

## Research Article

# The Influence of Iron Ions on the Aqueous Photocatalytic Oxidation of Deicing Agents

D. Klauson<sup>1</sup> and S. Preis<sup>2</sup>

<sup>1</sup> Department of Chemical Engineering, Faculty of Chemical and Materials Technology, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia

<sup>2</sup> Department of Chemical Technology, Lappeenranta University of Technology, P.O. Box 20, 53851 Lappeenranta, Finland

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An experimental research into aqueous photocatalytic oxidation (PCO) of the deicing compounds, 2-ethoxyethanol (2-EE), diethylene glycol monomethyl ether (DEGMME), and ethylene glycol (EG) was undertaken. The addition of iron ions to the acidic aqueous solutions to be treated displayed complex influence on the oxidation efficiency of the above mentioned substances, resulting in a sharp increase of the PCO efficiency at smaller concentrations of iron ions followed by a drastic decrease with the increasing iron ion concentrations. The phenomena observed can be explained by the electron scavenging effect of the iron ions and the competitive adsorption of iron ions and the oxidized substances on titanium dioxide surface. The carbonic acids determined as the PCO by-products allow outlining some reaction pathways for the substances under consideration.

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## 1. INTRODUCTION

The photocatalytic oxidation (PCO) of organic pollutants is based on the action of positively charged holes on the semiconductor surface [1]. However, the holes may recombine rapidly with conduction band electrons, decreasing the PCO efficiency. Therefore, prolongation of the holes' lifetime should increase the efficiency of PCO. For this purpose, multivalent metal ions may be added to the treated solutions or, more precisely, to the photocatalyst surface, to scavenge electrons at the surface of the titanium dioxide, thus preventing electron-hole recombination and improving the oxidation performance.

Several previous studies [2–5] have reported higher PCO rates following the addition of small amounts of ferrous ions. Sucrose, carboxylic acids, and textile azo dye were the organic pollutants in these studies. However, higher concentrations of ferrous ion reduced the decomposition rate significantly. A similar trend was observed with other multivalent metals influencing PCO of toluene and phenol [6, 7]. Our previous results showed a peculiar influence of ferrous ions to PCO of lignin, humic acids, and some oxygenated hydrocarbons, such as methyl *tert*-butyl ether [8]. The present paper analyses the effect of iron ions addition

on the PCO efficiency of the three most used glycolic deicing agents: ethylene glycol (EG, HO-CH<sub>2</sub>-CH<sub>2</sub>-OH), 2-ethoxyethanol (2-EE, CH<sub>3</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-CH<sub>2</sub>-OH), and diethylene glycol monomethyl ether (DEGMME, CH<sub>3</sub>-O-CH<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-CH<sub>2</sub>-OH).

Ethylene glycol is mainly used as an antifreeze, although substantial amounts of EG are consumed in polymer synthesis. 2-Ethoxyethanol is used as a solvent, a deicing agent for runways and aircrafts, and a deicing additive in the jet fuel. The usage of DEGMME is similar to that of 2-EE; it is also used as a diluent for hydraulic brake fluids. Massive use of the deicing substances, their leakage, accidental spillages and uncontrolled disposal of fuels, deicing and brake liquids, and antifreezes result in their occurrence in groundwater. All these substances act as central nervous system depressants and may inflict substantial kidney damage which can be fatal; they have also negative effects on respiratory and reproductive systems [9, 10]. Glycol-based deicing agents have been proven by earlier studies to be refractory against biodegradation, and thus they accumulate and remain intact in groundwater for long times [11]. Chemical oxidation methods, such as ozonation and treatment with Fenton's reagent, have been proven inadequate in dealing with glycolic pollution [12–15], resulting in insufficient pollutant

removal and poor mineralization, not to mention high treatment cost.

## 2. EXPERIMENTAL SECTION

The PCO experiments were carried out in two 200 mL simple batch reactors with inner diameter 100 mm (evaporation dishes), and aperture  $40 \text{ m}^2 \text{ m}^{-3}$ . The reactors were thermostatted at  $20 \pm 1^\circ \text{C}$  and mechanically agitated [16]. The reactor 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 the effect of water evaporation. A UV light source, Phillips TLD 15 W/05 low-pressure luminescent mercury UV lamp with the emission maximum at 360 nm, was positioned horizontally over the reactors, providing irradiance of about  $0.7 \text{ mW cm}^{-2}$  measured by the optical radiometer U VX at a distance corresponding to the level of the free surface of the reactor.

The experiments were carried out with synthetic solutions at a concentration of  $300 \text{ mg L}^{-1}$  of EG, 2-EE, and DEGMME. The concentrations of the substances were chosen to be consistent with their presence in polluted groundwater and experimental conditions applied previously [8]. All experiments were carried out at pH 3, adjusted with sulphuric acid. The treatment time, 24 hours, was chosen to reduce the concentration of EG, 2-EE, and DEGMME no more than 50% of the residual concentration, and was used in calculations of the process efficiency  $E$  (see (1)). All the experiments were carried out three times under identical conditions. The average deviation of data in parallel experiments did not exceed 5%.

The experiments were performed using Degussa P25 titanium dioxide as suspension at  $1 \text{ g L}^{-1}$ . Both ferric and ferrous ions were introduced as respective sulphates.

The decrease in the pollutant concentration was determined for EG, 2-EE, and DEGMME from the decrease in chemical oxygen demand (COD), measured by a standard method [17].

Adsorption experiments for glycols and ferrous ion on the  $\text{TiO}_2$  surface were conducted in the dark in closed flasks equipped with magnetic stirrers, thermostatted at  $20 \pm 1^\circ \text{C}$  and adjusted to pH 3. 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 the isotherms are the average of three experimental sets. The concentrations of iron ions were determined by a variation of photometric phenantrolin method described in [17], where phenantrolin was substituted by dipyriddy.

The PCO by-products of EG, 2-EE, and DEGMME, mainly carbonic acids, were qualitatively determined by the methods described in [18]. Resorcinol in amount of 200 mg was added to 5 mL of the sample in a test tube. After the resorcinol had dissolved, 10 mL of concentrated sulphuric acid was carefully inserted into the bottom of the test-tube. The colored rings corresponding to carbonic acids appeared in

the following sequence: the blue ring indicating oxalic acid appeared at the liquids' interface, the red ring below the blue one indicated glycolic acid, the orange ring above the blue one corresponds to formic acid. The rings were observed distinctively and repeatedly with both synthetic solutions of the acids and the samples of PCO-treated glycolic solutions. Oxalic acid was also separated from the PCO-treated 2-EE solution sample as calcium oxalate, and quantitatively determined by means of titration with potassium permanganate. Acetic acid was qualitatively determined with 2-EE as red crystals of iron (III) acetate precipitated as a result of addition of iron (III) chloride to the sample. The iron ions did not show any interference in these identifications, which was verified with individual carbonic acids with and without iron ions.

## 3. RESULTS AND DISCUSSION

The performance of PCO with artificial radiation sources was characterised 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 (1). The efficiency values were calculated after a period of time equal to the treatment time of 24 hours:

$$E = \frac{\Delta c \cdot V \cdot 1000}{I \cdot s \cdot t}, \quad (1)$$

where  $E$  is the PCO efficiency,  $\text{mg W}^{-1} \text{ h}^{-1}$ ;  $\Delta c$  is the decrease in the concentration of the pollutant,  $\text{mg O L}^{-1}$  for COD of EG, 2-EE, and DEGMME;  $V$  is the volume of the sample to be treated, L;  $I$  is irradiance,  $\text{mW cm}^{-2}$ ;  $s$  is irradiated area,  $\text{cm}^2$ ;  $t$  is treatment time, hours.

Both ferrous and ferric ions were tested in the experiments with EG. Sulphate was chosen as the counter-ion due to its low inhibitive effect on PCO efficiency, observed in [8]. Previously, the indifference of the PCO towards the oxidation state of iron ions was observed in the PCO of 2-EE [16]: one could see a similar trend in the dependence of PCO performance on the concentrations of both ionic species. Ferric ions were seen to have the same effect as ferrous ions, which may be explained with a dynamic equilibrium established between ferrous and ferric ions at the UV-irradiated  $\text{TiO}_2$  surface and, probably, in its closest vicinity, as described in [19].

In this research, the similar behaviour of iron species was observed in experiments with EG; the results are shown in Figure 1. As one can see also from Figure 2 obtained previously with 2-EE [16], ferrous and ferric ions appeared to play a significant role in PCO of EG and 2-EE. The addition of small amounts of  $\text{Fe}^{2+/3+}$ -ion, up to 0.09 mM, resulted, for example, in a drastic, up to 60%, increase in the 2-EE PCO efficiency (see Figure 2).

With further increase in the concentration of  $\text{Fe}^{2+/3+}$ , the PCO efficiency decreased dramatically. Therefore, the experiments were conducted with ferrous ions, the characterisation of which at  $t = 0$  and in aqueous solution was far simpler. During the PCO process, the dynamic equilibrium  $\text{Fe}^{2+}/\text{Fe}^{3+}$  took place very fast.

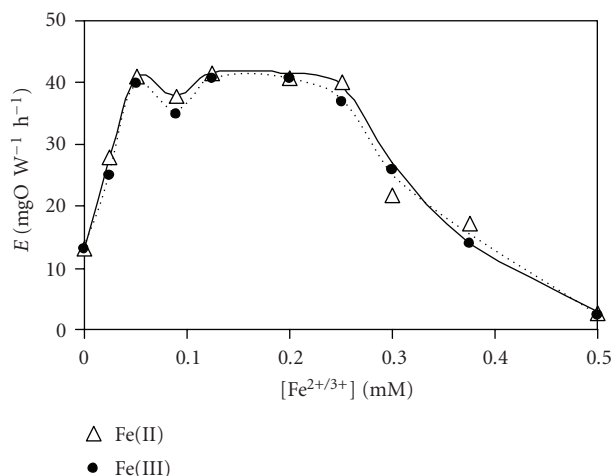


FIGURE 1: The efficiency of PCO of ethylene glycol (EG) in TiO<sub>2</sub> suspension versus concentration of Fe<sup>2+</sup> (Δ) and Fe<sup>3+</sup> (●) ions at pH 3.

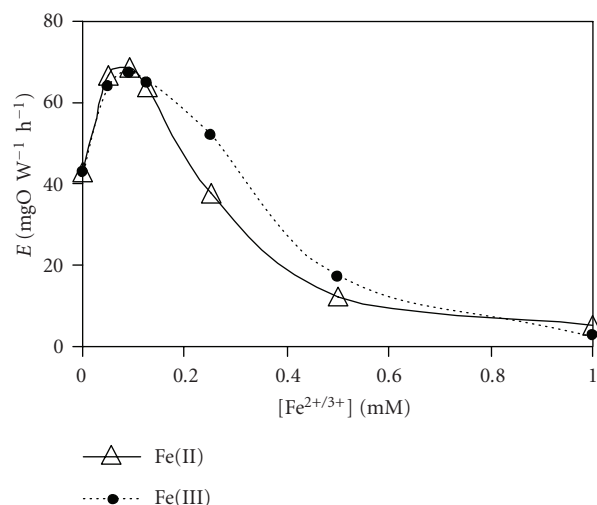


FIGURE 2: The efficiency of PCO of 2-ethoxyethanol (2-EE) in TiO<sub>2</sub> suspension versus concentration of Fe<sup>2+</sup> (Δ) and Fe<sup>3+</sup> (●) ions at pH 3.

A similar dependency pattern was observed with DEGMMME, although the concentration of iron ions corresponding to the efficiency peak was somewhat smaller than that of 2-EE, being 0.06 mM (Figure 3).

Ethylene glycol, however, showed a more complicated dependency of the PCO efficiency on the concentration of iron ions than 2-EE and DEGMMME (see Figure 1). An initial increase in the PCO efficiency of EG at smaller iron ion concentrations (up to 0.05 mM) was followed by a minor decrease between 0.05 and 0.09 mM Fe<sup>2+</sup>. The former PCO efficiency decrease was followed by yet another increase in the iron ion concentration range from 0.09 to 0.125 mM, when the efficiency returned approximately to the same values as at 0.05 mM Fe<sup>2+</sup>. Between 0.125 and 0.25 mM of iron ions' concentration the efficiency value remained stable, followed

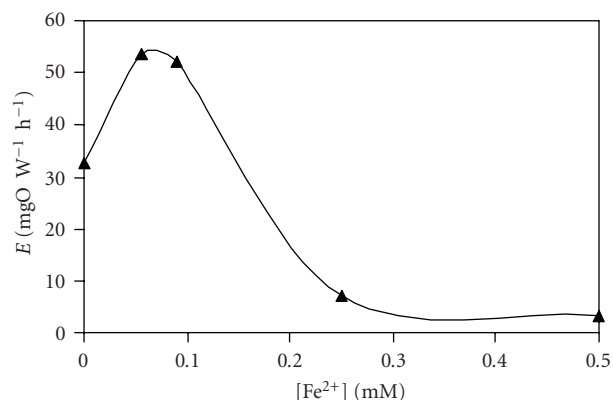


FIGURE 3: The efficiency of PCO of diethylene glycol monomethyl ether (DEGMMME) in TiO<sub>2</sub> suspension versus concentration of Fe<sup>2+</sup>-ions at pH 3.

by a drastic decrease above 0.25 mM. This observation did not find a proper explanation in the present work although the decrease in the PCO efficiency at Fe<sup>2+/3+</sup> concentrations between 0.05 and 0.09 mM was reliably established with both iron ionic species.

Photocatalytic oxidation is known to proceed via two different mechanisms [1]: direct subtraction of the adsorbed pollutant's electrons by the positively charged holes on the surface of titanium dioxide, and oxidation with hydroxyl radicals at the catalyst surface or in its vicinity. Both reactions may proceed simultaneously, although positively charged holes have an oxidation potential about 1.25 times bigger than OH-radicals [20]. Which mechanism dominates in PCO depends on the chemical and adsorption properties of the pollutant.

Glycolic substances were shown by previous studies [21, 22] to be resistant to radical-initiated oxidation reactions. The increasing PCO efficiency for monoalcoholic 2-EE and DEGMMME with the addition of ferrous ions in small concentrations (below 0.09 and 0.06 mM, resp.) may then be explained by the partial occupation of adsorption sites with Fe<sup>2+</sup>-ions, overpowered, however, with the electron scavenging by iron ions, extending the lifetime and thus improving the oxidation performance of the positively charged holes. A further increase in the concentration of iron ions results in the blockage of adsorption sites with a resultant drastic decrease in PCO efficiency. The difference in the concentration of iron ions at maximum PCO efficiency for 2-EE and DEGMMME may be explained by better adsorption of 2-EE (see below).

Ethylene glycol has two hydroxyl groups, which may result in a more complex mechanism of a stronger adsorption. It may be assumed that the adsorption of EG on the surface of titanium dioxide takes place partially with both hydroxyl groups. As it was shown below, the EG molecule attachment with two alcohol groups does not result in simultaneous oxidation of these groups, that is, the alcohol groups are attached with the bonds of unequal length and energy.

One can presume then that the alcohol group, which is adsorbed weaker to the photocatalyst surface, should be easier displaced from the  $\text{TiO}_2$  surface with the increasing iron ions concentration, thus making EG exhibiting fluctuations in its PCO efficiency. The surface concentrations of EG also are dramatically bigger than those of 2-EE and DEGMME (Figure 4), which explains a wide peak of the EG PCO efficiency versus the increasing  $\text{Fe}^{2+}$ -concentration.

In order to verify the viability of the hypothesis described above, series of adsorption experiments were conducted, in which the dependence of deicing agents' adsorption on the concentration of ferrous ions was examined. Also, the adsorption isotherm of ferrous ions on the surface of titanium dioxide was constructed. The results obtained are shown in Figures 4 and 5.

As one can see, the addition of small amounts of iron ions dramatically reduced the adsorption of EG, 2-EE, and DEGMME (Figure 4) on the surface of titanium dioxide. At these concentrations of iron ions, however, the growth of the PCO efficiency of these substances was observed, confirming the hypothesis of electron scavenging by iron ions.

The adsorption mechanism of the substances under consideration may be better explained with the analysis of the carbonic acids formed in PCO. Oxidation of 2-EE in absence of iron ions resulted in formation of glycolic, oxalic, acetic, and formic acids. This indicated the possible adsorption of 2-EE molecule at the protonated  $\text{TiO}_2$  surface with oxygen atoms of hydroxyl, ether, or both oxygenated groups. Since oxalic acid was formed in trace amounts and glycolic acid was also hardly detectable, the adsorption with the hydroxyl group appeared to predominate, although the adsorption with the ether oxygen or both oxygen atoms also took place. This found an indirect proof in the fact that in presence of iron ionic species, the PCO of 2-EE resulted in the formation of only acetic and formic acids. This may be explained by the decrease in 2-EE adsorption with iron ions adsorbed on the  $\text{TiO}_2$  surface: the absence of oxalic and glycolic acids indicates that 2-EE was adsorbed and oxidised only on the hydroxyl group.

The PCO of DEGMME resulted in formation of only glycolic and formic acids in the absence of iron ions. One can conclude that DEGMME molecule may adsorb also with either hydroxyl or one of the ether groups. However, since no oxalic acid was observed, the adsorption can take place only with one oxygen atom at a time, possibly due to geometrical obstacles for the long-chain DEGMME molecules. The last conclusion may be derived from the absence of oxalic acid among the PCO products of DEGMME: it was shown in the experiments that the PCO of glycolic acid does not result in the formation of oxalic acid. Therefore, the simultaneous adsorption and oxidation of both oxygenated groups in DEGMME molecule appear to be a prerequisite of the formation of oxalic acid. Obviously, no adsorption with ether groups was observed in presence of iron ions since no glycolic acid was detected in the treated samples, only formic acid appeared.

It might be assumed that PCO of EG adsorbed with both oxygen atoms should result in the formation of oxalic acid.

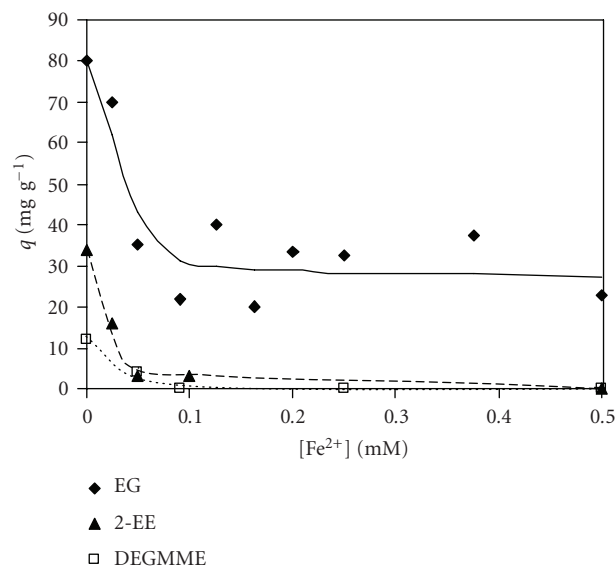


FIGURE 4: The surface concentrations of ethylene glycol (EG), 2-ethoxyethanol (2-EE) and diethylene glycol monomethyl ether (DEGMME) on  $\text{TiO}_2$  versus  $\text{Fe}^{2+}$ -ions equilibrium concentration at pH 3 ( $20^\circ\text{C}$ ).

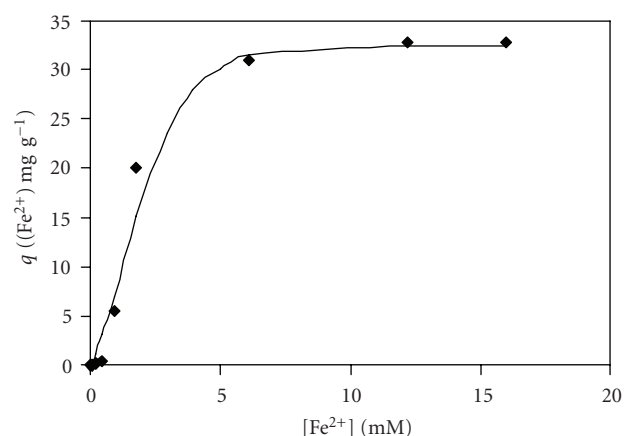


FIGURE 5: The surface concentration of  $\text{Fe}^{2+}$ -ions on  $\text{TiO}_2$  versus  $\text{Fe}^{2+}$ -ions equilibrium concentration at pH 3 ( $20^\circ\text{C}$ ).

However, this point was overrun by the experimental data: only glycolic and formic acids were formed. Also, the PCO of glycolic acid showed no oxalic acid among the products: only formic acid was determined as the product. This circumstance indicates that the EG molecule is oxidized on only one hydroxyl group, first with subsequent oxidation of glycolic acid to formic acid and further to ultimate oxidation products, carbon dioxide and water. This is presumably possible when the EG molecule is attached to the titanium dioxide surface with only one hydroxyl group or at least when two hydroxyl groups are connected to the surface by bonds of unequal length and energy. It is worth noticing that at higher iron ion concentrations the PCO efficiency on EG is negligible, however, at the same time, the amount of EG adsorbed

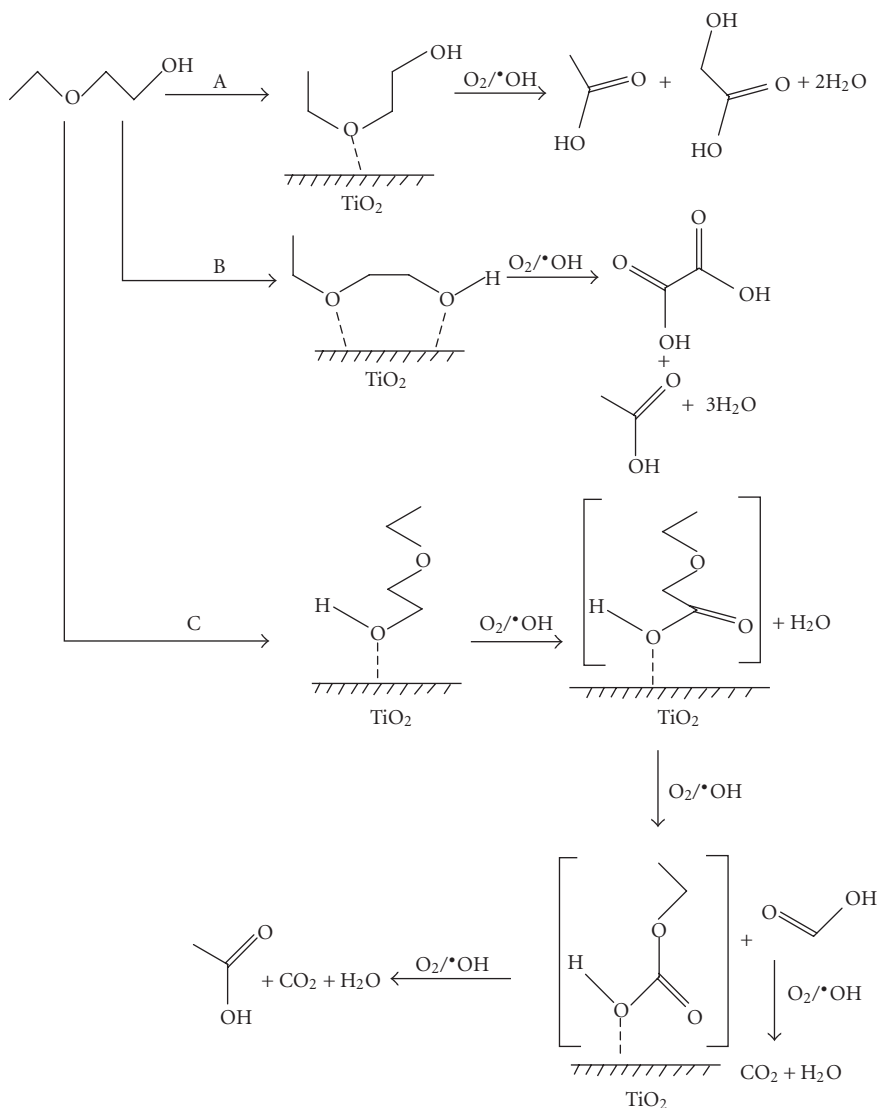


FIGURE 6: Outline of aqueous photocatalytic oxidation reaction of 2-ethoxy ethanol on  $\text{TiO}_2$ .

on the surface of titanium dioxide is significant. This contradiction may be explained by the “short circuit” phenomenon described in [4]: iron ions adsorbed in significant amounts scavenge the electrons at the  $\text{TiO}_2$  surface, and then are oxidised by the positively charged holes. The holes are therefore blocked by iron ions and the electrons keep circulating between iron ions and titanium dioxide. This way no pollutant oxidation can take place, regardless of its residual adsorption on the catalyst surface.

The adsorption of iron ions was of Langmuir type, reaching its maximum value at approximately  $34 \text{ mg L}^{-1} \text{ Fe}^{2+}$  (see Figure 5). One can see that all the efficiency changes under the experimental conditions take place at the surface concentration of iron ions growing with their concentration in the solution.

Alongside with adsorption mechanism clarification, the determination of PCO by-products allows to outline possible reaction pathways of the substances oxidised. The presence

of acetic and glycolic acids among the oxidation by-products indicates the adsorption of 2-EE with its ether oxygen and, therefore, electrophilic attack of positively charged holes to the ether bond (see Figure 6). This results in fracture of the 2-EE molecule into two fragments, the acetic and glycolic acids (reaction A). The formation of oxalic acid appears to be possible only when both oxygen atoms in the 2-EE molecules are adsorbed on the  $\text{TiO}_2$  surface and are under simultaneous attack of positively charged holes (reaction B). Acetic acid may also be a product of 2-EE stepwise oxidation starting from the alcohol group only (reaction C) with formic acid as a product of the last reaction. The ethoxy carbonic acids were not identified and were only shown as hypothetical by-products in rectangular brackets. It has been experimentally confirmed that glycolic acid cannot act as the precursor of oxalic acid; this circumstance brings the correction to the previously presented reaction pathway outline [23]. In presence of iron ions, the reaction may proceed only via



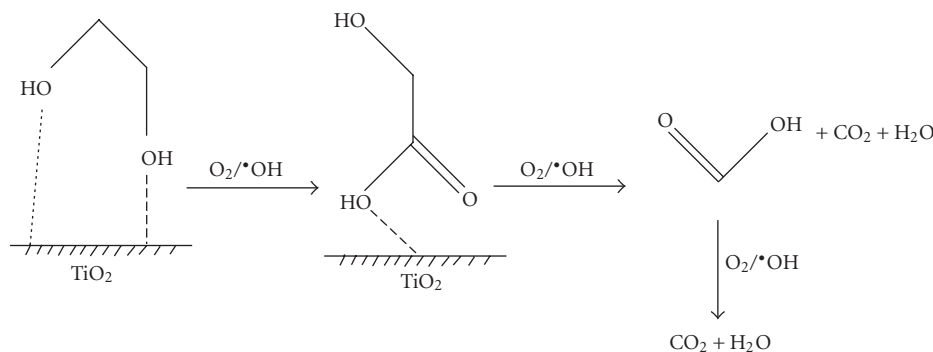


FIGURE 7: Outline of aqueous photocatalytic oxidation reaction of ethylene glycol on  $\text{TiO}_2$ .

the pathway C since formic and acetic acids were found, but neither glycolic nor oxalic acids were detected in the PCO-treated samples.

Further oxidation of reactive by-products, such as formic acid also observed in samples, may proceed with both positively charged holes and OH-radicals formed at the  $\text{TiO}_2$  surface, although their formation may be suppressed in acidic media. The OH-radical, although less reactive with 2-EE, may also participate in oxidation reactions initiated by positively charged holes at the  $\text{TiO}_2$  surface.

With DEGMME, adsorption of the molecule by any of the three oxygen atoms will eventually lead to the formation of glycolic and formic acids. Since no glycolic acid was observed in PCO samples in presence of iron species, no adsorption and, therefore, oxidation of ether groups took place. Formation of acetic acid was not observed as expected. Long-chain products, expected once the PCO starts fragmenting the DEGMME molecule with formation of formic acid, were not identified. Glycolic acid was presumably formed from the DEGMME molecule adsorbed with the oxygen of the ether bond in absence of iron ions.

The PCO on only one of the hydroxyl groups of EG leads to the formation of glycolic and formic acids (Figure 7). The dotted line on the figure shows the possibly weaker bond between one of the hydroxyl groups and the titanium dioxide surface, whereas the other hydroxyl group is connected to the catalyst by a shorter bond with higher energy. The addition of iron ions did not affect the composition of the PCO by-products: only glycolic and formic acids were observed with and without iron ionic species.

#### 4. CONCLUSIONS

The complicated influence of the addition of ferrous/ferric ions to the photocatalytic oxidation of the aqueous solutions of glycolic compounds, ethylene glycol (EG), 2-ethoxy ethanol (2-EE), and diethylene glycol monomethyl ether (DEGMME) was shown and explained. An optimum concentration range of ferrous ions for the highest PCO efficiency was observed.

The hypothesis of electron scavenging by iron ions of  $\text{TiO}_2$  surface with the increased PCO efficiency was proved.

It has been experimentally proven that the PCO efficiency optima are the result of the competitive absorption of the pollutants and iron ions on  $\text{TiO}_2$  photocatalyst surface: the PCO of EG, 2-EE, and DEGMME practically stopped when the adsorption sites at the  $\text{TiO}_2$  surface were blocked by iron ions.

#### ACKNOWLEDGMENTS

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