons, i.e. oxidation, with positively charged holes; 2) oxidation with hydroxyl radicals takes place at the catalyst surface or in its vicinity. Both reactions proceed simultaneously, although positively charged holes have an oxidation potential about 1.15 times higher than a hydroxyl radical [17]. What mechanism dominates in PCO depends on the chemical and adsorption properties of the pollutant.

The promotion of OH-radical was less effective in the oxidation of ethylglycerol derivatives [18, 19]. The increasing PCO efficiency for 2-EE with the addition of ferrous/ferric ions (at < 0.09 mM, concentrations may then be explained by the partial occupation of adsorption sites with Fe(II)-ions, overpowered, however, with the electron scavenging by these ions, extending the lifetime and thus the oxidation performance of the positively charged holes. A further increase in the concentration of metallic ions results in the blockage of adsorption sites with a resultant drastic decrease in PCO efficiency. The formation of hydroxyl radicals has little effect on the overall oxidation rate.

Methyl tert-butyl ether is less resistant towards oxidation with a hydroxyl radical. For example, oxidation methods, such as ozonation, exhibited poor performance in the abatement of MBTE, although introduction of OH-radical pretreatments significantly enhanced oxidation [20]. This makes both mechanisms of PCO effective in MBTE. Small concentrations of ferrous/ferric ions therefore enhance the direct oxidation of MBTE with positively charged holes, and also the formation of OH-radicals. Radical oxidation reactions contribute to the overall oxidation rate successfully until a certain concentration of metallic ions is achieved (1 mM).

Above this concentration, the formation of OH-radicals is probably obstructed by a "short-circuit" mechanism, described in [6], the blockage of the TiO2 adsorption sites with ferrous/ferric ions results in reduced generation of OH-radicals. The increase of the PCO efficiency with further increasing ferrous/ferric ions concentration is consistent with the observations reported by Chu et al. made in UV-assisted oxidation of 2,4-dichlorophenoxycetic acid [21] and may be explained by increased OH-radicals formation in the bulk solution initiated by the UV-irradiated Fe(III)-ions: we also preliminarily observed MBTE oxidized to some extent under UV-irradiation in aqueous solutions containing Fe(III)-ions with no TiO2 present, although this reaction was beyond the scope of the present paper. In the TiO2-free experiments the oxidation rate increased with increasing concentration of Fe(III)-ions. The authors presume that oxidation of MBTE.
with UV-irradiated Fe^{2+3+} may be enhanced in the presence of TiO₂. However, further experimental studies are necessary to confirm this statement.

Humic substances are known to be good scavengers of OH-radicals thus diminishing the role of radicals in the overall degradation [22]. One could then expect an increase in PCO efficiency for HS similar to 2-EE at small concentrations of ferrous/ferric ions. The observed solely inhibitory effect of ferrous/ferric ions to the PCO efficiency of the treatment of HS solution could be explained by the complications in adsorption: not only Fe^{2+3+}-ions block the adsorption sites at the TiO₂ surface, but also the partial chelation of carboxylic and phenolic groups of the humic molecules with the Fe^{2+3+}-ions may obstruct their adsorption at the TiO₂ surface. Under these circumstances, the prolonged lifetime of positively charged holes may have a weakened effect due to obstruction in the adsorption of chelated humic molecules.

To support the above-mentioned hypothesis concerning the role of ferrous/ferric ions in PCO performance determined by the adsorption properties and the sensitivity of the target compounds towards radical attacks, the impact of the Fe^{2+3+}-ions on the adsorption of a pollutant by TiO₂ was studied in a series of adsorption experiments. The ferrous/ferric ions content dependency of adsorption of 2-EE from a solution with an equilibrium concentration of 2-EE 300 mg L⁻¹ by the TiO₂ surface was determined experimentally. As one can see from Fig. 5, the surface concentration of 2-EE steadily decreases within the Fe^{2+3+}-ions equilibrium concentration range attributable to the peak zone of the PCO efficiency (Fig. 3).

An analogous dependence of the equilibrium surface concentration of Me(2+) was also observed: the MTBE surface concentration in equilibrium with an MTBE solution of 100 mg L⁻¹ decreased from 0.9 mmol g⁻¹ at zero concentration of Fe^{2+3+}-ions to 0.5 mmol g⁻¹ at 1 mM and 0.1 mmol g⁻¹ at 10 mM of Fe^{2+3+}-ions (Fig. 7). This explains the difference between the critical concentration values of Fe^{2+3+}-ions for 2-EE and MTBE: the adsorption of MTBE was less affected by the presence of Fe^{2+3+}-ions than 2-EE.

The last observation may be explained by differences in adsorption of 2-EE and MTBE. The list of carbonic acids determined qualitatively as PCO products of 2-EE include oxalic, acetic, formic and glycolic acids. The formation of glycolic acid confirms the adsorption of 2-EE by the oxygen atom of the other group, whereas the formation of oxalic acid indicates the adsorption of 2-EE with both oxygen atoms. In general, MTBE is noticeably better adsorbed to a TiO₂ surface than 2-EE. The greater sensitivity of 2-EE to the concentration...
Figure 6. The surface concentration of 2-EE at TiO₂ versus Fe²⁺/³⁺ ion equilibrium concentration at pH 3.0 (20°C).

Figure 7. The surface concentration of MTBE at TiO₂ versus Fe²⁺/³⁺ ion concentration at pH 3.0.
of Fe(II) ions may therefore be explained by weaker adsorption of 2-EE in an acidic aqueous solution.

Humic substances were adsorbed consistently with the PCCO efficiency dependence on the concentration of Fe(II) ions: the decrease in the surface concentration with increasing Fe(II)/Fe(III) ions concentration corresponds to the decrease in the HS PCCO efficiency. This observation confirms the small role of OH-radicals in PCCO of HS and the difficulties in adsorption can probably be accounted for by bonding of Fe(II) ions with HS.

The adsorption of ferrous/ferric ion on the surface of titanium dioxide was also studied. The results shown in Fig. 8 are consistent with the adsorption equilibrium of MTBE: the equilibrium aqueous concentration of Fe(II) for the minimum adsorption of MTBE approximately coincides with the maximum adsorption of Fe(II), which shows a direct connection between the occupation of adsorption TiO2 sites with iron ions and the performance of PCCO: the minimum PCCO efficiency for MTBE was observed around this concentration of Fe(II).

CONCLUSIONS

The complicated influence of the addition of multivalent ferrous/ferric ions to aqueous solutions of groundwater pollutants, 2-ethoxy ethanol (2-EE), methyl tert-butyl ether (MTBE) and humic substances (HS), was studied and explained. An optimum concentration range of ferrous/ferric ions was observed for 2-EE and MTBE. Ferrous/ferric ions exhibited only an inhibiting role in PCCO of HS.

Evidence was found that supported the hypothesis that the optimum are the result of the dual mechanism of oxidation: the surface of the TiO2 photocatalyst, including the direct oxidation of adsorbed pollutants with positively charged holes; and the radical oxidation: the PCCO of 2-EE resistant to radical oxidation practically stopped when the positively charged holes at the TiO2 surface were blocked by ferrous/ferric ions. The effective PCCO of less resistant MTBE at high concentrations of Fe(II) ions may be explained by the development of a radical oxidation mechanism. This radical mechanism exhibited poor performance with HS since they exhibit good radical scavenging ability.

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