

LAPPEENRANTA UNIVERSITY OF TECHNOLOGY

Department of Chemical Technology

Laboratory of Chemical Engineering

**PHOTOCATALYTIC OXIDATION OF AQUEOUS SOLUTIONS OF JET
FUEL AND ICING INHIBITORS**

Master of Science Thesis

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Suihkumoottoripolttoaineen ja jäänestoaineiden vesiliuosten fotokatalyyttinen hapetus

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Tässä työssä on perehdytty jäänestoaineiden vesiliuosten ja suihkumoottoripolttoaineen vesiuutteen fotokatalyyttisen hapetuksen kokeelliseen tutkimukseen. Diplomityö käsittää johdannon, kirjallisuuskatsauksen, materiaalien ja menetelmien kuvauksen, tulosten tarkastelun ja johtopäätökset.

Kokeet tehtiin käyttämällä etyleeniglykolista ja 2-etoksietanolista valmistettuja vesiliuoksia sekä suihkumoottoripolttoaineen vesiuutetta. Titaanidioksidi valittiin fotokatalyytiksi.

Fotokatalyyttisen hapetuksen mekanismien selvittämiseksi tutkittiin kontaminanttien alkukonsentraation, pH:n ja mineraalilisäyksen vaikutus sekä tert-butanolin vaikutus OH-radikaalien sitojana. Fotokatalyyysi auringonvalossa tehtiin kahdella eri tavalla: katalyyysi titaanidioksidisuspensiolla tai käyttämällä huokoisia lasipartikkeleita, joihin on kiinnitetty TiO₂.

Hapetuksen tehokkuus arvioitiin määrittämällä kemiallisen hapenkulutuksen (COD) alenema ja mittaamalla glykolikonsentraatio.

Fotokatalyyttisen hapetusprosessin tehokkuuden oletettiin olevan riippuvainen titaanidioksidisuspension koostumuksesta. Tästä syystä tutkittiin orgaanisten lisäaineiden, pH:n ja sekoituksen vaikutus.

Mineraalit (Ca²⁺, Fe^{3+/2+}, Mn²⁺, SO₄²⁻) ovat usein läsnä luonnon ja jätevesien systeemeissä tai niitä muodostuu orgaanisten kontaminanttien hävittämisen yhteydessä. Niiden vaikutus jäänestoaineiden fotokatalyyttiseen hapetukseen tutkittiin.

ABSTRACT

Lappeenranta University of Technology
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Photocatalytical Oxidation of Aqueous Solutions of Jet Fuel And Icing Inhibitors

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The paper consists of 77 pages, 35 figures, 5 tables, 4 appendices.

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Keywords: De-icing agents, 2-ethoxyethanol, ethylene glycol, jet fuel, photocatalytical oxidation, titanium dioxide.

The present paper is devoted to the results of experimental research undertaken into photocatalytical oxidation (PCO) of aqueous solutions of de-icing agents and aqueous extract of jet fuel. The report consists of introduction, literature review, description of materials and methods, discussion of results and conclusions.

TiO₂ was selected as a photocatalyst for the experiments with synthetic solutions of ethylene glycol, 2-ethoxyethanol and aqueous extract of jet fuel.

To explain the PCO mechanisms affecting certain behaviour of de-icing agent under distinctive conditions, the following factors were studied: the impact of initial concentration of pollutant, the role of pH, the presence of tert-butanol as OH[•]-radicals scavenger and mineral admixtures. PCO under solar radiation performed in two ways: catalysed by irradiated TiO₂ slurry or by TiO₂ attached to buoyant hollow glass micro-spheres. Special attention was paid to the energy-saving PCO with reduced intensity mixing of the slurry.

The effect of PCO was assessed by determination of residual chemical oxygen demand of solution (COD) and by measuring of concentration of glycols.

The PCO process efficiency was assumed to be dependent on the TiO₂ suspension fractional composition. Thus, the following effects of solutions' media were viewed: presence of organic admixtures, pH influence, mixing mode during the PCO.

The effects of mineral admixtures - Ca²⁺, Fe^{3+/2+}, Mn²⁺, SO₄²⁻ - that are often present in natural and wastewater systems or produced during the degradation of organic pollutants and which can affect the rate of PCO of de-icing agents, were also investigated.

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1 INTRODUCTION

1.1 Problem Background

One of the most serious environmental problems in Estonia is pollution of soil and groundwater with fuel hydrocarbons. Improper handling of jet fuel at abandoned military base in Estonia has resulted in heavy pollution of the soil and groundwater (Metsur et al., 1998).

Large pollution site is the former Soviet military airbase founded in 1957 in the vicinity of Tapa, Estonia. Numerous spills of aviation fuel resulted in extensive groundwater pollution. As a result of the disposal of jet fuel into the soil at the airbase, the groundwater in this region is heavily polluted. Nowadays the polluted area occupies about 16 km². The amount of spilled jet fuel is estimated to be from 1000 to 10000 m³. The polluted groundwater stratum is from 91 to 109 m deep. Pollution has reached the wells of the potable supply of Tapa town and, therefore, groundwater from the upper water-bearing strata is not in use. Presently, water from lower strata – from 130 to 160 m – is supplied (Metsur et al., 1998). The contamination of soil and groundwater includes not only fuel. Being toxic compounds miscible with water and constituting up to 1% vol. of jet fuel (Papok, 1962), de-icing chemicals contribute significantly to the pollution.

Large amounts of de-icing agents are used at many airports during the wintertime as fuel icing inhibitors. De-icing agents, containing glycols, are also being increasingly used for removal of frost and ice from aircraft and airfield runways. This may result also in soil and groundwater contamination. Therefore, the contamination of groundwater with de-icing agents is an international problem.

Human safety is an overriding concern at airports, and, for example, Federal Aviation Administration (FAA) requires the use of de-icing chemicals to ensure passenger safety during winter operations. However, while FAA is increasing its de-icing requirements, environmental organisations are increasing pressure for stormwater requirements. Airports and airlines are caught in the middle, but several management

alternatives are available for controlling the impact of de-icing chemicals on stormwater while maintaining safe and economically viable air transportation (Mericas and Wagoner, 1994). Mericas and Wagoner (1994) and Switzenbaum et al. (2001) described the detailed organisation of airport's de-icing and anti-icing.

Airport de-icing systems may be represented by four major components:

- materials application,
- stormwater collection and conveyance,
- stormwater storage,
- stormwater treatment, recycling and disposal (Mericas and Wagoner, 1994).

Ethylene glycol and its derivatives are regularly used as vehicular anti-freezes and de-icing compounds. Over two million tons of ethylene glycol are manufactured for commercial use each year (McGahey and Bouwer, 1992).

Airport runoff that contains significant concentrations of de-icing materials normally cannot be discharged directly into the environment. Instead, the runoff must be contained and treated to reduce pollutants before releasing the water to the environment. Airfield drainage may subsequently contaminate surface waters, abstracted for portable purposes or ingested by field or domestic animals, with undesirable levels of glycols. Additionally, because these de-icers may be intentionally or accidentally released into aquatic ecosystems, the possibility exists for direct or indirect adverse effect on aquatic organisms. As a result, the control of de-icing runoff is now being mandated by national regulatory agencies (i.e., stormwater permitting) to protect both human health and the environment.

Extensive investigations have proved that wastewater containing diethylene glycol may cause severe disturbances in sewage treatment. The discharge of such wastewater into municipal sewage treatment plant may lead – especially in case of shock loads and during cold temperatures when treatment plants are sensitive to COD overloading – can create hazards to domestic animals and wildlife when impounded, degrade water quality due to its high chemical oxygen demand (COD), or add

excessive COD to municipal wastewater treatment plants (McGinnis et al., 2000). The latter, however, is not considered serious at the levels likely to be encountered in the surface waters.

Historically, the principal concern associated with de-icing runoff has been dissolved oxygen impacts due to elevated BOD concentrations. For example, the 5-day carbonaceous biochemical oxygen demand (CBOD₅) of ethylene glycol ranges from 400 000 to 800 000 mg/L. Untreated domestic wastewater CBOD₅ ranges from 200 to 300 mg/L (Mericas and Wagoner, 1994). Veltman et al. (1998) measured BOD₅ as high as 245 000 mg/L on airport runoff.

There are toxicity concerns associated with certain glycols and with de-icing and anti-icing fluid additives as well. The physiological effects of icing inhibitors are central nervous system stimulation followed by depression and kidney damage, irritation effects on skin, eyes and oral routes (Sax, 1984). The physical properties of kerosene as jet fuel and some glycols follow.

Kerosene, that is used as jet fuel, is a fraction of oil distillation with boiling point range from 175 to 325° C; yellowish to water-white oily liquid miscible with other petroleum solvents with its flash point at 65.6-85° C and auto-ignition temperature at 210° C. Density of kerosene is from 0.80 to 1.0 g/cm³. Kerosene is a mixture of petroleum hydrocarbons, chiefly of the methane series having from 6 to 10 carbon atoms per molecule (Sax, 1984).

Ethylene glycol (C₂H₆O₂) is a colourless, sweet-tasting, hydrophilic liquid with its boiling point at 197.5° C, freezing point at 13° C, flash point at 111.1° C and auto-ignition temperature at 235° C. Density of ethylene glycol is 1.113 g/cm³. It is soluble in water, alcohol, ether, and acetone. Ethylene glycol has moderate irritation effects on skin, eyes and oral routes. Lethal dose for man reported to be 100 ml. If ingested it caused initial central nervous system stimulation followed by depression. Later it causes kidney damage, which can terminate fatally. It is very toxic in particulate form upon inhalation (Sax, 1984).

2-ethoxyethanol (C₄H₁₀O₂) is a colourless, practically odourless liquid with its boiling point at 134-137° C, flash point at 94.4° C and auto-ignition temperature at 235° C. Density of 2-ethoxyethanol is 0.931 g/cm³. It is soluble in water, alcohol, ether and acetone (Sax, 1984). 2-Ethoxyethanol (cellosolve) is toxic. It may impair fertility and may cause harm to the unborn child. It is also flammable, harmful by inhalation, contact with skin and if swallowed. It has moderate irritation effects via dermal and oral routes. It has the same physiological effect as ethylene glycol. Animal experiments indicate that exposure to air saturated with cellosolve vapour (0.6%) for periods of 18 to 24 hours may produce congestion and edema of the lungs and congestion of the kidneys. Exposure of humans to the same concentration for a few seconds resulted in irritation of the eyes (Sax, 1984).

Table 1.1. Toxicity Data (Sax, 1984)

Compound	Oral-rat LD ₅₀ , mg/kg	Skin-rabbit LD ₅₀ , mg/kg	Oral-guinea pig LD ₅₀ , mg/kg
Ethylene glycol	8540	19530	6610
2-ethoxyethanol	3000	3500	1400

As a result of contamination during the last several years, acute and chronic toxicity impacts have also been documented at several large airports. It is believed that materials added ethylene glycol to prevent corrosion, improve fluid viscosity, and promote shear from aircraft during take-off are significantly more toxic than either glycol. The possibility of toxicity limitations is an additional concern for airports facing the issuance of a national pollutant discharge elimination system (NPDES) permit or renewal (Switzenbaum et al., 2001).

Airport's abatement strategies were discussed by Switzenbaum et al. (2001). In general, strategies to control de-icing impacts on stormwater vary from airport to airport.

At modern airports a large proportion of the mixture of de-icing agents and meltwater is recycled and reused. There are several alternatives for the treatment and disposal of

de-icing runoff. These alternatives are divided into three primary categories: off-site, on-site and recovery options. The off-site category consists of alternatives where the airports discharge stormwater into a collection system or pay for trucking to a treatment/disposal facility. The on-site category consists of aerobic and/or anaerobic treatment facilities that can be constructed at the airport for the pretreatment or treatment and disposal of the de-icing runoff. The recovery category utilizes filtration, reverse osmosis, and distillation to recover glycol from runoff, while there are a lot of disadvantages in application (Switzenbaum et al., 2001).

However, there is no appropriate treatment method for groundwater pollution. For example, investigations into various sewage treatment plants show that diethylene glycol was either almost completely or not at all biodegradable i.e. only special species of bacteria are able to use diethylene glycol in their metabolism (Evans and David, 1974).

Returning to the problem of groundwater contamination in Estonia, the only treatment work, applied to the Tapa airfield, was pumping of the free petroleum layer from the surface of water and soil. But all of water-soluble compounds remain in water and soil, including de-icing compounds. The problem for developing the appropriate purification method makes the investigations in this field essential.

1.2 Previously Acquired Knowledge

The present project continues the research, carried out by the author in 1999-2000 (Malygina, 2000). Main points of the research are outlined in the article (Krichevskaya et al., 2001).

The following conclusions were made in the course of the previous research:

- water, polluted with jet fuel and de-icing agents readily yields to PCO under artificial radiation;
- neutral medium is preferable for the process efficiency;

- Degussa P25 photocatalyst has shown better performance compared to Aldrich anatase;
- titanium dioxide attached to buoyant hollow glass micro-spheres shown lower photocatalytical activity than its slurry;
- under conditions of experiments in the present study the process efficiency increases with the concentration of pollutant;
- the biodegradability of aqueous solution of 2-ethoxyethanol increased with PCO proceeding;
- insignificant acceleration was observed as a result of H₂O₂ addition under acidic conditions.

Present project is dedicated to investigation of additional factors influencing PCO of aqueous solution of de-icing agents and jet fuel aqueous extract.

1.3 Objectives

One of the observations of the previous research was as follows: the role of •OH-radicals was found to be negligible in PCO of 2-ethoxyethanol and ethylene glycol as well as jet fuel aqueous extract. Poor mineralisation in the alkaline medium confirms an insignificant role of •OH-radicals in the oxidation. Simultaneously, the PCO efficiency of de-icing agents appeared to be dependent on pH.

The objective of the present research was to explain the PCO mechanisms affecting the certain behaviour of de-icing agent under distinctive conditions.

The experiments on the influence of initial concentration of pollutant, presence of tert-butanol as •OH-radicals scavenger and PCO under solar radiation were performed in two ways: PCO with the irradiated TiO₂ slurry and with TiO₂ attached to the buoyant hollow glass micro-spheres. The efficiency of PCO of aqueous solutions of de-icing agents and jet fuel aqueous extract were studied dependently on the mentioned factors. Special attention was paid to the energy-saving PCO with the reduced intensity mixing of the slurry.

The hypothesis of this research was the influence of the dispersion composition of suspension to the PCO efficiency. In other words, the PCO process efficiency was assumed to be dependent on the TiO₂ suspension fractional composition. Thus, the following effects of solutions' media on the TiO₂ catalyst properties were viewed:

- the pH influence on the fractional composition of TiO₂ catalyst slurry in aqueous medium;
- the pH influence on the fractional composition of TiO₂ catalyst slurry in aqueous solutions of de-icing agents;
- the pH influence on the fractional composition of TiO₂ catalyst slurry in aqueous solutions of PCO by-products of de-icing agents;
- the dependence of fraction composition of TiO₂ catalyst slurry on mixing mode during the PCO.

Among the other parameters it was necessary to realise the influence of different mineral admixtures on the rate of PCO of aqueous solutions of icing inhibitors. Mineral admixtures are often presented in natural and waste water systems or produced during the degradation of organic pollutants. Therefore, as the reaction proceeds, the increasing concentration of these anions may play a crucial role in the degradation of the parent compound.

2 LITERATURE REVIEW

2.1 Pollution Abatement Strategies

Abatement strategies for fuel hydrocarbons as water pollutants such as kerosene recovery, air stripping, steam distillation and microbial degradation are unlikely to be effective in the removal of icing inhibitors.

Recycling, biodegradation and UV/H₂O₂ systems have been proposed for treatment of wastes containing ethylene glycol. Regulatory requirements, economics and the

quality of recovered solutions currently limit recycling as a treatment method (Mericas and Wagoner, 1994).

There have been made some investigations to find the appropriate method for groundwater purification from glycols. Ethylene glycol has been shown to degrade in $\text{H}_2\text{O}_2/\text{UV}$ systems (Wang et al., 1992). Authors proposed that $\bullet\text{OH}$ -radicals produced by ultraviolet light (UV) absorbed by H_2O_2 is a system that will degrade ethylene glycol. However, the actual mechanism, by which ethylene glycol was mineralised, was not described. The requirement for $\bullet\text{OH}$ -radicals can only be presumed. $\text{H}_2\text{O}_2/\text{UV}$ systems require a relatively high doze of H_2O_2 and long UV-exposure time.

The use of $\bullet\text{OH}$ -radicals generating systems is of interest since they may be effective despite the combination of low temperatures and high ethylene glycol concentrations associated with de-icing waste. Other systems producing $\bullet\text{OH}$ -radicals include Fenton and photo Fenton reactions as summarized in equations (1) and (2) by McGinnis et al. (2000):



Authors discovered that the photo Fenton reaction has been shown to be very pH sensitive, a condition often explained as a dependence on specific iron species. The optimal pH was 3.0, with significant decreases in the degradation rates below 2.8 and above 3.2. Iron species such as the iron hydroxy complex $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$, the dominant monomeric ferric iron species at pH 2.5-5.0, have been shown to significantly adsorb light in the UV range and efficiently produce $\bullet\text{OH}$ -radicals (Faust and Hoigne, 1990). Analysis of possible intermediate products indicated that ethylene glycol was converted to formic acid with detectable amounts of acetic acid and glycoaldehyde occurring. Oxalic acid, glycolic, glyoxylic acid, acetaldehyde, ethanol, methanol and formaldehyde were not detected (McGinnis et al., 2000).

Despite the differences between the UV/ H_2O_2 and photo Fenton system, it was presumed that the reaction of $\bullet\text{OH}$ -radicals produced in both systems with ethylene

glycol would involve production of similar intermediate products. The intermediates detected by Leitner and Dore (1997) in both systems were consistent with the pathway described in Figure 2.1.1 and with previously described pathways for similar compounds.

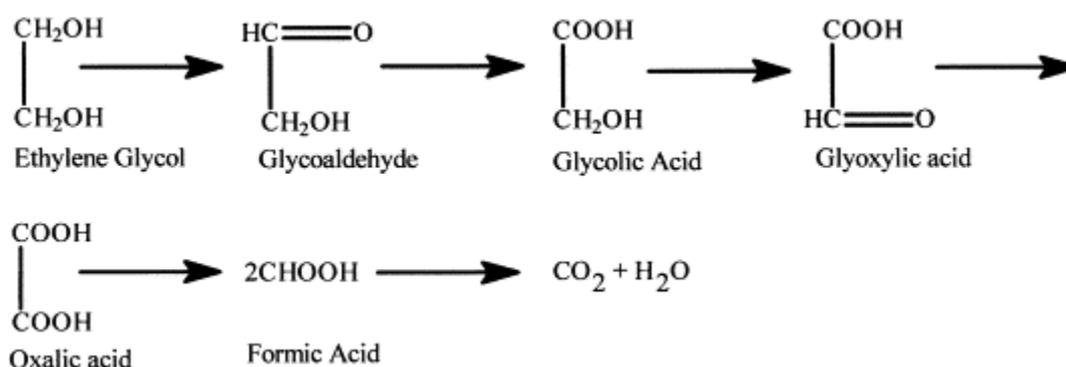


Fig. 2.1.1. Possible pathway for mineralisation of ethylene glycol in the UV/H₂O₂ system.

These results indicate a stepwise oxidation of ethylene glycol by reaction with •OH-radicals following the pathways suggested by Leitner and Dore (1997) for •OH-radicals attack of glycolic, glyoxylic and oxalic acid. The results of McGinnis et al. (2000) investigations show that in the UV/H₂O₂ system, nearly 75% of the TOC was lost compared to less than 10% in the equivalent photo Fenton system, suggesting increased mineralisation or loss of volatile intermediates. In the photo Fenton systems, the lack of oxalic acid demonstrates the importance of the formation and photodecomposition of ferrioxalate.

The results of the UV/H₂O₂ system indicate that TOC reduction in ethylene glycol solutions may be possible in the photo Fenton system if it is optimised to increase •OH-radicals production or to increase retention time. Accumulation of oxalic acid in the UV/H₂O₂ and not in the photo Fenton system indicates that the formation of ferrioxalate may be significant in the degradation of ethylene glycol intermediate products. The residual formic acid concentration found in the photo Fenton system can be reduced by •OH-radicals oxidation as demonstrated in the UV/H₂O₂ system. In addition, the results of Murphy et al. (1989) demonstrated mineralisation of formic

acid in Fenton systems with longer retention times and potentially higher •OH-radicals concentrations (McGinnis et al., 2000). Consequently, both of these methods have its drawbacks: require high dosage of •OH-radicals or long retention time.

The relatively high removal rates (McGahey and Bouwer, 1992; Union Carbide Chemicals, 1992) and low microbial toxicity (Kilroy et al., 1992) of ethylene glycol make biodegradation a possibility. The literature provides evidence that ethylene glycol can be biologically removed from solution by various adapted strains of bacteria, municipal wastewater treatment activated sludge and aerobic and anaerobic bacterial consortia.

On the other hand, the effects of environmental factors (substrate concentration, soil type, temperature, nutrient level) have to be taken into consideration. Soil and groundwater bacteria were shown to biodegrade ethylene glycol, and soil type was shown to significantly impact biodegradation rate. Investigations have shown consistently that ethylene glycol is rapidly biodegradable under a range of experimental conditions by a wide variety of inocula and can be biologically degraded to simple end-products: carbon dioxide, acetate and ethanol. Increasing substrate concentration was found to decrease the biodegradation rate. Increasing ethylene glycol concentration to 1000 ppm further lowered the rate constant (McGahey and Bouwer, 1992).

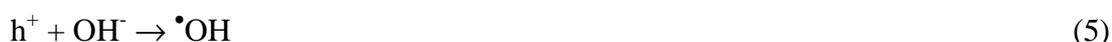
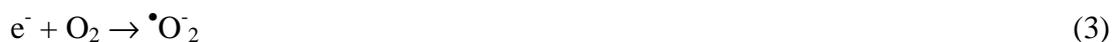
Despite of the advantages there have been observed a lot of drawbacks too. Temperature would be expected to have a direct relationship on biomass activity. Generally, this relationship takes from of a doubling of the metabolic rate for each 10 degree Celsius increase in temperature. Changing the microcosm temperature from 25 °C to 10 °C led to a decrease in the rate constant (McGahey and Bouwer, 1992).

Continuing the drawbacks, biological treatment of used de-icing solutions can be limited by high concentrations, 5% is typical, of ethylene glycol in de-icing waste streams (Mericas and Wagoner, 1994) and microbial inhibition due to low temperatures associated with de-icing (Evans and David, 1974). This method seems to be inefficient for groundwater treatment.

At the same time, the method of photocatalytical oxidation (PCO) gives the unique possibility to use so powerful and cheap energy source like solar radiation. This makes investigations in this treatment method very attractive.

2.2 Photocatalytic Oxidation of Organic Compounds

The process of PCO is initiated by the photogeneration of hole/electron pairs in the semiconductor valence and conduction bands, respectively, upon adsorption of UV light with energy equal to or higher than the corresponding band gap (>3.2 eV). Energized electrons and holes may either recombine, dissipating energy, or be available for redox reactions with electron donor or acceptor species adsorbed on the semiconductor surface or being nearby in the electrical double layer surrounding the particle (Pozzo et al., 1997).



If these charge carriers reach the catalyst surface before recombination, they can be used for chemical reactions, i.e., for oxidation or reduction of pollutants (Dillert et al., 1999).

Holes possess extremely positive oxidation potential and should thus be able to oxidise almost all chemicals, even toxic ones. Even the one-electron oxidation of water resulting in the formation of hydroxyl radicals should be energetically feasible:



It is generally accepted that the primary steps initiating the subsequent degradation processes are the formation, by hole trapping, of extremely reactive radicals (such as $\bullet\text{OH}$), in the highly hydroxylated semiconductor surface, and/or the direct oxidation of the pollutant species. Charge balance would be sustained by electron consumption via reduction of adsorbed oxygen species derived from dissolved molecular oxygen, or other electron acceptors (Pozzo et al., 1997).

Wavelengths shorter than 400 nm are essential for the excitation of TiO_2 , at present the most suitable semiconducting material for photocatalysis (Dillert et al., 1999). Its use as a catalyst support or as a catalyst and photocatalyst itself is well known. Titanium dioxide acts not only as a catalyst support, but also interacts with the supported phase as a promoter (Martin et al., 1995).

Titanium dioxide generally exhibits the highest photocatalytic activity amongst metal oxides. The anatase modification of titanium dioxide shows much higher photocatalytic activity than the rutile form, which has been explained by a faster recombination of charge carriers in rutile and also by a considerably lower amount of reactants adsorbed on the surface of a rutile particle. Adsorption of the toxic molecules onto the catalyst particle is a prerequisite for a highly efficient detoxification (Bahnemann et al., 1991).

Titanium dioxide (anatase) has an energy bandgap of 3.2 eV and can be activated by UV illumination with a wavelength up to 387.5 nm. At the ground level, solar irradiation starts at a wavelength of about 300 nm. Therefore only 4-5% of the solar energy reaching the surface of the earth could in principle be utilised as direct and diffused components when TiO_2 is used as photocatalyst. Solar irradiation is capable of mineralising organic compounds under a wide range of weather conditions with various irradiance numbers (Zhang et al., 1994).

The surface chemistry of titanium dioxide immersed in aqueous solutions can be rationalized in terms of the surface complexation approach. In this description, partially hydrated surface titanium ions interact with dissolved solutes, in a way that resembles solution chemistry. Thus, surface OH groups, formed upon dissociative

chemisorption of water molecules, undergo protonation-deprotonation reactions, for example



and adsorbing ligands form outer- and/or inner-sphere surface complexes.



Weisz et al. (2001) describe these surface equilibria by mass-action-law constants (for a more sophisticated description of the surface complexes). While outer-sphere surface complexation is essentially electrostatic, inner-sphere complexation is driven chemically.

There are many factors, influencing PCO efficiency. pH has a dominant effect on the photocatalytic reaction because many properties, such as the semiconductor's surface state, the flat-band potential, the dissociation of organic contaminant, are all strongly pH dependent.

Solution matrix can influence the photocatalytic reaction rate of a particular compound in several ways. A change in pH causes a shift in the Fermi level of the semiconductor so that the photocatalyst becomes a better oxidant with decreasing pH. Solution matrix parameters such as pH and ionic strength determine speciation and subsequent chemical behaviour of dissolved components, strongly influencing the photocatalyst surface charge and affecting the sorption of ionic compounds (Schmelling et al., 1997).

The precise mechanism of photocatalytical oxidation over UV irradiated titanium dioxide is supposed to be very complicated and electrochemical methods are required to analyse the band energy shift on TiO₂. In addition, Nishida and Ohgaki (1994) proposed to continue investigation of the following problems:

- 1) electric and ionic profile of the catalyst and the substrate;
- 2) reactivity of various substrates with radicals;
- 3) features of the change in pH value through the reaction;
- 4) influence of ionic intermediates.

Investigating factors that influence PCO, Zhang et al. (1994) reported an interesting observation: the catalytic effect of the slurry depends on the preparation method, catalyst type and dosage. Three methods for preparing concentrated slurry were compared to each other: without sonication, sonication with common laboratory sonicating bath, and sonication with sonic dismemberator. The last one gave the best degradation results.

In principle, photocatalysts can be employed either as finely divided powders suspended (slurried) in the aqueous media or immobilized on a suitable support material (quartz sand, glass, silica gel, optical fibers, alumina clays, ceramics), operating in either fixed or fluidised bed configurations. According to various reports, mainly from laboratory scale investigations, slurry type reactors seem to be more efficient than those based on immobilized catalyst (Pozzo et al., 1997). From an engineering point of view the second alternative is preferable, so as to avoid costly particle-fluid separation stages downstream. Also, because of the small particle size of catalyst powders usually synthesised by in industry (somewhere between 30 and 300 nm in diameter), the operating costs of this downstream operation may become prohibitive, thus invalidating the energy saving of these decontaminating processes altogether (Pozzo et al., 1999).

It was observed that excess catalyst, suspended in the aqueous solution, could cause a shielding effect on the light. The optimum range of the catalyst concentration for the photocatalytic reaction is about 1 - 3 g/L depending on types of reactor and TiO₂ powders (Way and Wan, 1991, Tseng Huang, 1990). However, for the very concentrated solutions, “suspended solution”, the concentration of the catalyst of 200 g/L was found effective (Hidaka et al., 1992).

To ensure efficient conversion of incident photons to charge carriers, the appropriate design of a solar reactor is of utmost importance. For example, it has been reported that light concentrating systems, such as parabolic-trough reactors, do not necessarily exhibit advantages over non-light concentration systems. It is known that in the wavelength range of the solar spectrum that can be used for the excitation of TiO_2 , the diffuse and direct portion of the solar radiation reaching the surface of the earth are almost equal. This means that a light concentrating system cannot employ much more than half of the solar radiation available for catalyst activation. Moreover, even under the most favourable operating conditions for a parabolic-trough reactor, its solar radiation collection efficiency cannot be larger than 70% of that corresponding to a flat-plate reactor of the same photon harvesting area (Dillert et al., 1999).

Photocatalytic oxidation of aqueous solutions of hazardous organic compounds may be carried out using either artificial UV-irradiation or solar radiation. As an example of photocatalytic reactor with artificial UV source photoreactor, fabricated by Nulite (Al-Ekabi et al., 1990) can be presented. This reactor is comprised of a stainless steel jacket, a lamp and a photocatalytic sleeve. The lamp emits ultraviolet light in the 300-400 nm range and is mounted coaxially within the jacket. Around the lamp lies a sleeve formed of fibreglass mesh that is coated with titanium dioxide. Contaminated water flows through the fibreglass mesh parallel with the lamp.

There has been great interest in developing solar photocatalytic oxidation facilities for commercial applications. Some authors have utilised solar concentrators to photocatalytically destroy contaminants in water. However, the prohibitive cost associated with solar concentrators limits their potential for industrial applications when compared against competing wastewater treatment technologies.

In contrast, non-concentrating reactors have the potential for low cost development. Additionally, concentrating reactors make use only of the direct component of the UV solar radiation, while non-concentrating reactors utilise both the direct and diffuse components. The diffuse component of UV radiation in some climatic regions can be as much as, or in some cases even greater than, the direct component (Wyness et al.,

1994). Since water vapour does not absorb UV radiation, non-concentrating reactors may also be used during cloudy atmospheric conditions.

Three different types of non-concentrating photoreactors have been fabricated and tested over a range operating conditions (Wyness et al., 1994; Klausner and Goswami, 1995):

- flat-plate reactor;
- shallow pond reactor;
- tubular reactor.

It has been demonstrated that the three non-concentrating reactors demonstrate satisfactory performance in solar photocatalytic oxidation facilities when tested over a wide range of operating conditions. The following guidelines should prove useful for selecting a suitable reactor design for a given application:

- on a volumetric basis, shallow pond reactors are the least expensive to manufacture. The shallow pond reactor design is only useful for destroying non-volatile organic compounds since its surface is open to the atmosphere. However, it should be possible to cover the reactors with a thin Kynar sheet so, that reactors may also be useful for treating volatile compounds.
- when considering enclosed reactors in a large scale facility, the tubular design is preferable to the trickle reactor design since the tubular reactors may be connected in series without requiring a pump between each reactor (Klausner and Goswami, 1995).

Dillert et al. (1999) described a new design of reactor. Double-skin sheet reactor (DSSR) consists of a flat and transparent structured box made of polymethylmethacrylate. The suspension containing the pollutant(s) and the photocatalyst is pumped through a meandering channel inside the reactor. Once the degradation process is completed, the suspended photocatalyst has to be removed

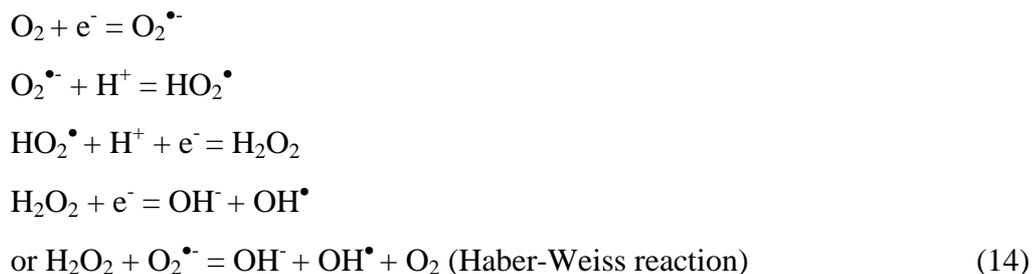
from the liquid. This type of reactor can utilize both the direct and the diffuse portion of the solar radiation.

Returning back to factors, influencing PCO, the penetration length of light in the solid-liquid medium is another important parameter, which is a function of particle size, catalyst charge (slurry concentration in one case, support surface coverage in the other) and support transparency to radiation, among other variables. Actually, given the complexity of the photocatalytic process, and the multiplicity of variables involved it is not an easy task to carry out an effective variable control and to find a common ground for comparison of supported vs. unsupported catalyst performances (Pozzo et al., 1997).

The efficiency of PCO was found to depend on irradiation intensity. The incident radiation intensity (irradiance) is measured usually in Einstein/s (moles of photons/s) or power units, e.g. mW, per area unit, e.g. m^2 or cm^2 . Investigations utilising concentrated solar radiation often operate with “suns” as units of irradiance.

Bahnemann et al. (1991) reported that at low fluxes of radiation (less than 1 sun) a linear dependence of the reaction rate on the illumination intensity is expected. Often, yields of reaction products are found to increase with the square root of the increasing illumination intensity. The described square root law is valid in an intermediate regime. The square-root dependency between reaction rate and light intensity was explained by a competition between the oxidation of the pollutant molecule and the combination of charge carriers generated by the subsequent absorption of two photons by a single semiconductor particle.

The authors who investigated the problem noticed that there is a difference between oxidation efficiencies in the presence and in the absence of dissolved oxygen. In the absence of oxygen practically no oxidation is observed. That phenomenon is explained by the role of oxygen as an electron scavenger which prevents the recombination reaction between surface species - holes and electrons - and, additionally, by the role of oxygen in the OH^\bullet -radicals generation:



Klausner and Goswami (1995) also found that there is no need to bubble the air through the reaction mixture, the performance does not depend on aeration. The absorption of oxygen by the surface of solution is sufficient for photooxidation. It means that the absorption of oxygen by the liquid phase is not the stage limiting the process rate.

The influence of temperature on PCO efficiency was found to depend on the compound. The temperature dependence of a photocatalytic degradation process was examined in case of chloroform in the range of 15 - 75°C at two different, relatively low light intensities. A decrease of the detoxification rate with increasing temperature is observed which is especially pronounced at the higher illumination intensity. This result is at the first sight in contradiction with other results reported in literature (salicylic acid and phenol showed an increase in the rate of oxidation with increasing temperature) (Bahnemann et al., 1991).

In contrast, the values of photooxidation rates of organochlorine compounds were found independent on temperature in the range from 20 to 50°C. This may be explained, according to Koster et al., by the decrease of the organochlorines adsorption on the titania particles with increasing temperature and the reaction rate.

The important question in the study of heterogeneous photooxidation mechanism is the role of the organics adsorption on the surface of titanium dioxide particles. The important role of adsorption may be illustrated by the following examples. Photodegradation of surfactants significantly depends on their ionic character. So anionic surfactants yield better to photooxidation on the titanium dioxide surface than non-ionic. Cationic surfactants show the lowest oxidisability (Hidaka et al., 1992).

Consequently, a photocatalysed degradation technique with titanium dioxide is one of the most remarkable ways for treatment of wastewater containing organic contaminants owing to a complete mineralisation of the organic contaminants under the mild conditions such as ambient temperature and ambient pressure.

From the practical viewpoint, the identification of the intermediate products of the photocatalytic degradation of organic pollutants is clearly essential, since generally the treatment cannot be carried out to the total mineralisation in a cost-effective manner. These identifications are also of great interest for a better understanding of the reactions that are involved in photocatalysis (Pichat, 1997). Most of the time, intermediates are degraded as fast as or even faster than the original pollutant, since they are already transformed en route to mineralisation.

In the course of mineralisation of any organic contaminant, oxidation will logically involve a series of intermediates of progressively higher oxygen-to-carbon ratios on the way to CO₂. Such intermediates make the conversion process multicomponent, even if only a single contaminant exists in the feed. Hence demonstration of the formation and elimination of intermediates also is important for showing complete removal of undesirable compounds (Ollis et al., 1991).

However, isolation and, therefore, identification of intermediates beyond ring opening up to CO₂ formation is very difficult due to the nature of these intermediates (hydroxylated acids are probably formed) and their low concentrations. The overall picture is that the organic pollutants undergo oxidation with or without cleavages (including ring openings), substitutions by hydroxyl groups, deprotonations, and decarboxylations. These photocatalytic transformations can obviously be accompanied by hydrolysis reactions at each stage. As a result, intermediate products can include phenol, alcohol, aldehyde, ketone, amide and acid functionalities (Pichat, 1997).

2.3 Properties of TiO₂ Catalyst in Aqueous Suspensions

The stability and rheological behaviour of dilute and concentrated dispersions of TiO₂ powders in aqueous solution have been investigated by many researches. Due to the conditions of the production process, the titanium dioxide powders are very fine with an average primary particle size of about 21nm. However, in aqueous media the particles form aggregates within the micron range.

An important factor influencing the stability of aqueous dispersions is the surface potential of the particles. The repulsive interaction between electrical double layers around the particles hinders the particles from agglomeration, endowing the dispersion a certain degree of stability (Turian et al., 1997 and Chen et al., 1998). Gösele (1995) confirmed that in this range of particle size solid-liquid separation is influenced by interfacial effects of the aggregates rather than by the size of the primary particles. The change of electrostatic repulsive and van der Waals attractive interactions between particles may result in the flocculation of the particles and lead to a formation of flocks and produce a good separation.

Therefore, the classical solid-liquid separation processes, such as sedimentation, flotation and filtration may in principle find application in the separation of submicron TiO₂ particles from a liquid if the controlling parameters such as pH-value, solid concentration, ionic strength, etc., which determine the coagulation/flocculation state of TiO₂ particles are optimised (Xi and Geissen, 2001).

Being an oxide, TiO₂ has H⁺ and OH⁻ ions as its potential determining ions, and hence the pH of aqueous medium has a substantial effect on the stability of aqueous dispersion of TiO₂ powders (Chen et al., 1998). Stability of the TiO₂ dispersions shows a minimum at their isoelectric point, and, correspondingly, the viscosity at infinite shear rate and the yield value of the concentrated TiO₂ dispersion reach their maximum at about the same pH. Either increasing or decreasing the pH will result in the enhancement of the stability of the TiO₂ dispersion, and, concomitantly, a decrease in the viscosity and yield value of the concentrated TiO₂ dispersion.

A literature survey reveals that the isoelectric point reported for TiO₂ varies from pH 4.0 to 6.1. The isoelectric point is the pH at which the electrophoretic mobility is

zero, which occurs when there is no net surface charge on the colloidal particle. The electrophoretic mobility parameter, which is a measure of the velocity of a charged particle in an electric field, is dependent on the ionic strength, the presence of the dispersant, and the presence of an inorganic coating on the TiO₂ particles (Mikulasek et al., 1997). As a result, the adsorption is the largest at the same pH, therefore, the PCO efficiency should be the highest. Since impurities are difficult to eliminate completely it is common to find a range in the isoelectric point quoted for the same material in literature. At pH below the isoelectric point, the surface charge for most metallic oxides, including titania, is positive which is attributed to the protonation of the surface hydroxyl group.

The confirmation of the above mentioned statement one can see on Fig. 2.3.1. It can be seen that the dispersion is most unstable at pH around 4. Either increasing or decreasing pH will lead to the improvement of the stability of TiO₂ (Tianjin Chemical) dispersions.

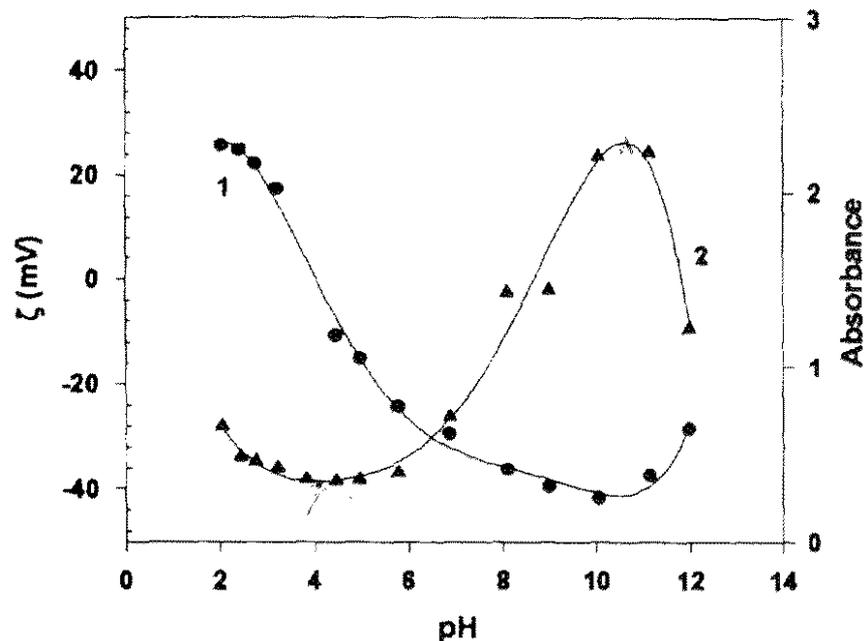


Figure 2.3.1 Stability and zeta potential of dilute aqueous TiO₂ dispersion. 1. Zeta potential; 2. Absorbance.

The corresponding zeta potential-pH curve in Fig. 2.3.1 indicates that the isoelectric point of TiO₂ particles is about 4 and either increasing or decreasing pH will enhance

the absolute value of the zeta potential, demonstrating that the electrostatic stabilization is the essential factor stabilizing the aqueous dispersion of TiO₂ powders. The absolute value of the negative zeta potential of TiO₂ particles again decreases at high pH (pH>11) and leads to a corresponding deterioration in the stability of TiO₂ dispersion. This may be a consequence of the surface charge density on the particle surface no longer increasing as the pH increases to a high pH range since the ionisation of the particle surface has reached a saturation, but the double electrical layers around the particles are depressed due to the concomitant increase of the electrolyte concentration with the increasing pH, eventually resulting in the decrease of the zeta potential and dispersion stability (Chen et al., 1998).

Other investigations of TiO₂ catalyst properties in aqueous suspensions were made by Mikulasek et al. (1997). Observations showed that a change in the particle size (fraction composition) leads for titanium dioxide dispersions to totally different rheological behaviour, that is, the effects of moving from an electrostatically stabilized to a sterically stabilized dispersion. The addition of surfactant into the solution and increasing the pH level caused an increase in ionic strength of the system.

The titanium dioxide used in experiments was rutile supplied by Tioxide Group LTD., England.

The results in Fig. 2.3.2 show that the dispersions are shear-thinning and are characterized by non-linear flow curves that converge at low shear rate to the yield stress of the dispersion. The position of the shear-thinning flow curves is pH-dependent. This is due to the different degrees of flocculation in the dispersion at different pH. The high shear stress behaviour at extremely high pH (pH13), as observed in Fig. 2.3.2, may be explained by the fact that the high ionic strength of the system (due to NaOH addition) can lead to a reduction of the electrical double layer thickness, and flocculation reoccurs due to van der Waals forces (Mikulasek et al., 1997).

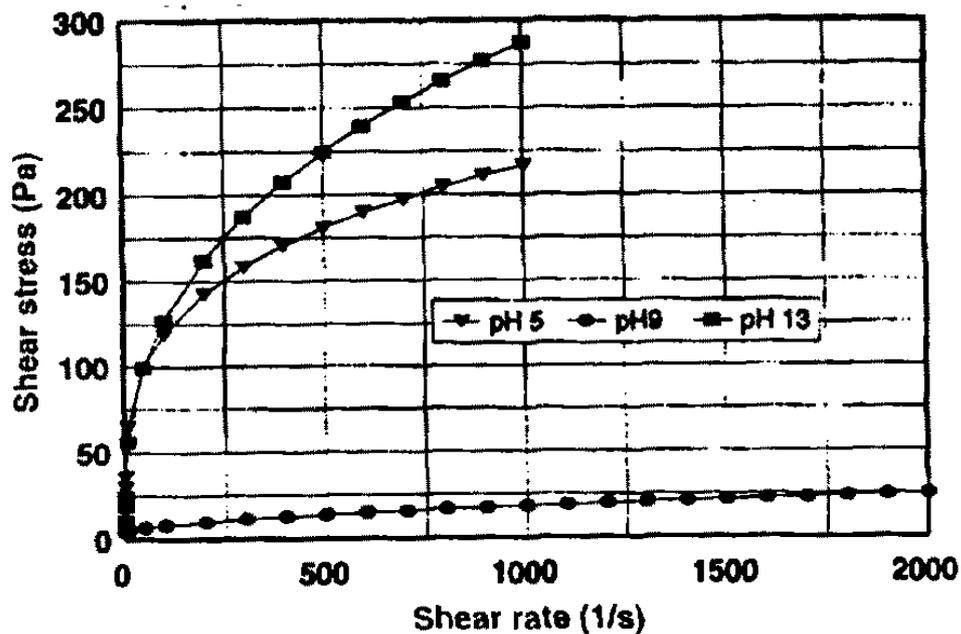


Figure 2.3.2. Effect of pH on the flow properties of 30 vol% titanium dioxide dispersions at temperature 20 °C.

According to Mikulasek et al. (1997) the isoelectric point is at pH 4.2 for TiO₂ particles.

Turian et al. (1997) have compared the properties, the settling rate and rheological behaviour of concentrated aqueous slurries of titanium dioxide, laterite, gypsum and silica flour. The results showed that titanium dioxide suspension needs approximately ten times bigger period to settle till the same volume, like other investigated suspensions (Fig. 2.3.3).

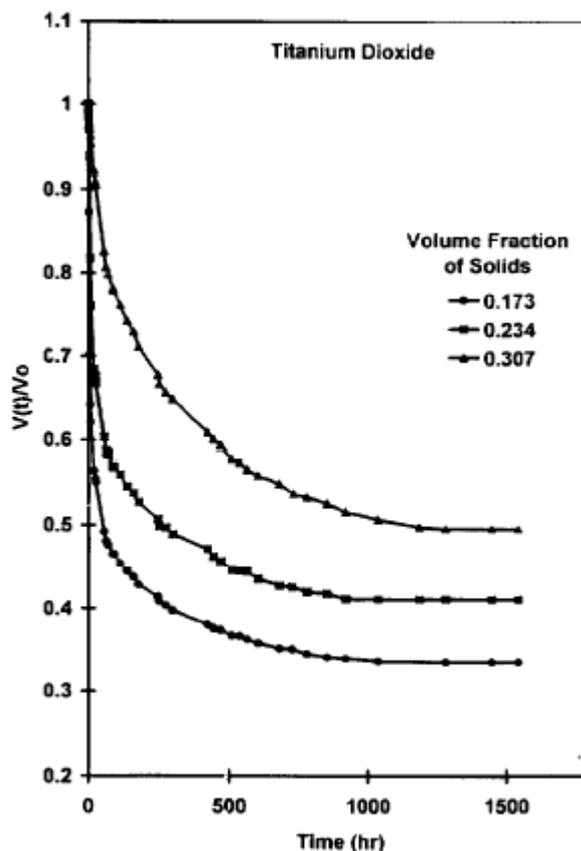


Fig. 2.3.3. Settling-rate curves for titanium dioxide – effect of particle concentration.

When compared with the maximum packing concentration it was observed, according to Turian et al. (1997), that the titanium dioxide suspensions, once destabilized, tend to form compact sediments on separation. The titanium dioxide suspensions, before dilution, had been stabilized through addition of polymers to effect steric stabilization. The stability behaviour of these industrial suspensions is clearly quite complex.

For titanium dioxide and gypsum suspensions exponent in hindered settling behaviour was higher than that for spherical particles. The higher value of the exponent is an indication of strong interparticle interaction effects. The results of yield stress measurements showed, that for low concentrations the yield stress increases slowly first and then very rapidly with the increasing concentration of solids. Aside from concentration, the yield stress also depends on suspension chemistry (pH) (Turian et al., 1997).

The results of investigations made by Turian et al. (1997) for titanium dioxide seem anomalous: the sediment value is higher than the maximum packing obtained by centrifugation. However, this slurry was obtained as a sterically stabilized suspension using polymeric additives. The polymeric coating over the particles evidently wears off if the suspensions are stored for long periods in high-temperature environments. A broad particle size distribution leads to enhanced particle interactions and, therefore, enhanced hindrance of the particle settling rate. The results for titanium dioxide particles do not lend themselves to any obvious inference about shape. This is perhaps due to the particle aggregation, which tends to invalidate the applicability of the hindered settling correlations, which are strictly applicable to monodispersed systems.

Kagaya et al. (1999), Bhattacharya et al. (1995), Xi and Geissen (2001), Koliadima and Karaiskakis (1990), Geissen et al. (2001) and Cardot et al. (2001) described methods, used for catalyst sedimentation.

The future application of photocatalysis is very strongly depending on the specific treatment costs. As an example, Xi and Geissen (2001) calculated that specific treatment costs of less than 1 to 2 US \$ m⁻³ should be aimed at for the posttreatment and reuse of wastewater.

2.4 The Influence of Mineral Additives

PCO process rate is quite slow and its acceleration represents a challenge. Therefore, among the other parameters, it is necessary to realize the influence of different ions on the rate of PCO. The following ions, which can affect the rate of PCO, are the subjects of interest: Ca²⁺, Mg²⁺, Mn^{2+/x+}, Cu^{+/2+}, Fe^{2+/3+}, NH₄⁺; HCO₃⁻, Cl⁻, NO₃⁻ and SO₄²⁻. As it follows from the different literature sources, different ions affect the rate of PCO of different model solutions differently.

4.2.1 Effect of Cations

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 wastewaters already before the purification process and is necessary to know what influence the metal ions has on the degradation of pollutants.

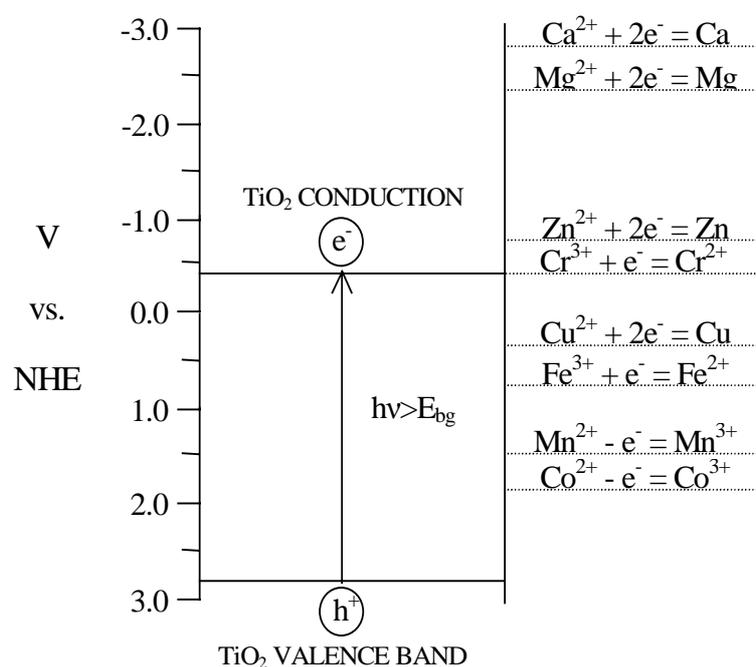


Figure. 2.4.1. Schematic illustration of valence and conduction band potentials in TiO₂ (anatase) at pH=7 with the corresponding photochemical generation of reduction sites (e^-) and oxidation sites (h^+) along with the standard reduction potentials of metal ions

In the presence of metal ions M^{n+} the photogenerated electrons and holes may be involved in the surface reduction and oxidation processes (Butler and Davis, 1993).



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 TiO₂ as schematically depicted in Figure 2.4.1.

The reduction of metal cations can result in the photodeposition of metal on TiO₂ surface, which can significantly change the surface properties (Herrmann et al., 1993). Both cation species Mⁿ⁺ and M⁽ⁿ⁻¹⁾⁺ may be also dissolved in water (e.g. Fe³⁺/Fe²⁺, Co³⁺/Co²⁺, Mn³⁺/Mn²⁺), and their reaction with generated hydrogen peroxide (Butler and Davis, 1993) and surface peroxidic groups via the Fenton reaction, represents the additional source of hydroxyl radicals:



Effect of Mn^{2+/x+}

The influence of Mn ion on the PCO is questionable: there are data on improving the performance of PCO by adding manganese, while others showed its detrimental effect. Chen et al. (1999) write that the experimental results indicate that dissolved manganese ions can increase the rate of chlorophenols oxidation in the TiO₂ photocatalytic system; however, it did not conspicuously increase the mineralisation rate of chlorophenols. Manganese ions enhance the oxidation rate by surface reaction increasing photo-generated electrons, holes and inhibiting electron/hole recombination. Increase of oxidation rate of chlorophenols in the presence of manganese ions could also be explained by the photo-Fenton-reaction. This complex reaction increases the hydroxyl radical production with thermodynamic consideration because at low pH it is favoured in increasing the formation of hydroxyl radicals.

However, Brezova et al. (1995) found out that the effect of Mn²⁺ and Co²⁺ on the phenol degradation rate is detrimental. The rate of phenol degradation in irradiated TiO₂ suspensions may be well explained by the electron transfer from metal ions to the photogenerated holes (16) in the valence band (Figure 2.4.1). This process probably decreases the yield of hydroxyl radicals' production resulting in the lower phenol degradation rate in these systems.

Effect of Ca^{2+} and Mg^{2+}

The presence of Ca^{2+} , Mg^{2+} had no influence on the phenol degradation rate according to Brezova (1995): 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. 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.

However Preis et al. (2002) reported that the minor COD reduction occurred as a result of the addition of CaO at any stage of phenolic compounds oxidation when pollutants were treated under alkaline conditions. For example, addition of CaO to samples of 5-methylresorcinol (5-MR) solution with initial concentration of 200 mg/L PCO-treated under pH 12 for 48 h reduced COD for 8%. On the other hand, under acidic conditions oxidation by-products readily removable with calcium ions were formed: COD of photocatalytically oxidised solutions decreased noticeably as a result of the addition of CaO. For example, reduction of COD for described 5-MR solution was 10 and 6% under pH 3 and 5 respectively. No more than 3 % of COD reduction was observed as a result of addition of CaO to the solutions of 5-MR and 2,4-xylydine treated by PCO in the presence of hydrogen peroxide, a generator of $\bullet\text{OH}$ radicals, under any pH tested.

Effect of Cu^{2+}

The Cu^{2+} ion has the different influence on PCO of different model solution. For example, Hua et al. (1995) reported that the behaviour of Cu^{2+} ions was shown to have different effects on the photocatalytic degradation of monochrotophos (MCP). It depends on the concentration of Cu^{2+} ion added during the reaction. At low concentrations ($< 10^{-5}$ M) an enhancement in the degradation was found. This finding is in agreement with the previous works. Authors have reported the promotion of photocatalytic oxidation of organics by the inclusion of Cu^{2+} ion in the test solution.

The enhancement was proposed to occur via the trapping of photogenerated electrons in the TiO₂ by the Cu²⁺, thereby reducing the extent of deleterious electron-hole recombination.

Whilst this explanation seems to explain the enhancement at low copper ion concentrations but it does not account for the curious effect observed when the concentration of Cu²⁺ is greater than 10⁻⁵ M. At higher Cu²⁺ concentrations, a dramatic lowering of the rate of degradation was observed. Here, a reduction in photocatalytic degradation of MCP was observed. Similar observations were found for phenol and 4-chlorophenol where the crossover point for the two effects occurred at 10⁻⁴ M. A plausible explanation for this phenomenon may be due to the short-circuiting mechanism of the coupled reaction, which occurs only at Cu²⁺ concentration above a certain level. The coupled reaction is shown below as



On the other hand Brezova et al. (1995) have got such results in which the dissolved Cu²⁺ ions (concentration of 0.28-1.1 mM) significantly hindered the phenol degradation in the irradiated TiO₂ suspensions. The inhibition effect of Cu²⁺ on phenol decomposition is important for Cu²⁺ concentrations higher than 1 mM, where the photo-deposition of copper species on TiO₂ surface is evident.

Effect of Fe^{3+/2+}

Brezova et al. (1995) found out that the highest efficiency of PCO of phenols was observed in the presence of ferric ions: the addition of Fe³⁺ ions in the oxygen-saturated TiO₂ suspensions caused the significant decrease of phenol half-times. The lowest half-time (5.8 min) was achieved for Fe³⁺ concentration of 0.57 mM. Further increase of dissolved Fe³⁺ did not improve the rate of phenol degradation. During irradiation of photocatalytic TiO₂ systems with added ferric ions the formation of Fe²⁺ ions was confirmed.

The presence of redox couple $\text{Fe}^{3+}/\text{Fe}^{2+}$ in TiO_2 suspension strongly influences the reaction of the generated hydrogen peroxide and surface peroxidic groups. The reaction of Fe^{2+} with hydrogen peroxide (17) represents a supplementary source of hydroxyl radicals (Butler and Davis, 1993) 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 peroxy titanium species by the competitive reaction of photogenerated electrons with Fe^{3+} ions, thus the phenol half-times became higher (Brezova et al., 1995).

In the irradiated homogeneous aqueous solution of Fe^{3+} ions, the hydroxyl radicals are formed according to the mechanism ascribed by equation (17) and (20)



and the generated hydroxyl radicals cause the degradation of phenol molecule (Brezova et al., 1995).

Sclafani et al. (1991) also investigated the influence of Fe^{3+} , Fe^{2+} and Ag^+ on phenol photodegradation performed in aqueous polycrystalline TiO_2 (anatase) and TiO_2 (rutile) dispersions. These ions can react very easily with peroxy species produced on the catalyst surface and/or in the solution. Maximum photoactivity was observed for TiO_2 (anatase) in the presence of oxygen and $[\text{Fe}^{3+}] = 5 \times 10^{-4}$ M. The behaviour of Fe^{2+} was similar to Fe^{3+} for the same experimental conditions.

4.2.2 Effect of Anions

One of the strategies for inhibiting e^-/h^+ recombination is to add irreversible electron acceptors to the reaction. In many highly toxic wastewaters where degradation of organic pollutants is the major concern, the addition of an inorganic anion to enhance the organic degradation rate may be justified. For better results, these additives should fulfil the following criteria: dissociate into harmless by-products and lead to the formation of $\bullet\text{OH}$ or other oxidising agents (Malato et al., 1999). Mineralisation rates

may be greatly diminished if the anion either adsorbs strongly to the photocatalyst surface or is an effective hydroxyl radical scavenger (Schmelling et al., 1997).

The study of the effects of anions on the photocatalytic degradation of organic pollutants is important in two respects. Firstly, anions are often present in natural water systems, and secondly, CO_3^{2-} , PO_4^{3-} , and NO_3^- anions are produced during the degradation of organic pollutants and as the reaction proceeds, the increasing concentration of these anions will play a crucial part in the degradation of the parent compound.

The presence of common inorganic ions such as nitrate, chloride, sulphate and phosphate might alter the adsorption-desorption equilibrium attained on the surface of the photocatalyst, TiO_2 , the reaction rate is expected to change with respect to the presence of these inorganic anions. During the photocatalytic degradation of humic acid in the presence of the anions an initial stage adsorptive removal occurred for chloride, nitrate and sulphate ions (also observed in the dark experiments that were carried out to assess the dark adsorption rate), but in the presence of phosphate ions direct inhibition was observed (Bekbölet, 1998).

By adding chloride, sulphate, nitrate and hydrogen carbonate, and sodium as counter-ion, into a 0.155 mM solution of 3-chlorophenol (3-CP) at pH 8, D'Olivera et al. (1993) detected no change in the initial rate of disappearance of this pollutant was found within experimental accuracy. This observation also suggests that sodium ions, although they are close to the negatively charged surface, do not hinder the reaction between 3-CP and the oxidative species formed by the optical excitation of TiO_2 .

Sökmen and Özkan (2002) obtained the results in which the effectiveness of TiO_2/UV system was significantly decreased in the presence of inorganic anions. While the adsorption of astrazone orange textile dye on TiO_2 was promoted in the presence of all salts, the photodecomposition was retarded with HPO_4^{2-} , SO_4^{2-} , NO_3^- , and the presence of NaCl had little effect on it.

Xia et al. (2002) carried out the experiments to study the effects of several anions on the photocatalytic degradation rates of sodium dodecylbenzene sulphonate (DBS) with TiO_2 as catalyst. The results revealed that Cl^- , SO_4^{2-} , NO_3^- and HCO_3^- retarded the rates of DBS degradation to different degrees. For the opposite to the experiments carried out by Bekbölet et al. (1998), PO_4^{3-} increased the DBS degradation rate at low concentrations and decreased it at high concentrations; H_2PO_4^- accelerated the rate of DBS degradation.

The mechanism of the effects of anions on DBS degradation, according to Xia et al. (2002), was concluded as follows: anions compete for the radicals; anions are absorbed on the surface of catalyst and block the active site of catalyst; anions added to the solution change the pH value and influence the formation of $\bullet\text{OH}$ radicals and the adsorption of DBS on catalyst.

Effect of Cl

Usually, the chloride ion influence on the rate of PCO is negative. The present of chloride ions caused relevant reduction in the reaction rate since they are rapidly adsorbed by the catalyst. The rate constants decreased by 25% and 20% for Color₄₃₆ and Color₄₀₀ respectively (Abdullah et al., 1990).

Wang et al. (2000) used UV light of 365 nm and titanium dioxide in aqueous suspension to study the photocatalytic reaction of o-methylbenzoic acid. In the previous works, Chen et al. (1997) and Zhang et al. (1998) have shown that the influence of the anions is dependent on the pH of the aqueous solution. The study by Wang et al. (2000) indicated that in the presence of anion additives, the inhibitive effect of chloride ions was larger than that of sulphate ions under acidic condition for Degussa brand titanium dioxide. The authors report that the main explanation is the acid/base properties of TiO_2 -P25 surface (adsorption with TiOH_2^+ at low pH and repulsion of Cl^- ion by TiO^- at basic pH).

For chloride ions, the Degussa type had stronger adsorption and reduced the reaction sites due to the presence of Ti-OH_2^+ . For sulphate ions, the above phenomenon also

prevailed, but in a lesser extent, since sulphate ions underwent the following photolysis reactions (Abdullah et al., 1990):



At pH 7 and 11 the addition of chloride ions did not influence the reaction, while the presence of sulphate ions slightly promoted the reaction. Ti-O⁻ is predominant at pH 7 and 11 for Degussa TiO₂, so the adsorption of chloride and sulphate can be neglected. The slight promotion of sulphate might be caused by the elimination of negative ion adsorption and a small extent of the participation of sulphate radicals produced from a series of reactions following photolysis of water (Wang et al., 2000).

With Cl⁻, there appears to be more than one factor influencing the reaction in the rate of degradation, since the rate reduction profile has a distinct double hump. The general effect of Cl⁻ was found to reduce the degradation of monocrotophos (MCP) (Hua et al., 1995).

The research work made by Piscopo et al. (2001) showed that at low chloride concentration, the behaviour of benzamide (BA) and *para*-hydroxybenzoic acid (4-HBZ) are sensitively different ([Cl⁻] < 0.02 mol/l). 4-HBZ is only weakly dependent on the chloride concentration. The evolution can be explained on the basis of adsorption of 4-HBZ.

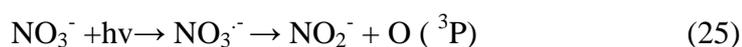
In contrast, the degradation of BA is strongly affected by the Cl⁻ ions concentration, especially at low chloride concentrations ([Cl⁻] < 0.02 mol/l). The decrease of degradation rate according to chloride concentration has been described by Wang et al. (1999) and could explain the results obtained in the BA degradation:

- 1) at pH 5 to 6, TiOH_2^+ and TiOH were the main functional groups on the catalyst surface, and the Cl^- ions competed with organic species for active sites and lowered the reaction rate;
- 2) Cl^- ions competed with oxygen for electron, which reduced the formation of superoxide radicals and then blocked the chain reaction for free hydroxyl radicals;
- 3) according to Abdulah et al. (1990), chloride recombines with free radicals during reaction, and thus, abruptly the reactive chain between pollutant and free radicals.

However, at high chloride concentrations, the behaviour of both compounds are the same and there is a stability of the rate constant degradation after $[\text{Cl}^-]=0.4 \text{ mol/l}$ (Piscopo et al., 2001).

Effect of NO_3^-

The effect of nitrate on the PCO is presumably favourable. Some literature sources reported that nitrate improves PCO efficiency: the most pronounced effect was observed as an increase in the presence of nitrate ions. It is known that the irradiation of nitrate in water ($\lambda=320\text{nm}$) gives the following reactions:



The $\bullet\text{OH}$ radicals formed in natural waters react principally with dissolved organic matter, namely humic acids. Aqueous OH is highly non-selective and can abstract an H atom from many sites of organic molecule or add to any C-C double bond or accept an electron (Hoigne, 1990). Thus, presence of NO_3^- in surface waters can induce the oxidation of humic substances (Abdullah et al., 1990).

However, other authors report that neither chloride nor nitrate appreciably hindered mineralisation. This was expected, since neither is an effective hydroxyl radical scavenger at alkaline pH, complexation of chloride to TiO_2 at alkaline pH is

negligible and nitrate does not typically hinder photocatalytic oxidation of organic compounds (Abdullah et al., 1990; D'Oliveira et al., 1993). As a result, the presence of inorganic anions did not substantially hinder TNT transformation at alkaline pH (D'Oliveira et al., 1993). HNO_3 was used to acidify the medium, because NO_3^- ions don't affect initial rate for the pollutants studied (3-CP, benzamide (BZA), nitrobenzene (NBz)).

At the same time Hua et al. (1995) reported that with NO_3^- , the rate of degradation of MCP has slowed down or even decreased with its increase in concentration.

Effect of SO_4^{2-}

In the presence of sulphate ion the rate of PCO increased with the increasing of sulphate ion concentration: at pH 6.8, sulphate ions are present in the HSO_4^- form. The presence of sulphate ions were expected to decrease the reaction rates, but in contrary a slight increase in the reaction rate constant was observed (<10%). The reason may be the enhanced rate of oxidation due to the formed $\bullet\text{SO}_4^-$ -radicals by the reaction of the sulphate ions with $\bullet\text{OH}$ radicals (Abdullah et al., 1990).

Hua et al. (1995) reported that the photocatalytic oxidation rate of monocrotophos was increased by increasing the sulphate ion concentration. It should be pointed that the enhancement effect of SO_4^{2-} on the photocatalytic degradation of MCP was contrary to the previous findings on the degradation of aniline, ethanol, and salicylic acid. This could be attributed to the difference in the structural property of MCP from the other compounds. Previously, acetate ion was also reported to enhance photocatalytic degradation of certain organic compounds (Hua et al., 1995).

Effect of HCO_3^-

In the presence of bicarbonate ions the rate of PCO of humic acid decreased, and Bekbölet and Balcioglu (1996) reported that since $\bullet\text{OH}$ -radicals are known to oxidise even carbonate ions and thus become scavenged, the protective effect of carbonate ions was also tested experimentally. By the increasing concentration of HCO_3^- the

PCO rate for humic acid significantly decreased. This inhibition was undoubtedly due to the scavenging of hydroxyl radicals. If the PCO is going to be used, the removal of these ions will be necessary before application. But on the other hand, D'Oliveira (1993) reported that the absence of hydrogen carbonate effect is an advantage of the photocatalytic method with respect to the O₃-UV and H₂O₂-UV systems, because in homogeneous phases HCO₃⁻ ions scavenge •OH radicals. Also, if these radicals are among the species formed at the surface of TiO₂, an evidence of their reaction with the pollutant in the adsorbed phase predominantly, and not significantly at a distance from the surface, allowing them to be scavenged by HCO₃⁻.

The present review illustrates that the influence of ions on the PCO has certain doubts and contradictions. The additional research into the influence of different ions on the rate of PCO of the target compounds should be undertaken.

3 EXPERIMENTAL SECTION

3.1 Experimental Techniques and Methods

PCO experiments were carried out using exact amount of synthetic solution of ethylene glycol monoethyl ether (2-ethoxyethanol) and ethylene glycol, as well as aqueous extracts of commercial jet fuel. Several factors, influencing the process performance, were investigated (see Table 3.1).

Table 3.1 Plan of experiments

Substance Factor	2-ethoxyethanol	Ethylene glycol	Aqueous extract of jet fuel
Initial concentration of pollutant	Examined	Not examined	Not examined
Mixing mode with different pH of pollutant	Examined	Examined	Examined
Tert-butanol presence	Examined	Not examined	Not examined
Mineral admixtures presence	Examined	Examined	Not examined

The impact of tert-butanol, well known as •OH-radical scavenger, on PCO of de-icing agents was investigated to find out, if the oxidation process goes by radical mechanism.

The influence of mixing mode and pH to the efficiency of PCO of de-icing agents were studied experimentally (see Table 3.2). These experiments were carried out to find the optimum conditions for energy-saving way of PCO of wastewaters, contaminated with the de-icing agents.

Table 3.2 Energy saving PCO

pH	Mixing mode	2-ethoxyethanol	Ethylene glycol	Aqueous extract of jet fuel
3	Constant mixing	Examined	Not examined	Not examined
	Periodical mixing	Examined	Not examined	Not examined
	Without mixing	Examined	Not examined	Not examined
6	Constant mixing	Examined	Examined	Examined
	Periodical mixing	Examined	Examined	Examined
	Without mixing	Examined	Not examined	Examined
11	Constant mixing	Examined	Not examined	Not examined
	Periodical mixing	Examined	Not examined	Not examined
	Without mixing	Examined	Not examined	Not examined

Table 3.3 shows some characteristics of synthetic solutions and jet fuel aqueous extract, used at the present research.

Table 3.3 Characteristics of ethylene glycol, 2-ethoxyethanol aqueous solutions and jet fuel aqueous extract

Substance	NN	Characteristics	Unit	Range
Ethylene glycol	1	Concentration	mg/L	100
	2	COD	mgO ₂ /L	130
	3	pH	-	5.3-5.7
2-ethoxy-ethanol	1	Concentration	mg/L	50-2000
	2	COD	mgO ₂ /L	98-3910
	3	pH	-	3.0-12.0
Jet fuel aqueous extract	1	Concentration	mg/L	-
	2	COD	mgO ₂ /L	180-215
	3	pH	-	4.8-5.5

Experiments were performed in a 0.20-L capacity thermostatted batch glass reactor, having an inner diameter of 100 mm, and thus an exposed surface to volume ratio (aperture) equal to $39.9 \text{ m}^2/\text{m}^3$, supplied with a magnetic mixer. The revolution frequency of standard 25-mm mixer was 300 rev/min. In case of experiments for energy saving PCO timer controlled periodical mixing. A 365 nm UV-lamp was positioned horizontally over the reactor (irradiance was about $1.1 \text{ mW}/\text{cm}^2$, measured by UVX Radoimeter).

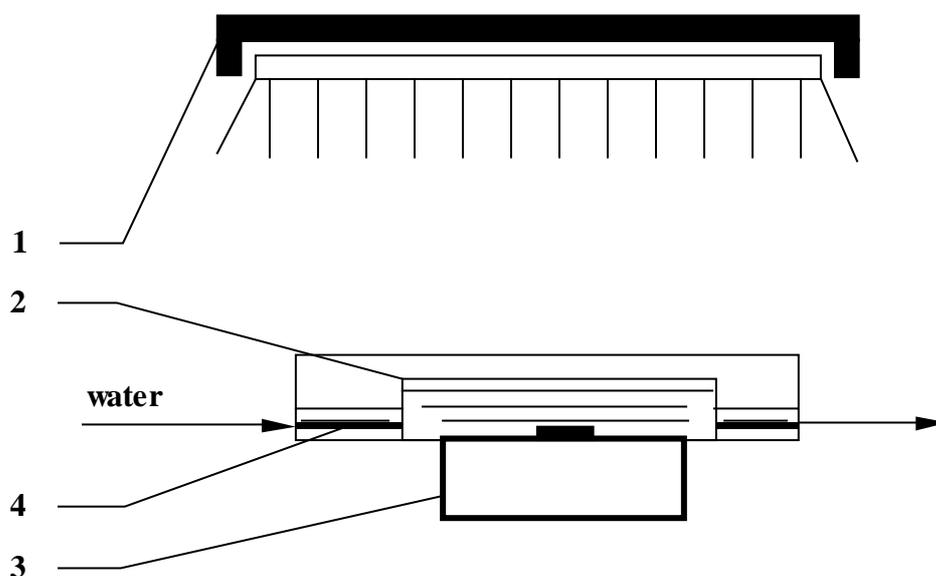


Figure. 3.1 Scheme of experimental facility:

1 - UV-lamp; 2 - reactor; 3 - magnetic stirrer; 4 - thermostat.

Titanium dioxide under near-UV irradiation was selected as a photocatalyst for the experiments. PCO was performed in two ways: catalysed by irradiated TiO_2 slurry (Degussa P25, 1 g/l) or by TiO_2 attached to buoyant hollow glass micro-spheres (the product of LP-ImpEx, Estonia). Titanium dioxide was attached to the surface of the micro-beads by thermal method (Jackson et al., 1991).

All experiments were compared with reference samples, treated under identical conditions except UV-radiation. The pH value was controlled by the addition of either sulphuric acid or sodium hydroxide. All experiments were conducted at $18 \pm 1^\circ\text{C}$. The volume of samples withdrawn was 10 ml (for sedimentation experiments 50 ml/sample).

Tert-butanol was added at the very beginning of the experiments in molar equivalent amount regarding the concentration of a target compound.

The experiments, investigating fraction composition of TiO₂ catalyst under different conditions, were carried out using pure water or synthetic solution of 2-ethoxyethanol. PCO experiments were performed like it was described above except the fact, that the capacity of thermostatted batch glass reactor was 0.25 l. The concentration used was 1 g/L of catalyst (Degussa P25). Sample requirement was 10-14 ml, depending on particle size and density. Sample was diluted in the apparatus up to 1.7 L. Analyses were repeated three times to ensure results. Investigating pH influence, the pH of sampling unit in the apparatus was also controlled by the addition of either sulphuric acid or sodium hydroxide.

The experiments, investigating the effect of mineral admixtures on PCO efficiency of ethylene glycol and 2-ethoxyethanol, were conducted as it was described before and the experimental conditions are shown in Table 3.4.

Table 3.4. Series of experiments with mineral admixtures

Ion	Concentration, mol/L		
	<i>0,001</i>	<i>0,01</i>	<i>0,1</i>
Fe ²⁺ (FeSO ₄)	pH 3	pH 3	pH 3
Fe ³⁺ (Fe ₂ (SO ₄) ₃)	pH 3	pH 3	pH 3
Mn ²⁺ (MnSO ₄)	pH 3	pH 3	pH 3
SO ₄ ⁻ (Na ₂ SO ₄)	pH 3,6,11	pH 3,6,11	pH 3,6,11

The effect of Ca²⁺ ion (5 g/L) was investigated at pH 12.

3.2 Analyses

Chemical oxygen demand (COD) and glycols concentration change analyses were determined after the PCO experiments. In the experiments with mineral admixtures

only COD was determined. Before COD determination, ferric, ferrous and manganese ions were removed by addition of sodium hydroxide and filtration.

COD was measured by standard procedures (Standard Methods, 1989). Concentrations of glycols, as oxidation by-products, were measured with 3-methyl-2-benzothiazolinone hydrazone HCl hydrate (MBTH) by the method, described by Evans and Dennis (1973) (see Appendix I).

The fractional composition of TiO_2 particles in slurry was determined by means of particle size analyser Coulter LS130.

The principle of Coulter LS130 work is as follows. The Fourier lens forms the moving diffraction patterns of the particles traversing the diffraction sample cell to change into a stationary composite diffraction pattern that can be measured by a stationary set of detectors arrays. The composite diffraction pattern is used to measure the particle size distribution.

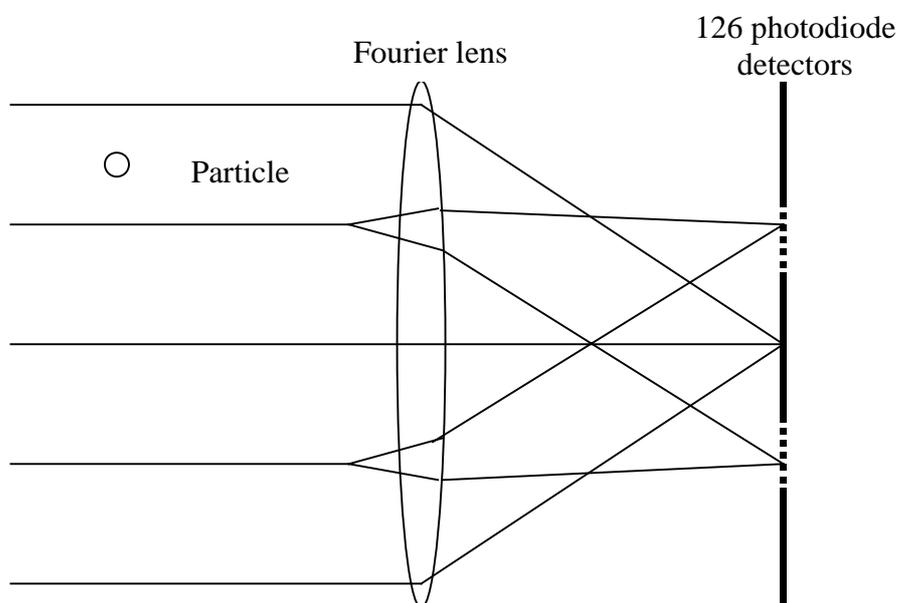


Figure 3.2. Principle of Coulter LS130 work

4 RESULTS AND DISCUSSION

4.1 PCO of de-icing agents and jet fuel aqueous extract

The performance of PCO with artificial radiation sources was characterised by the process efficiency E . The efficiency E was defined as the decrease in COD divided by the amount of energy reaching the surface of the treated sample:

$$E = \frac{\Delta c \cdot V \cdot 1000}{I \cdot s \cdot t} \quad (27)$$

E – PCO process efficiency, mg/Wh;

Δc - COD decrease, mgO₂/L;

V – the volume of sample to be treated, L;

I - irradiation intensity, mW/cm²;

s - solution irradiated surface area, cm²;

t - treatment time, h.

1.4.1 Influence of initial concentration of pollutant

As was previously established by our studies (Krichevskaya et al., 2001), neutral medium is preferable for optimum process efficiency for both de-icing agents and jet fuel aqueous extract. Therefore, PCO of 2-ethoxyethanol solutions with initial concentrations of 50, 100, 250, 1000 and 2000 mg/l at pH 6 was carried out (see Appendix II, Table 4.1). The results of 2-ethoxyethanol PCO with maximum and minimum initial concentration are presented in Appendix III, Fig. 4.1 – 4.3. As one can see, COD values decreased noticeably. Fig. 4.1 shows that with the initial concentration 50 mg/L and 100 mg/L final COD values varied about zero.

The dependence of PCO efficiency on the initial concentration of 2-ethoxyethanol is shown in Fig. 4.1.1.

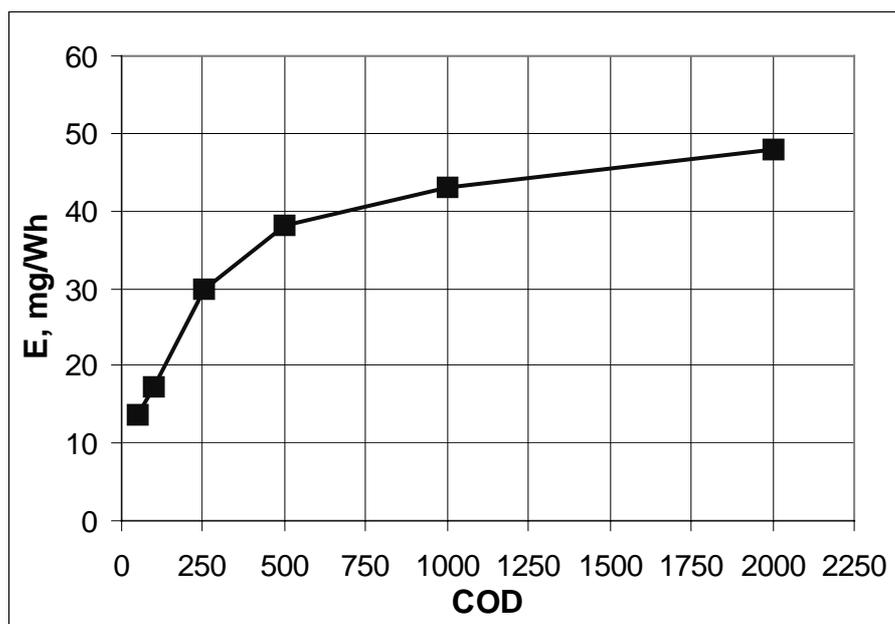


Figure 4.1.1. Influence of initial concentration of 2-ethoxyethanol on PCO efficiency at pH 6

One can see from Fig. 4.1.1 that the efficiency of PCO depends on the initial concentrations of 2-ethoxyethanol. The process efficiency enhances with the increasing of 2-ethoxyethanol concentration. Presumably, the maximum efficiency, usually observed with aromatic compounds (Preis et al., 2002), was not achieved within the studied concentration range, even with initial concentration of pollutant 2000 mg/L, due to the absence of UV-screening effect of pollutants.

1.4.2 Influence of tert-butanol addition

Tert-butanol (82 mg/L), well known as an OH^\bullet -radicals scavenger, was added to the solution of 2-ethoxyethanol with initial concentration of 100 mg/L (see Appendix II, Table 4.2). Preliminary experiments (carried out by the IAESTE scholar at Lappeenranta University of Technology, Miss Marta Lopez Velasco, the student of the University of Barcelona, Spain) showed, that the efficiency of PCO of tert-butanol in aqueous solutions is comparable by its order of magnitude with the one of 2-ethoxyethanol: at pH from 3.5 to 5.0 and initial concentration of tert-butanol of about

100 mg/l the efficiency was 20-22 mg COD/Wh, whereas for 2-ethoxyethanol PCO gives 18 mg COD/Wh under analogous conditions. In alkaline solution PCO of tert-butanol showed the poorest performance – 10-12 mg COD/Wh. In the present research measurements of 2-ethoxyethanol concentration were made during the oxidation (see Appendix I). The influence of tert-butanol presence on efficiency of PCO of 2-ethoxyethanol is presented in Fig. 4.1.2.

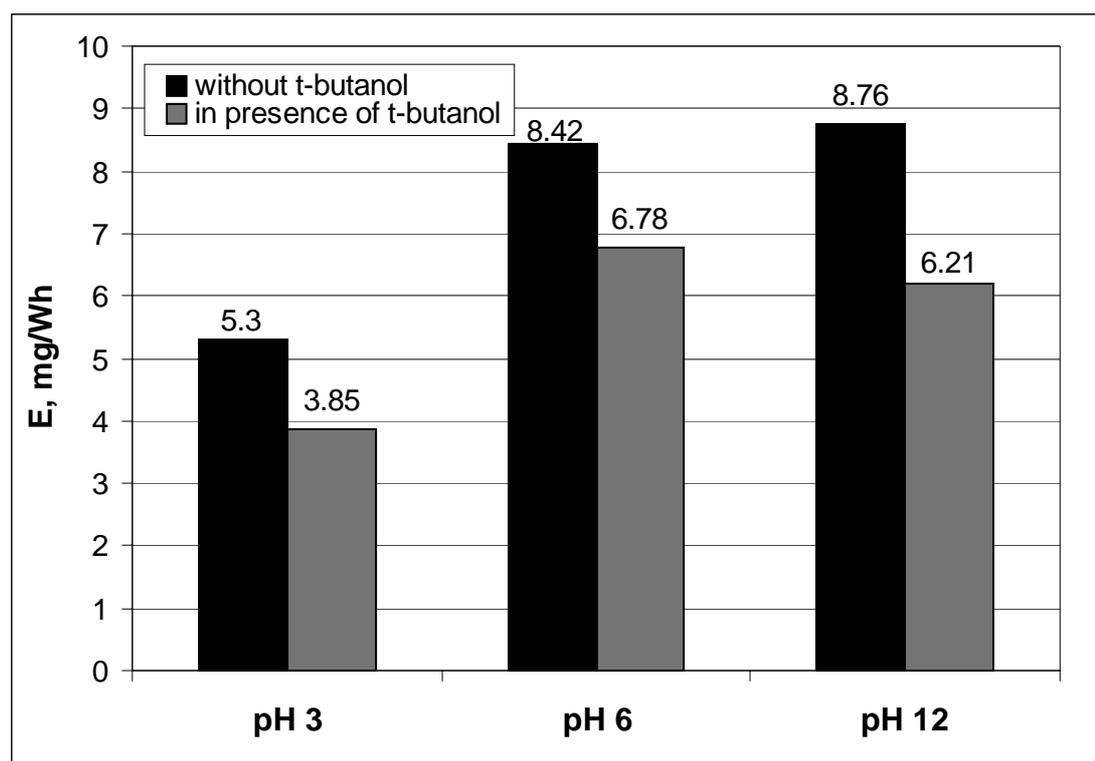


Figure 4.1.2. Influence of tert-butanol (82 mg/L) presence on PCO efficiency of 2-ethoxyethanol (100 mg/L)

As one can see from Fig. 4.1.2, the addition of tert-butanol under acidic and neutral media conditions had smaller effect on the PCO efficiency of 2-ethoxyethanol (10-18% reduction), than in alkaline solution (35%). This indicates the difference in the mechanism of oxidation in acidic and alkaline media: the radical mechanism plays certain, although not dramatic, role in PCO of 2-ethoxyethanol. The effect of tert-butanol addition in acidic and neutral media may be explained by competitive simultaneous oxidation of tert-butanol and 2-ethoxyethanol.

1.4.3 Influence of mixing mode

Special attention was paid to the energy-saving PCO with reduced mixing of the slurry. The reduced mixing was applied in a form of episodic mixing for 7.5, 15 or 30 min/h, controlled by the timer, switching the mixer's appliance on and off. The idea of such study was to establish the ability of TiO₂ slurries to maintain PCO of sufficient efficiency without or with episodic mixing.

The experiments with ethylene glycol and jet fuel aqueous extract were carried out at pH 6 (see Appendix II, Table 4.3 and Table 4.4). Besides, additional investigations were made with 2-ethoxyethanol synthetic solution, exploring the impact of different mixing time on PCO efficiency with different pH values (Appendix II, Table 4.5-Table 4.8).

➤ Aqueous solution of ethylene glycol

The results of PCO of ethylene glycol are shown in Appendix III, Fig. 4.4-4.5.

Figure 4.1.3. presents the dependence of ethylene glycol PCO efficiency on mixing mode. One can see, that PCO efficiency of ethylene glycol is higher in case of constant mixing. However COD analysis showed insignificant difference between PCO efficiency within constant or periodical mixing.

The observation, that the PCO efficiency in the ethylene glycol removal is more sensitive to the mixing mode than that in COD reduction, found no explanation in the present paper. The author may presume, that since the reduction rate of ethylene glycol removal is significantly higher than that of COD reduction, it may be more sensitive not only to the irradiated surface of TiO₂, but also to the factors, influencing the mass transfer of ethylene glycol and oxygen to the TiO₂ surface.

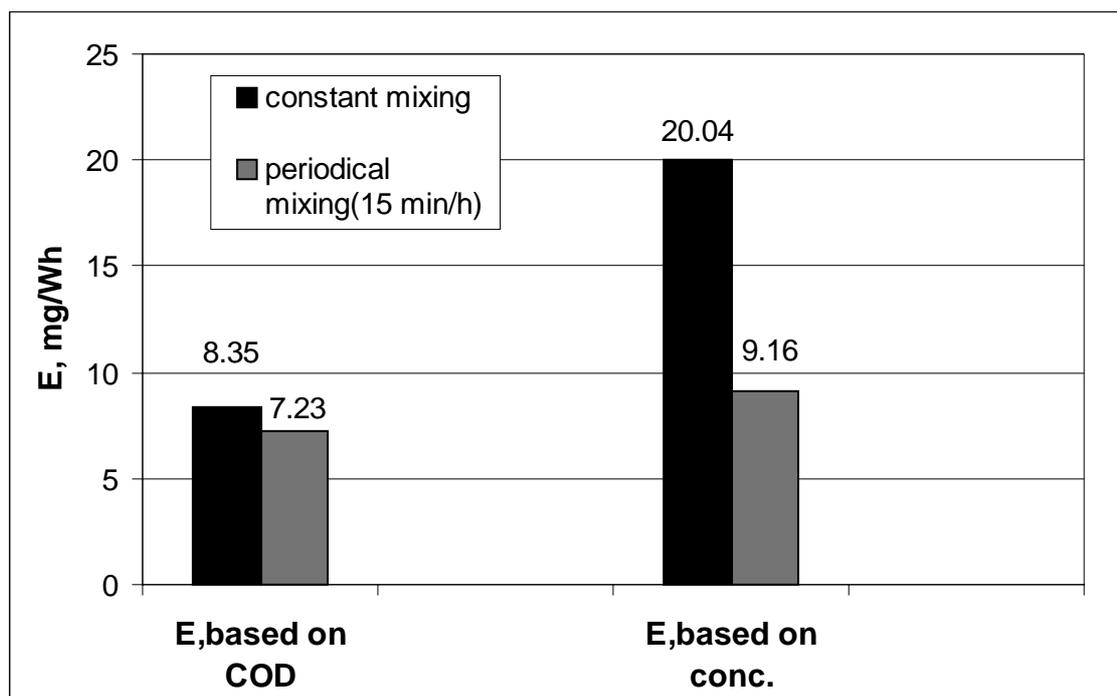


Figure 4.1.3. Influence of mixing mode on ethylene glycol (100 mg/L) PCO efficiency without pH regulation

➤ **Jet fuel aqueous extract**

Results of PCO of jet fuel aqueous extract can be seen in Appendix III, Fig. 4.6-4.7. It reflects the visible reduction in COD values within the increasing mixing time.

For the jet fuel aqueous extract the established results demonstrates a slight difference in PCO efficiency between constant mixing and mixing for 30 min/h (see Fig. 4.1.4). The 50% loss in PCO efficiency was observed when no stirring was applied compared to constant stirring.

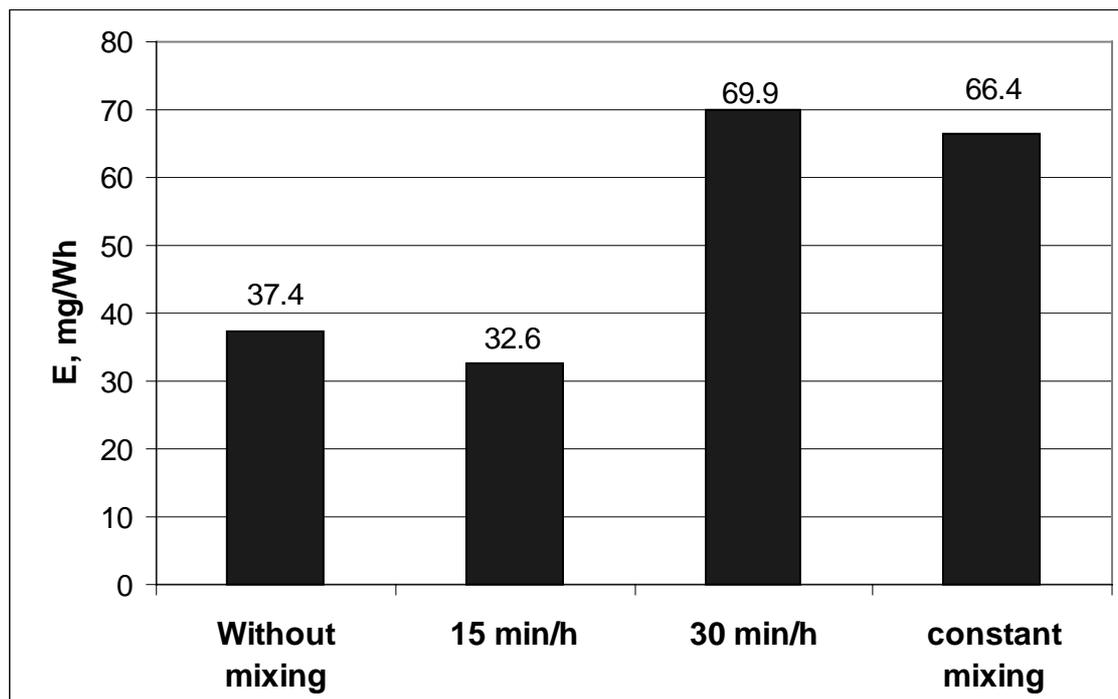


Figure 4.1.4. Influence of mixing mode on jet fuel aqueous extract (75 ml/L) PCO efficiency without pH regulation

➤ **Aqueous solution of 2-ethoxyethanol**

Experiments, carried out with 2-ethoxyethanol, were performed investigating the influence of mixing mode at different pH values. Oxidation results can be seen on Fig. 4.1.5-4.1.9. Additional information about oxidation results one can find in Appendix II (Fig. 4.8-4.10 at pH 3, Fig. 4.11-4.15 at pH 6 and Fig. 4.16-4.18 at pH 11). The experiments confirmed that neutral medium is preferable for oxidation. Therefore, more thorough investigations were made at pH 6.

The results of the experiments showed that the efficiency of oxidation without mixing is smaller than with constant mixing independently from pH (see Fig. 4.1.5 - 4.1.7). The determination of data of 2-ethoxyethanol PCO is presented for two analyses: based on COD and based on the change of glycol's concentration during the experiment. Both of them showed the decrease in efficiency of oxidation within decreasing mixing time.

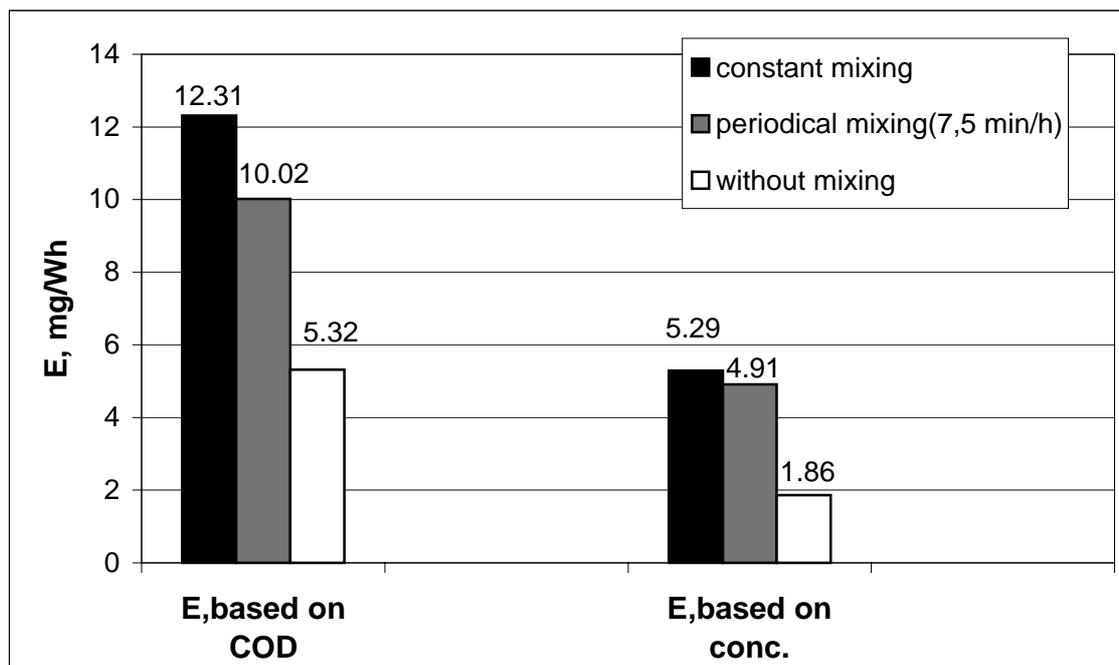


Figure 4.1.5. Influence of mixing mode on 2-ethoxyethanol (100 mg/L) PCO efficiency at pH 3

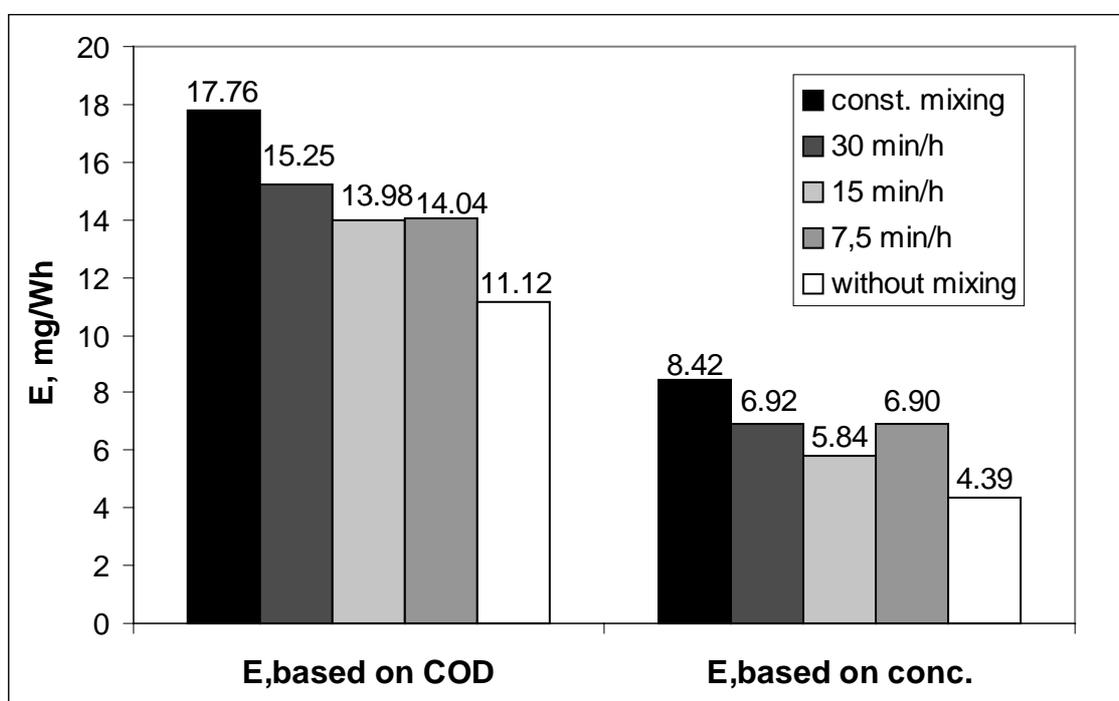


Figure 4.1.6. Influence of mixing mode on 2-ethoxyethanol (100 mg/L) PCO efficiency at pH 6

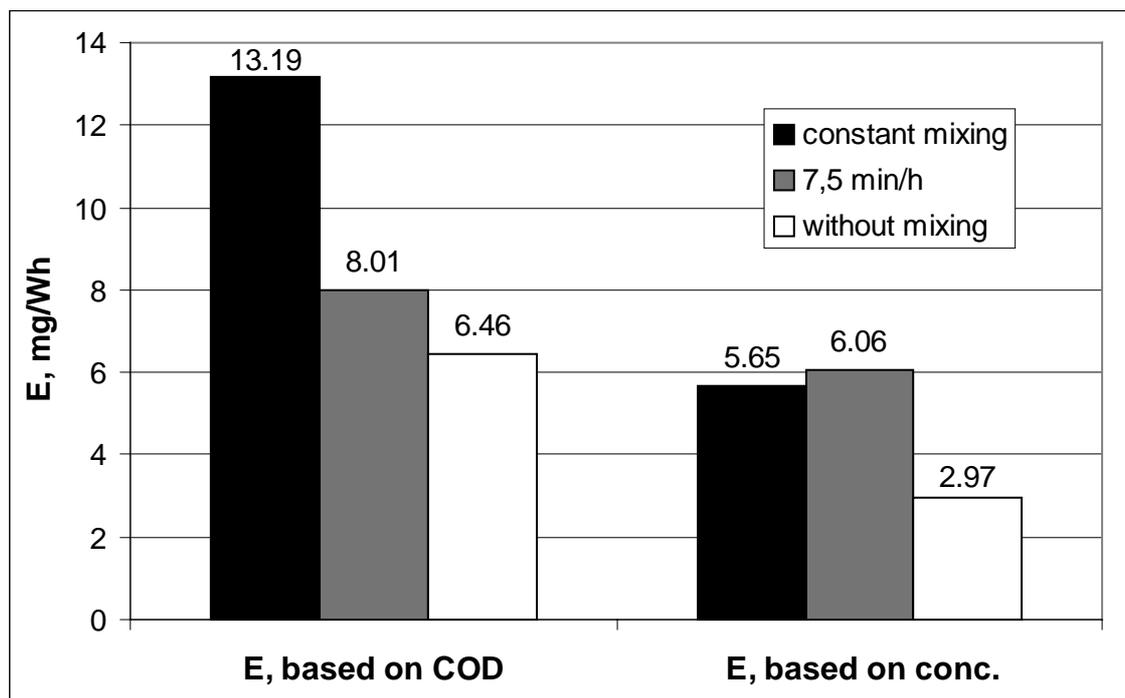


Figure 4.1.7. Influence of mixing mode on 2-ethoxyethanol (100 mg/L) PCO efficiency at pH 11

More detailed investigation of PCO of 2-ethoxyethanol solution without pH regulation indicated that more uniform small-sized TiO_2 suspensions, attained in 2-ethoxyethanol solutions, gave only 35% reduction in PCO efficiency for non-agitated slurries (Fig. 4.1.6). Periodical mixing for 7.5 min/h and 15 min/h presents a slight difference between the oxidation efficiencies.

Also, the influence of mixing mode on the PCO efficiency of 2-ethoxyethanol solutions was studied in dependence on pH. The decrease in PCO efficiency with reduced mixing appeared to be independent from pH. Both analyses – COD and concentration change – confirm these results (see Fig. 4.1.8-4.1.9).

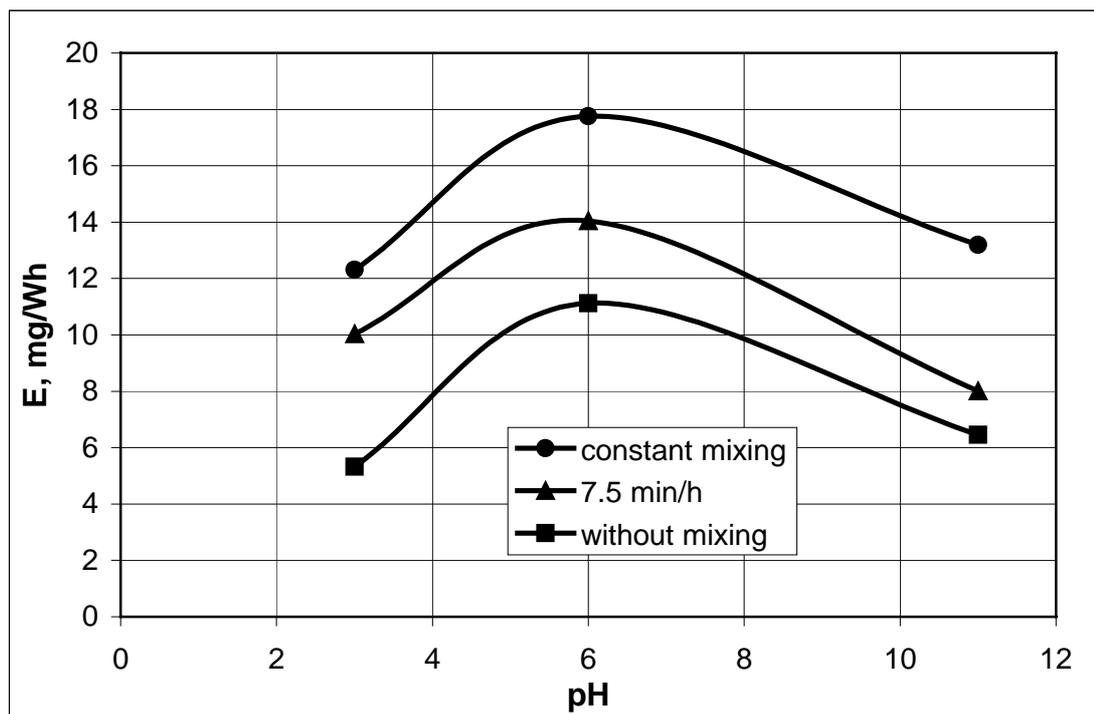


Figure 4.1.8. Dependence of 2-ethoxyethanol (100 mg/L) PCO efficiency on different mixing modes and pH, based on COD

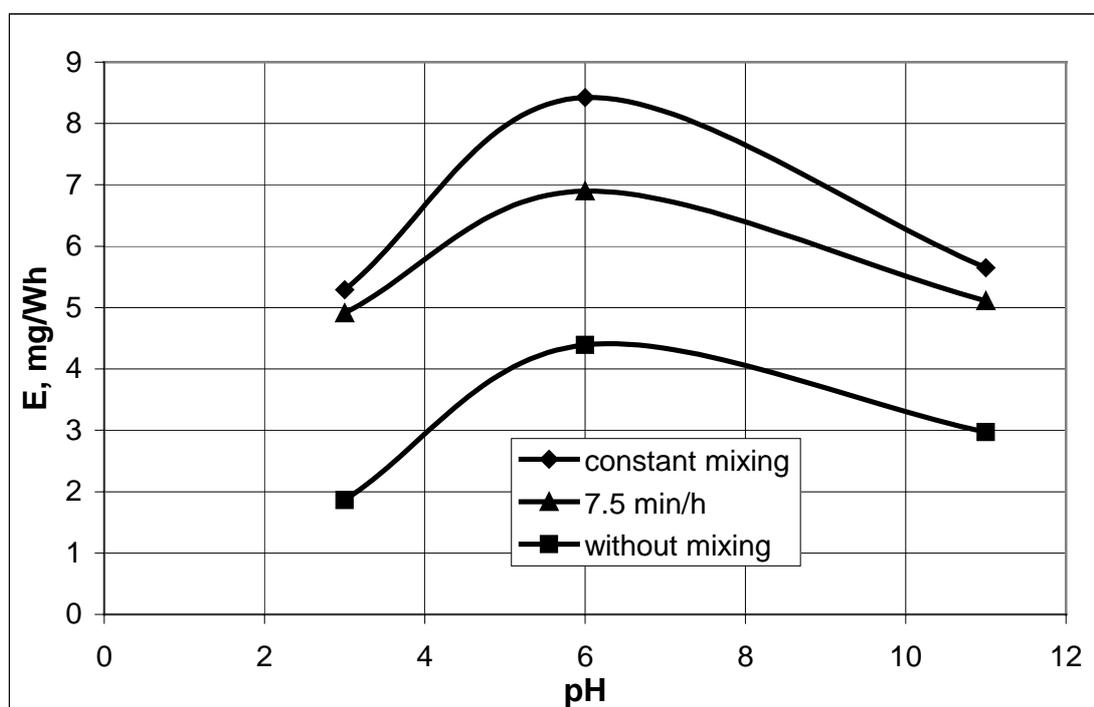


Figure 4.1.9. Dependence of 2-ethoxyethanol (100 mg/L) PCO efficiency on different mixing modes and pH, based on 2-ethoxyethanol concentration change

1.4.4 PCO under solar radiation

Experiments on PCO of jet fuel aqueous extract and aqueous solution of 2-ethoxyethanol under solar radiation (May to June 2001) were carried out using fixed catalyst (attached to buoyant glass microspheres) or its non-agitated slurry (Fig 4.1.10-4.1.11). UV-irradiance under solar radiation was not measured in the present research.

One can see from Fig. 4.1.10 that comparative experiments with samples demonstrated almost no difference in the rate of COD reduction in jet fuel aqueous extracts.

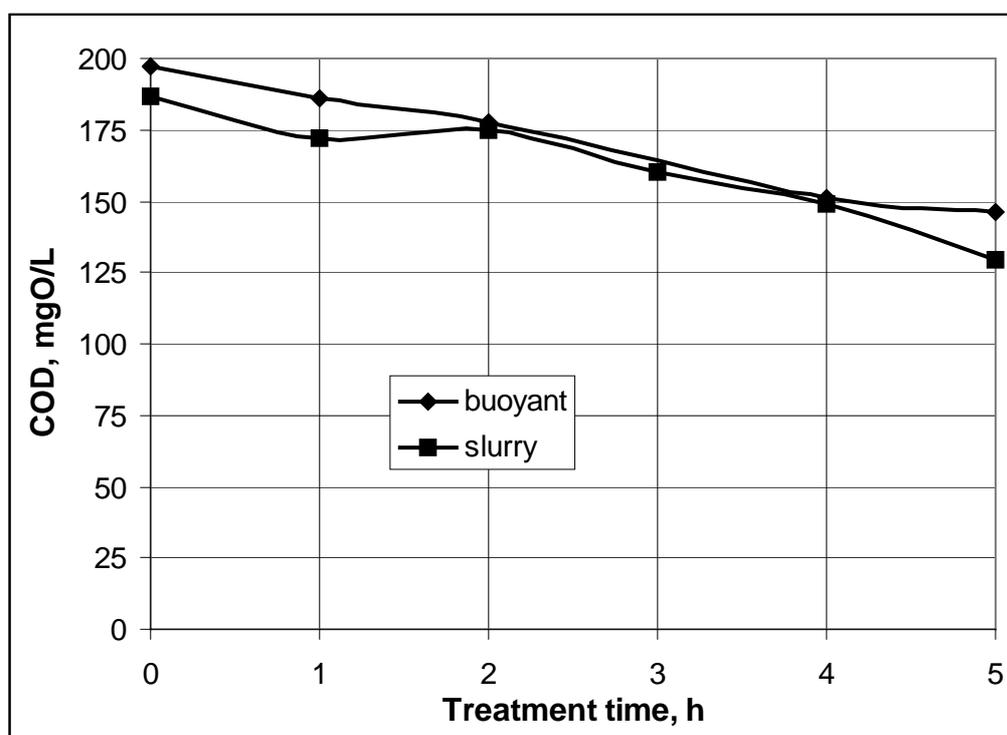


Figure 4.1.10. Dependence of jet fuel aqueous extract on treatment time under solar radiation using TiO_2 as slurry or as buoyant catalyst

During the PCO of 2-ethoxyethanol solution, the buoyant photocatalyst showed a lower activity than non-agitated slurry (see Fig. 4.1.11).

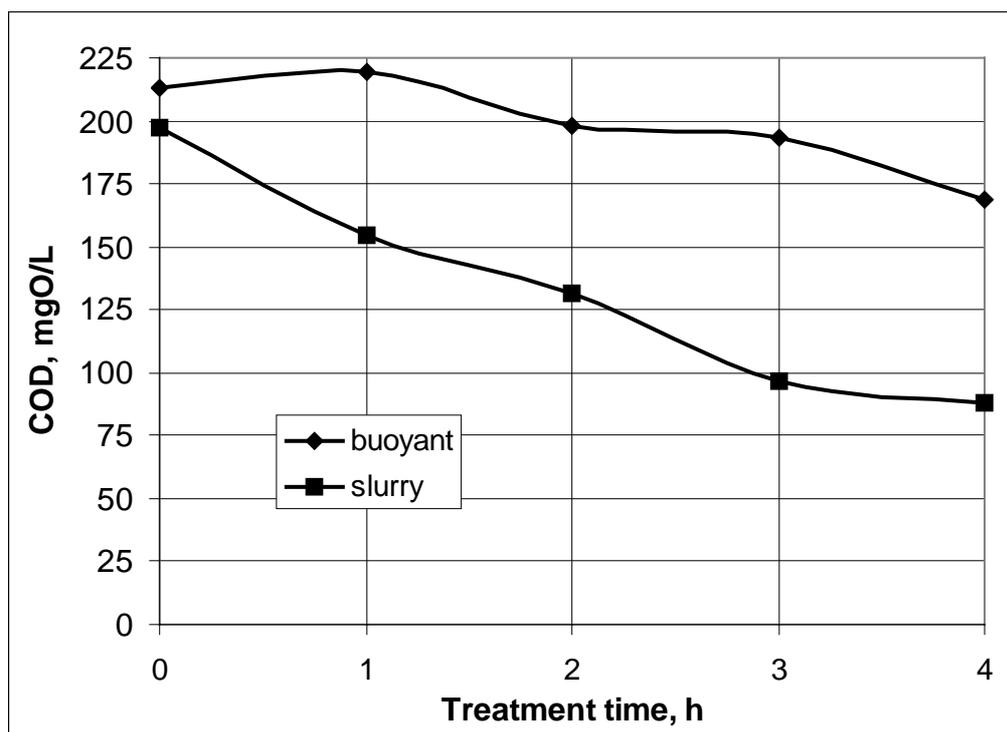


Figure 4.1.11. Dependence of aqueous solution of 2-ethoxyethanol (100 mg/L) on treatment time under solar radiation using TiO_2 as slurry or as buoyant catalyst

As it was established in the energy-saving PCO experiments under artificial irradiation, a drastic loss (50%) in PCO efficiency was observed during PCO of jet fuel aqueous extract, when no mixing was applied compared to constant mixing. Therefore the rate of PCO of jet fuel aqueous extract with buoyant catalyst approaches the rate of the PCO in non-agitated slurry. This fact may be explained by optical activity of jet fuel aqueous extract in UV range, partially screening the UV from penetration to the bottom of the reactor, where TiO_2 particles settle in hydrodynamically inactive medium. This was established by spectrophotometric analysis of jet fuel aqueous extract. This makes PCO efficiency at bottom-settled TiO_2 comparable to the one of less efficient buoyant photocatalyst.

UV-transparent solution of 2-ethoxyethanol demonstrates no screening effect for radiation thus making PCO efficiency with non-agitated TiO_2 slurry still noticeably higher, than with buoyant photocatalyst. This difference has its effect on the solar PCO rate, as can be seen on Fig.4.1.11.

4.2 Investigation of Fraction Composition of TiO₂ Suspension

Titanium dioxide (Degussa P25) was selected for the investigation of factors, influencing catalyst behaviour. TiO₂ was used in amount of 1 g/L, which was found to be the optimum dose for PCO process (Preis et al., 2002).

2.4.1 Influence of Organic Admixtures Presence

➤ *Aqueous suspension*

The aim of the experiments, establishing properties of TiO₂ suspension in water, was to identify the dispersion behaviour with the impact of pH. The results are presented in Fig. 4.2.1 and Appendix II (Fig 4.19 and Table 4.9).

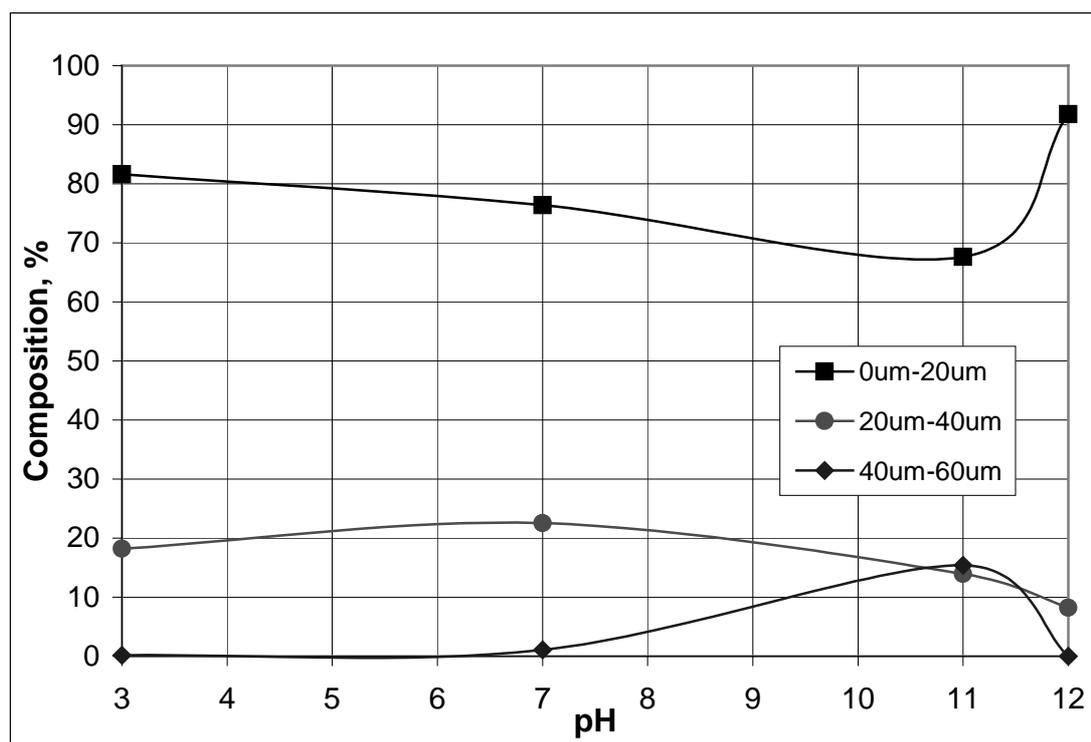


Figure 4.2.1. Dependence of TiO₂ (1 g/L) fraction composition in aqueous suspension on pH

Experimental results showed that the finest fraction of TiO₂ particles (0μm-20μm) prevails in the suspension under strong acidic or alkaline conditions (pH 3 and pH

12). There is no large fraction (40 μm -60 μm) at these pH values. On the other hand, at pH 11 the largest fraction (40 μm -60 μm) has been found in the solution. The percentage of medium fraction (20 μm -40 μm) was found to be the largest at neutral conditions and the smallest at pH 12.

➤ *Aqueous solution of 2-ethoxyethanol*

The influence of 2-ethoxyethanol presence in TiO₂ aqueous suspension on the catalyst behaviour was investigated during the experiment. Results can be seen in Fig. 4.2.2, Table 4.10 and Fig. 4.20. One can see from Fig. 4.2.2 that fraction of fine particles (0 μm -20 μm) predominates under acidic and alkaline media. Only neutral medium is favourable to medium size particles (20 μm -40 μm), containing 15 % of those.

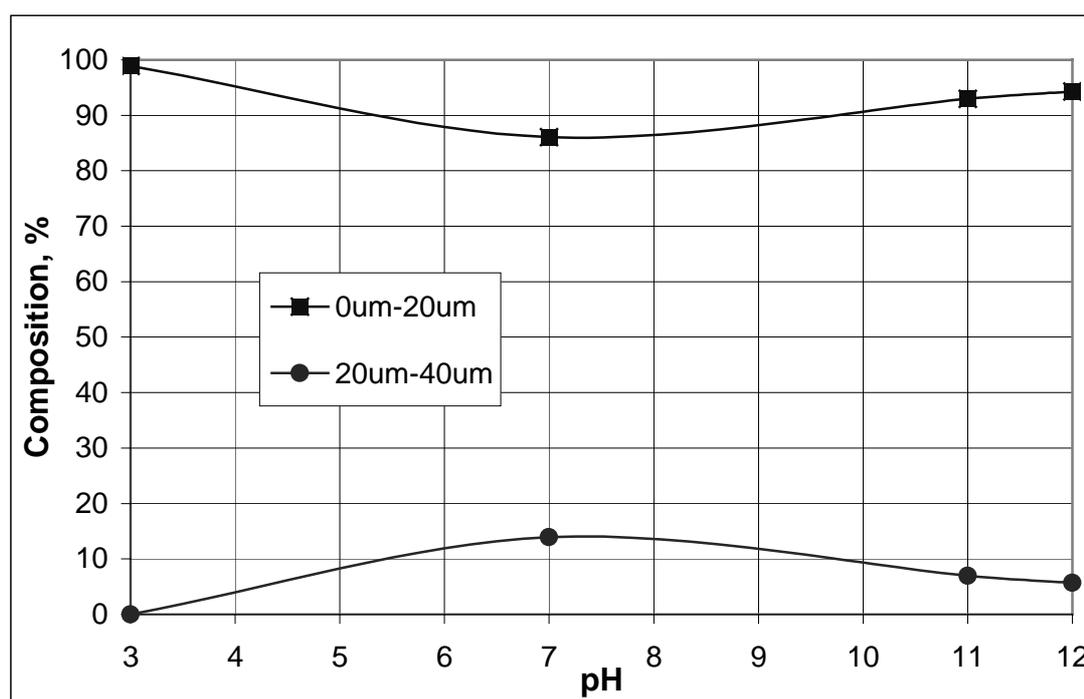


Figure 4.2.2. Dependence of TiO₂ (1 g/L) fraction composition in aqueous solution of 2-ethoxyethanol (100 mg/L) on pH

Presence of 2-ethoxyethanol makes aqueous suspension of TiO₂ slurry more dispersed independently of pH, comparing with pure aqueous suspension of catalyst.

➤ *Aqueous solution of 2-ethoxyethanol PCO by-products*

The experiments were made to establish the behaviour of TiO₂ catalyst suspension during the PCO of 2-ethoxyethanol solution (100mg/L) and the influence of its by-products on the fraction composition of dispersed particles. Results can be seen in Fig. 4.2.3-4.2.6, Table 4.11-4.12 and Fig. 4.21-4.23, given in Appendix II.

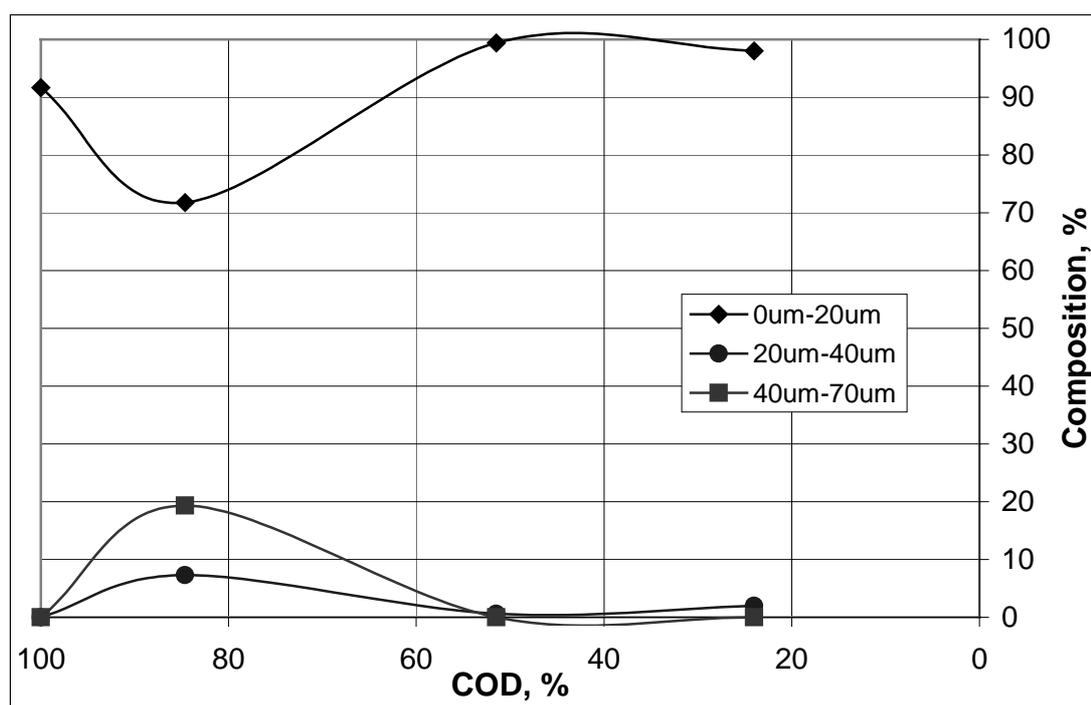


Figure 4.2.3. Dependence of TiO₂ (1 g/L) fraction composition on the presence of by-products of 2-ethoxyethanol (100 mg/L) PCO at pH 3

The size of TiO₂ particles was found to increase during the PCO of 2-ethoxyethanol at pH 3. At COD 85 % of initial the large fraction (40μm-70μm) was presented. However, the following reduction in particle sizes can be seen in Fig. 4.2.3. The percentage of highly dispersed fraction (0μm-20μm) was up to 98 % at the end of PCO. The content of coarse particles increased as PCO proceeded (maximum is at COD 85 % of initial), and then decreased to the value characteristics for the suspension at given pH without organic admixtures. This observation indicated flocculation character of PCO by-products.

Experiments in neutral medium (Fig. 4.2.4) detected changes in particles' fraction distribution. At COD 68 % of initial the agglomeration of particles was the largest. The presence of by-products during the following oxidation made fraction more dispersed (at COD 39 % of initial about 92 % of dispersed fraction). Further oxidation agglomerated catalyst again and at the end of PCO at about 8 % of initial COD the largest fraction (60 μ m-100 μ m) was observed to be 15 %. The measurements of final fraction composition of catalyst exhibited agglomeration of particles, comparing with suspension with no organic admixtures.

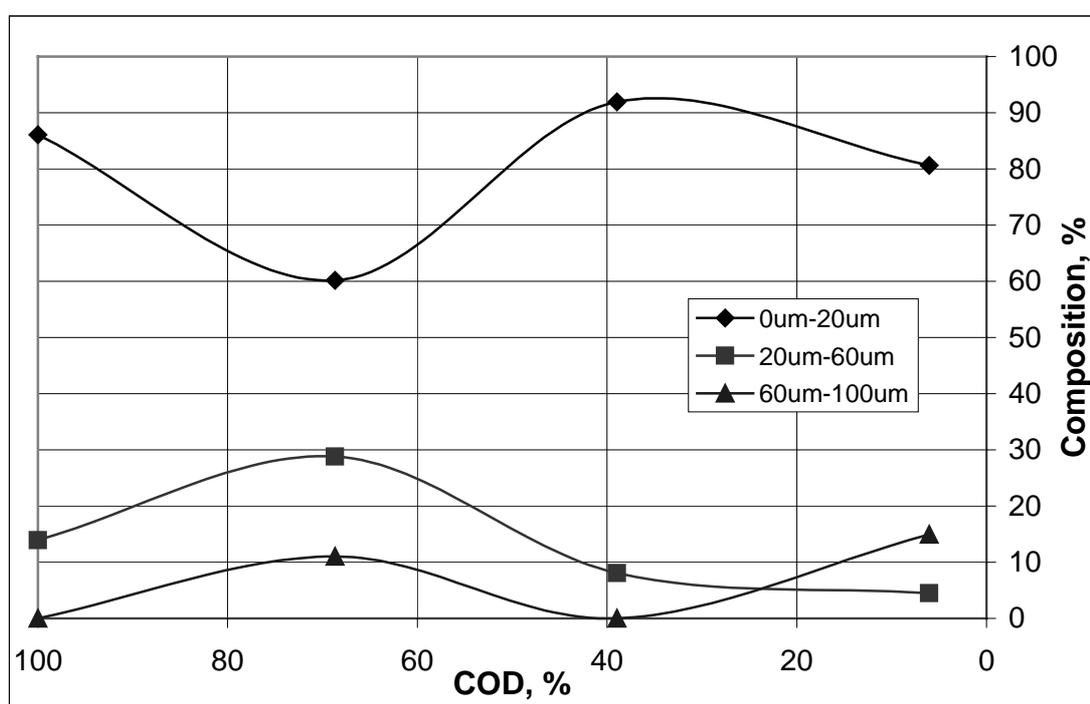


Figure 4.2.4. Dependence of TiO₂ (1 g/L) fraction composition on the presence of by-products of 2-ethoxyethanol (100 mg/L) PCO at pH 7

The presence of 2-ethoxyethanol makes TiO₂ aqueous suspension more dispersed: the finest fraction (0 μ m-20 μ m) is presented up to 100%. However, during the PCO of 2-ethoxyethanol, starting at COD 40 % of initial, agglomeration of particles can be observed (see Fig. 4.2.5). Though, comparing with pure TiO₂ aqueous suspension the reduction of catalyst's particle sizes occurred during PCO process.

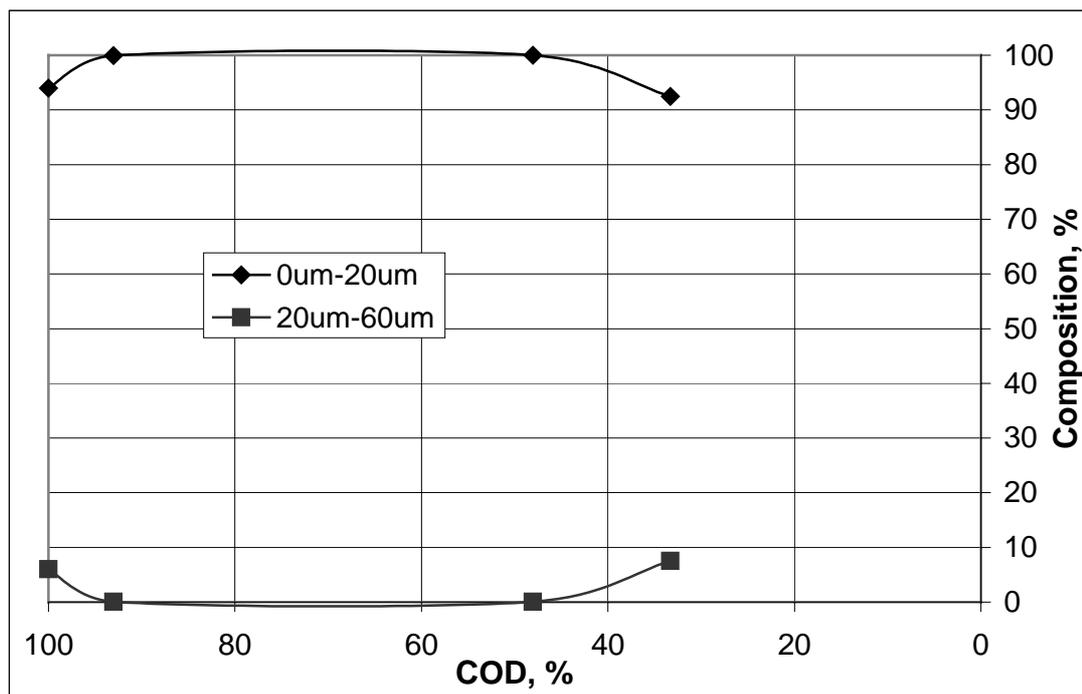


Figure 4.2.5. Dependence of TiO₂ (1 g/L) fraction composition on the presence of by-products of 2-ethoxyethanol (100 mg/L) PCO at pH 11

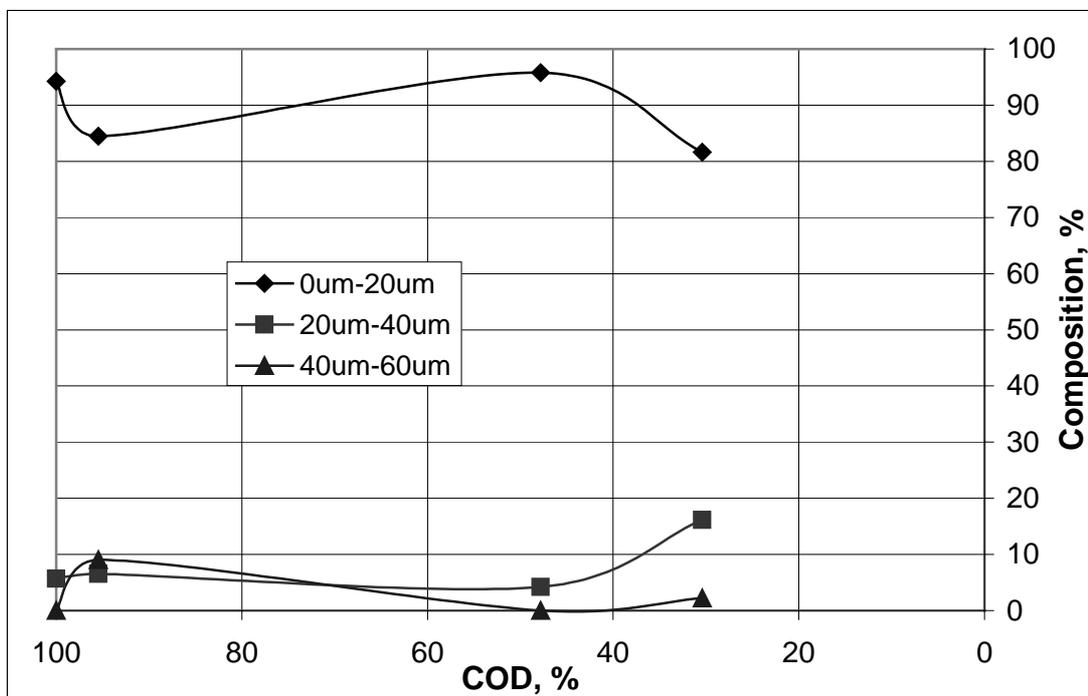


Figure 4.2.6. Dependence of TiO₂ (1 g/L) fraction composition on the presence of by-products of 2-ethoxyethanol (100 mg/L) PCO at pH 12

During the oxidation of 2-ethoxyethanol under strong alkaline conditions no changes in TiO₂ fraction composition were determined up to COD 45 % of initial. Following oxidation indicated particles' agglomeration (see Fig. 4.2.6). The comparison of TiO₂ aqueous suspension without organic admixtures and in presence of 2-ethoxyethanol PCO by-products exhibits insignificant reduction in particles' sizes.

➤ **The Comparison of the Different Organic Admixtures' Impacts at Different pH**

The comparison of the impacts of different conditions on the fraction composition of TiO₂ suspension at different pH was done. The results can be seen in Fig. 4.2.7-4.2.10 and Appendix II (Table 4.13 and Fig. 4.24-4.27).

The TiO₂ suspension fraction composition was found to be dependent on pH and the presence of organic admixtures. One can see from Fig. 4.2.7-4.2.10 that the most dispersed fraction predominates in every solution independently of its conditions. Although the percentage of all fractions depends on character of solution: presence of organic compounds and by-products of PCO.

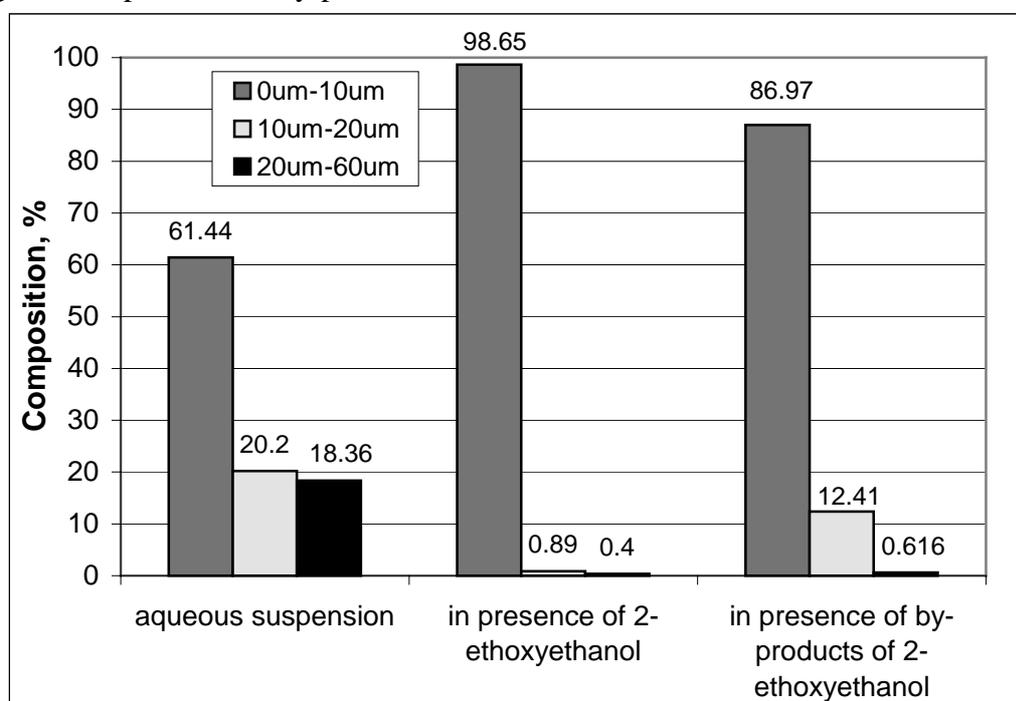


Figure 4.2.7. Dependence of TiO₂ (1 g/L) fraction composition on the presence of 2-ethoxyethanol (100 mg/L) and its by-products (after 7 h of PCO) at pH 3

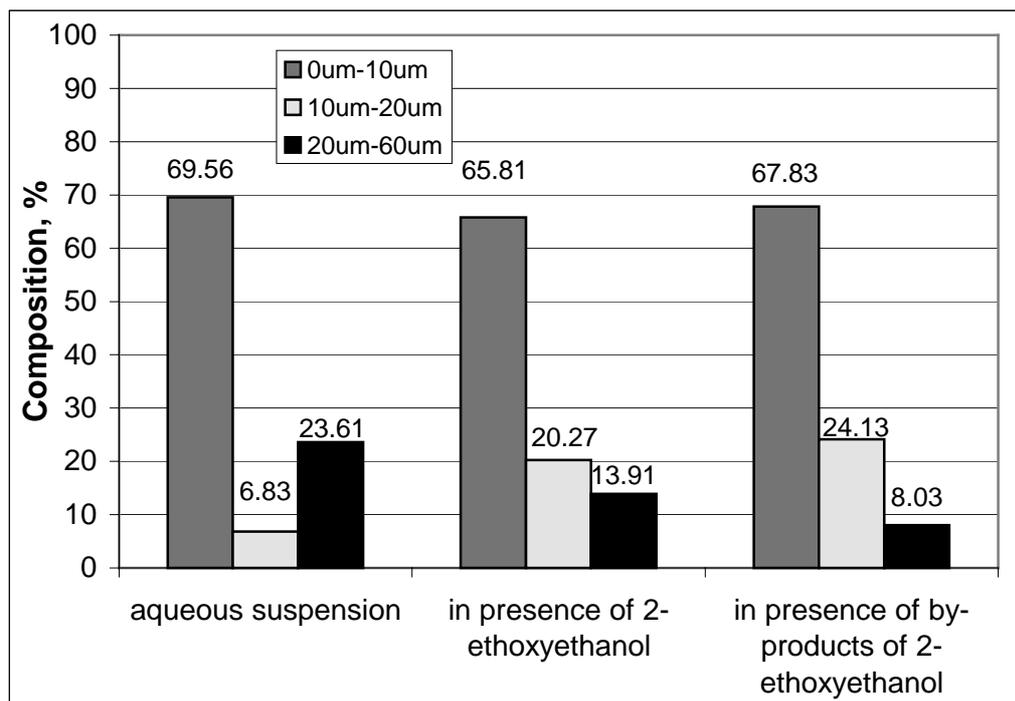


Figure 4.2.8. Dependence of TiO_2 (1 g/L) fraction composition on the presence of 2-ethoxyethanol (100 mg/L) and its by-products (after 7 h of PCO) at pH 7

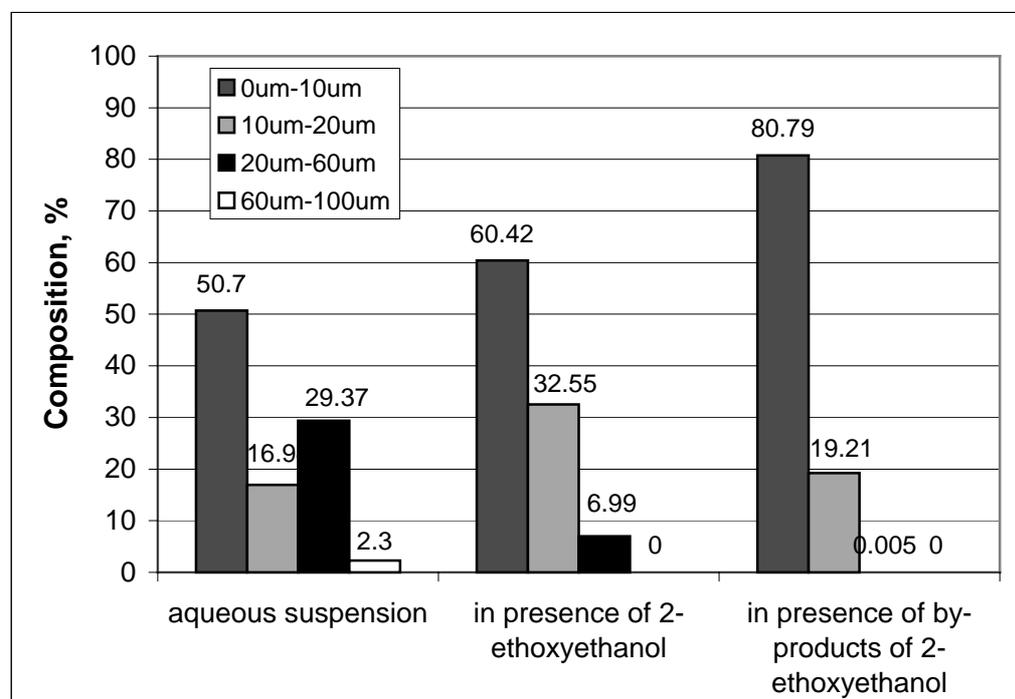


Figure 4.2.9. Dependence of TiO_2 (1 g/L) fraction composition on the presence of 2-ethoxyethanol (100 mg/L) and its by-products (after 7 h of PCO) at pH 11

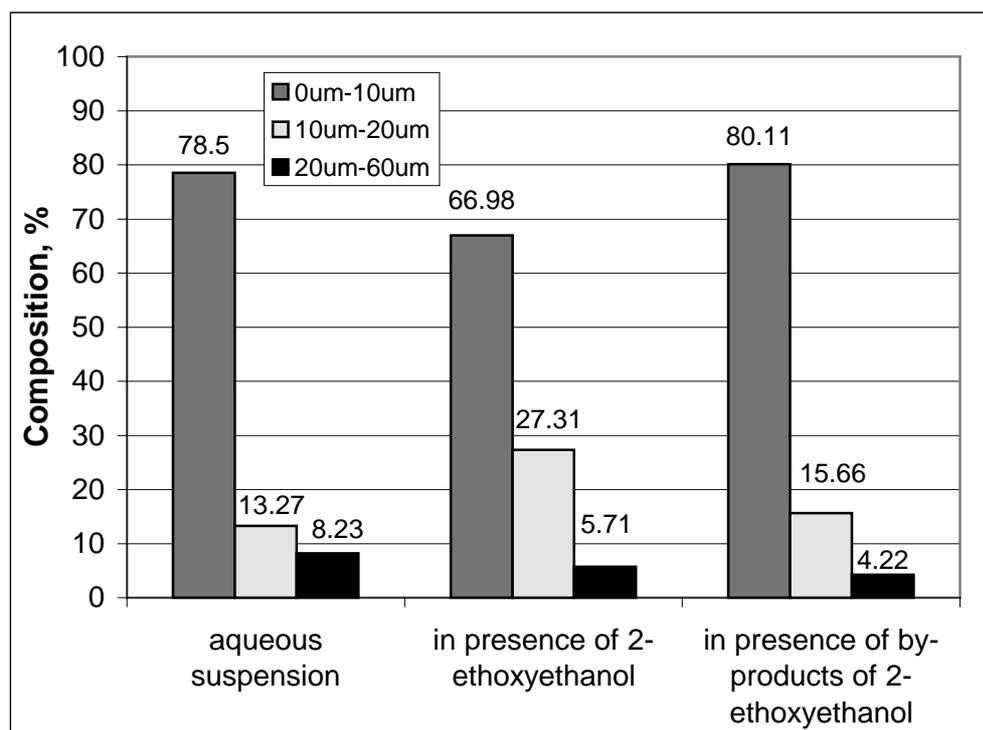


Figure 4.2.10. Dependence of TiO_2 (1 g/L) fraction composition on the presence of 2-ethoxyethanol (100 mg/L) and its by-products (after 7 h of PCO) at pH 12

The monitoring of the catalyst behaviour showed the increase of coarse particles content as the PCO of 2-ethoxyethanol proceeded. The percentage of this fraction reached its maximum at the treated sample COD of 60-85% from the initial value and then decreased to the value characteristic of the suspension at the given pH with no organic admixtures.

Additionally, the pH influence on the particle's distribution is as follows: the highest percentage of fine particles was established for acidic medium at pH 3 (about 90% of size from 0 to 20 μm). At the same time the highest sedimentation was observed visually in acidic medium. However, acidic medium appeared to be less effective in PCO of both de-icing agents and jet fuel aqueous extract (Krichevskaya et al., 2001). Moreover, the titanium dioxide suspension in a 2-ethoxyethanol solution in neutral or slightly acidic medium, favourable for PCO of icing inhibitors, contains maximum fraction of coarse particles – 15% from 20 to 40 μm , which is natural for TiO_2 suspensions at the isoelectric point (Chen et al., 1998). This observation shows that the particle size distribution in TiO_2 slurry, dependent on pH, is unlikely to determine the PCO efficiency: the effect of pH is attributed to adsorption issues.

2.4.2 Influence of Mixing Mode

Experiments were conducted to determine the impact of mixing mode on fraction composition of TiO₂ catalyst during PCO of 2-ethoxyethanol. All the experiments were performed at pH 7. One can see the results in Fig. 4.2.4, 4.2.11 – 4.2.12 and in Appendix II (Table 4.14 and Fig. 4.28-4.30).

The dependence of TiO₂ (1 g/L) fraction composition on the presence of by-products of 2-ethoxyethanol (100 mg/L) during PCO with constant mixing can be seen on Fig. 4.2.4. One can see an interesting picture of catalyst particles distribution during PCO of 2-ethoxyethanol with constant mixing. At COD 68 % of initial the fraction of agglomerated particles increased. However, the presence of by-products during the following oxidation made suspension more dispersed: at COD 39 % of initial about 92 % of fine fraction was detected. As PCO proceeded, agglomeration of the particles was established again and at the end of the experiment (about 8 % of initial COD) the largest fraction (60µm-100µm) was observed to be 15 %. Consequently, the agglomeration of TiO₂ particles was found to occur during the PCO of 2-ethoxyethanol in neutral medium.

One can observe the reduction of the TiO₂ particles sizes during the PCO of 2-ethoxyethanol with mixing 15 min/h (Fig. 4.2.11). At COD 58 % of residual the most dispersed fraction (0µm-20µm) reached 100 % and no changes were observed till the end of the oxidation. Periodical mixing may crash the largest fractions and does not allow particles to agglomerate again.

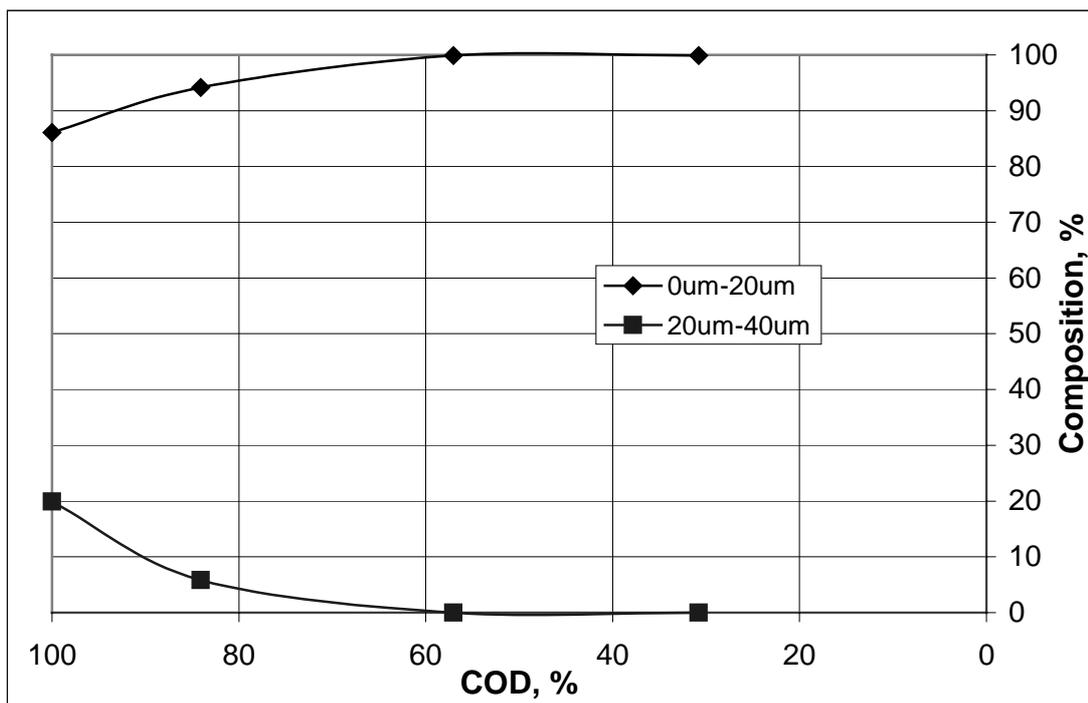


Figure 4.2.11. Dependence of TiO₂ (1 g/L) fraction composition on the presence of by-products of 2-ethoxyethanol (100 mg/L) during PCO with mixing 15 min/h

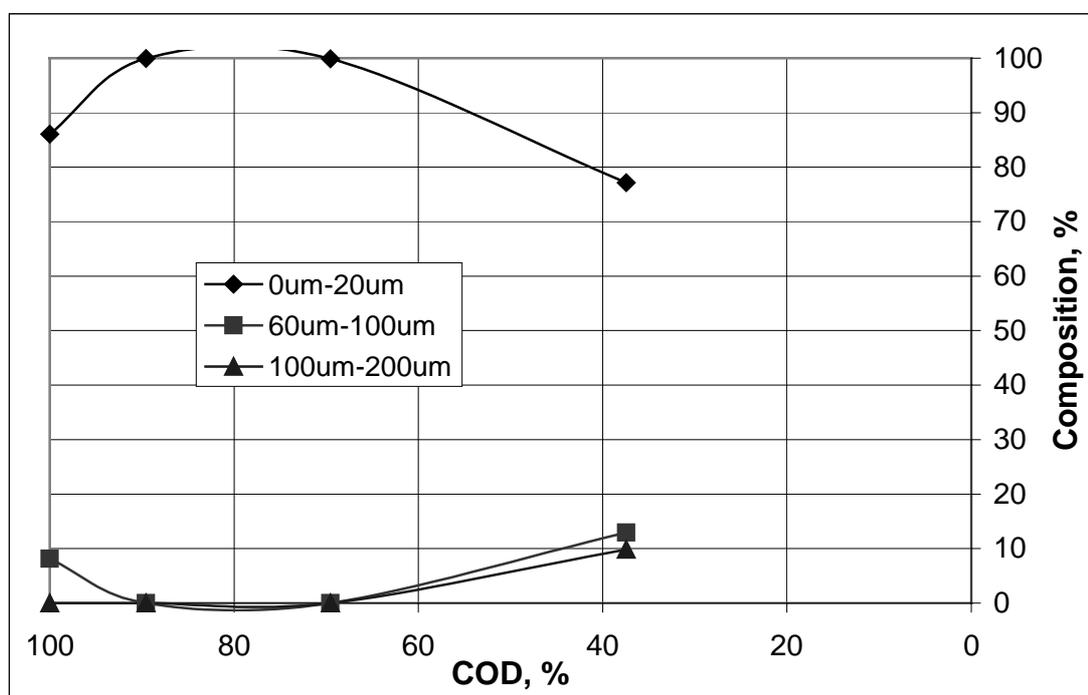


Figure 4.2.12. Dependence of TiO₂ (1 g/L) fraction composition on the presence of by-products of 2-ethoxyethanol (100 mg/L) during PCO without mixing

Slight agglomeration of the particles was established during PCO of 2-ethoxyethanol without mixing (Fig. 4.2.12). Agglomeration reaches maximum at the end of oxidation at about 38 % of initial COD, when the fraction of large particles (100 μm -200 μm) was detected. Consequently, within the decreasing mixing time the agglomeration of particles occurred.

4.3 Mineral Additives Presence

3.4.1 Influence of Ferric, Ferrous and Manganese Ions

The effect of multivalent metallic ions (ferric, ferrous and manganese) presence on the PCO of ethylene glycol and 2-ethoxyethanol aqueous solutions was studied for the concentrations up to 100 mM under acidic conditions (Fig. 4.3.1 and Fig. 4.3.2; Appendix II, Tables 4.15-4.20).

The literature survey showed the beneficial effect of ferric ions on phenol PCO efficiency (see paragraph 2.4.1 from the literature review). However the results of present research demonstrate the injurious influence on ferric ions on the degradation rate of the de-icing agents.

The experimental results indicate that dissolved ferric ions had an evident detrimental effect on the used de-icing agents degradation. The addition of 1 mM of ferric ions reduced the degradation efficiency of ethylene glycol solutions for 68%, and for 2-ethoxyethanol solution – for 75%. With the increasing ions' concentration, further gradual reduction of PCO rate was observed (Fig. 4.3.1 and Fig. 4.3.2).

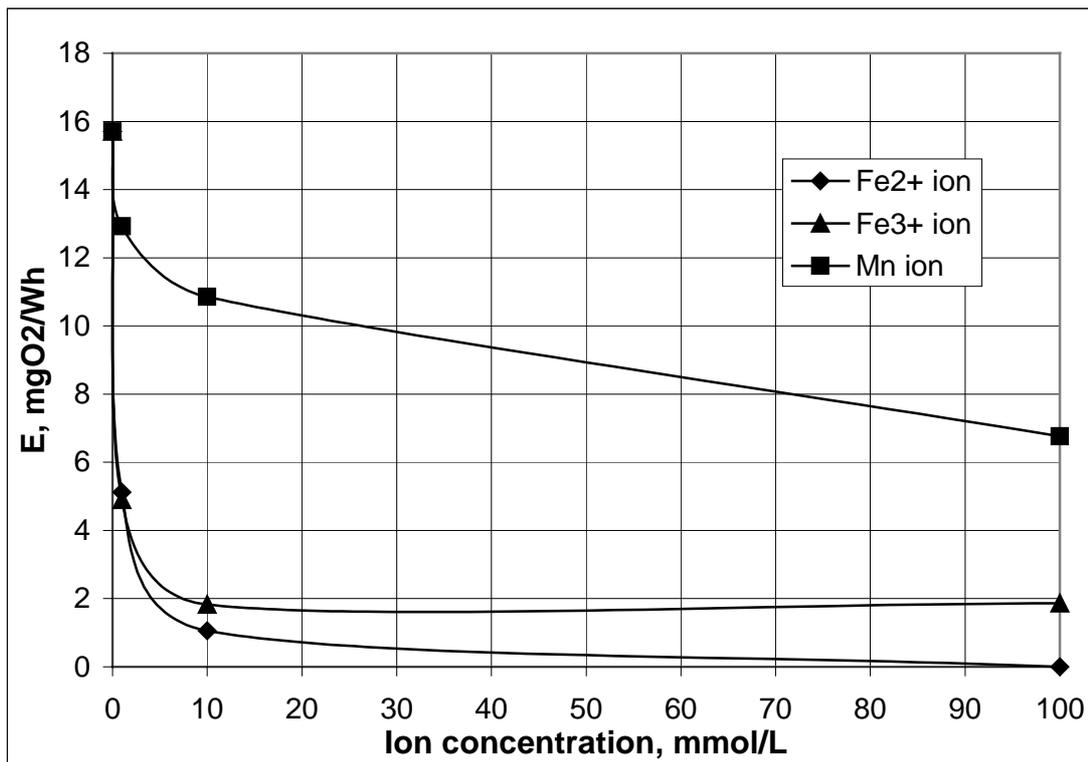


Figure 4.3.1. Dependence of PCO efficiency of ethylene glycol ($C_{\text{initial}}=100$ mg/L) on concentration of ferric, ferrous and manganese ions at pH 3 for 12-hours treatment

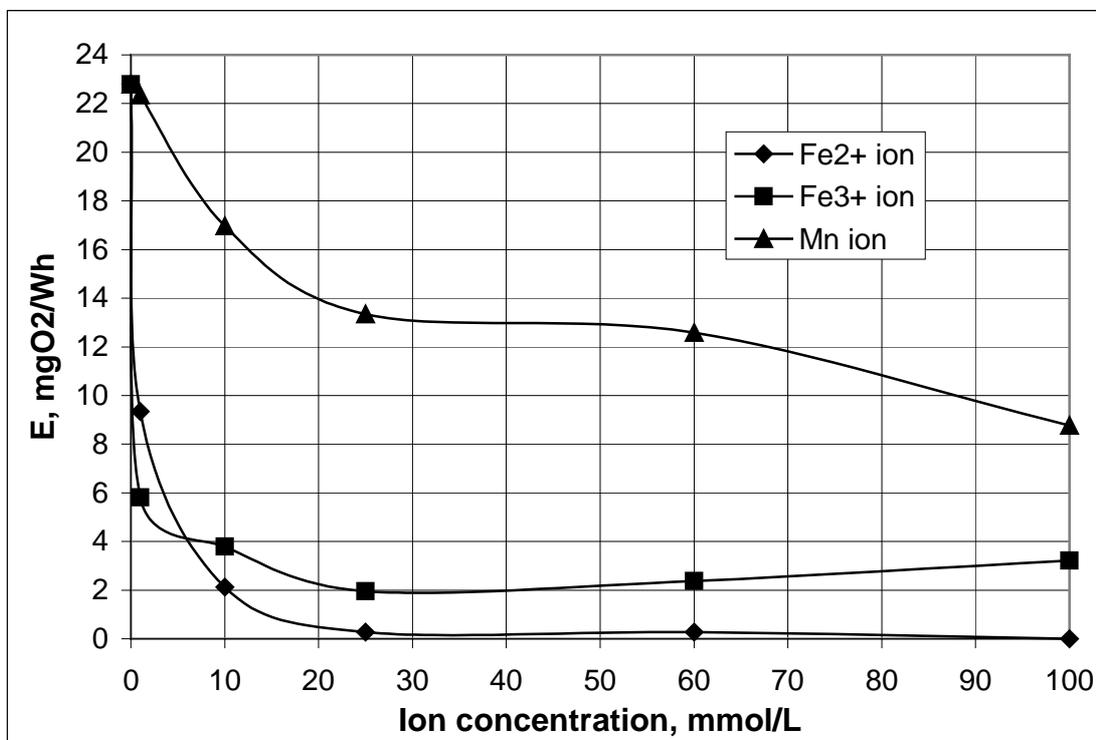


Figure 4.3.2. Dependence of PCO efficiency of 2-ethoxyethanol ($C_{\text{in}}=100$ mg/L) on concentration of ferric, ferrous and manganese ions at pH 3 for 12-hours treatment

Possible inhibition effect of ferric, ferrous and manganese ions on the de-icing agents' degradation rate can be explained by competitive adsorption between cations and the target compound. Multivalent metal ions may also create acceptor and donor surface centers that behave as recombination centers for the photogenerated charge carriers (Brezova et al., 1995).

This judgment confirms the strong interaction of TiO₂ surface with multivalent metal ions, which probably causes the decrease of PCO efficiency of de-icing agents solution.

The results of the experiments with manganese ion presence showed the gradual reduction in PCO efficiency of experimental solutions and are in agreement with the research results of Brezova et.al. (1995). The dependence of degradation rates of target solutions on manganese ion presence at the concentration up to 1 mM is negligible. However, with the enhancement of these ions concentration the degradation rate becomes slower.

The decrease in degradation rate may be explained by electron transfer from metal ions to the photogenerated holes in the valence band. Such process possibly reduces the yield of •OH radicals production resulting in the lower substances degradation rate in present systems (Brezova et al., 1995).

3.4.2 Influence of Calcium Ion

As a result of PCO of organic compounds carbonic acids may be often indicated as by-products. To remove some of them from reaction zone by forming insoluble salts the addition of calcium ions is needed. Therefore, the addition of CaO to the PCO reactor may decrease COD of the treated solution.

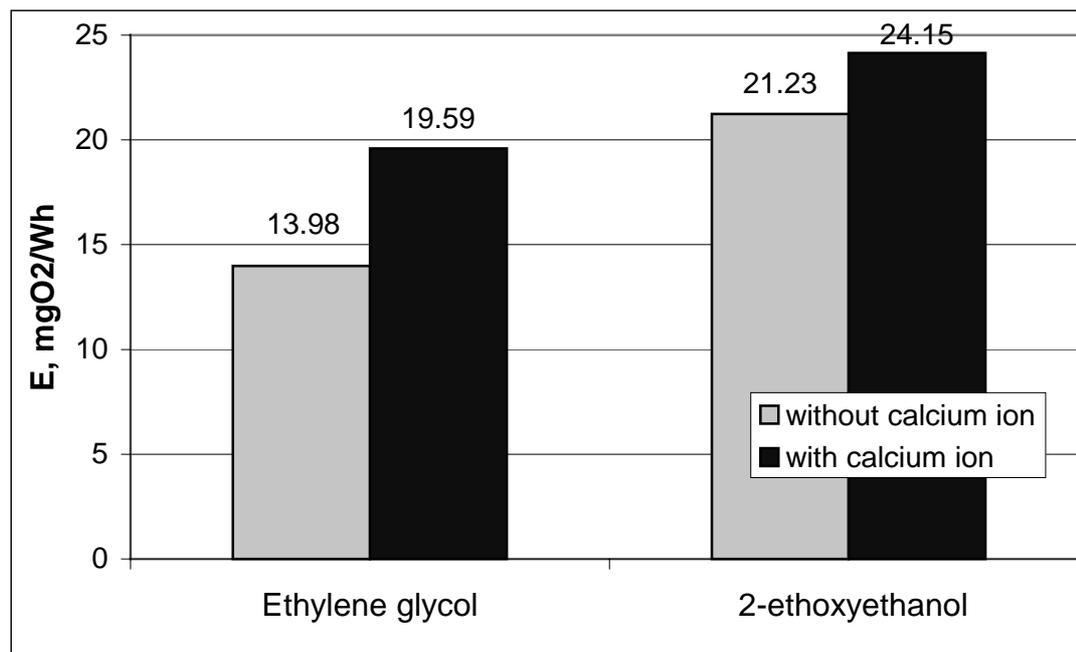


Figure 4.3.3. Influence of calcium ion concentration on PCO efficiency of ethylene glycol and 2-ethoxyethanol ($C_{in}=100$ mg/L) at pH 12 for 12-h treatment

The influence of calcium ions on PCO of aqueous solutions of de-icing agents was investigated using the concentration of CaO – 5 g/L of solution. The results are shown in Figure 4.3.3 and Appendix II, Table 4.21. Presence of calcium hydroxide in the solution increased the degradation efficiency of ethylene glycol and 2-ethoxyethanol – for 40% and 15 % respectively. This fact may be explained by forming of insoluble calcium salts of organic acids and their removal from the solution.

3.4.3 Influence of Sulphate Ion

The dependence of PCO efficiency of ethylene glycol and 2-ethoxyethanol solutions on sulphate ion concentration was experimentally studied at pH 3, 5, 7 and 10, with adding of sulphate ion at concentrations up to 100 mM.

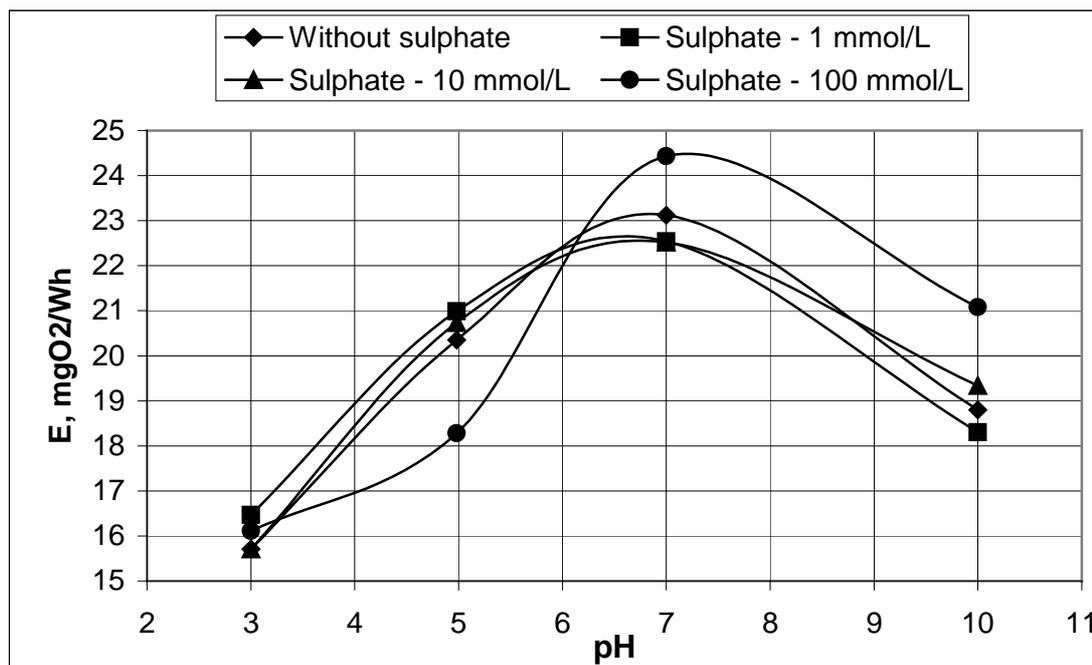


Figure 4.3.4. Dependence of ethylene glycol ($C_{in}=100$ mg/L) PCO efficiency on pH at different concentrations of sulphate ion for 12-h treatment

The effect of sulphate ions on PCO efficiency of ethylene glycol and 2-ethoxyethanol was found to be different and, in general, complex (see Fig. 4.3.4 and Fig. 4.3.5; Appendix II, Tables 4.22-4.29). One can see from Figure 4.3.4 that the dependence of ethylene glycol degradation on the presence of sulphate ion in lower concentrations - up to 10 mM - was negligible. This can be attributed to a competitive adsorption on the surface of the catalyst of these anions and molecules of ethylene glycol - the sulphate also might react with $\bullet\text{OH}$ radicals to produce sulphate radicals (Abdulah et al., 1990).

The exception was observed for the sulphate ions concentration of 100 mM/L at pH 5, 7 and 10. At pH 5 an inhibitive effect of SO_4^{2-} ions addition (10 %) was observed. However the enhancement of PCO efficiency of ethylene glycol was detected at pH 7 (6 %) and pH 10 (12 %). Such slightly promotion of oxidation at high concentration of sulphate (100 mg/L) might be caused by the elimination of negative ion adsorption and a small extent of the participation of sulphate radicals from a series of reactions following photolysis of water (Wang et al., 2000).

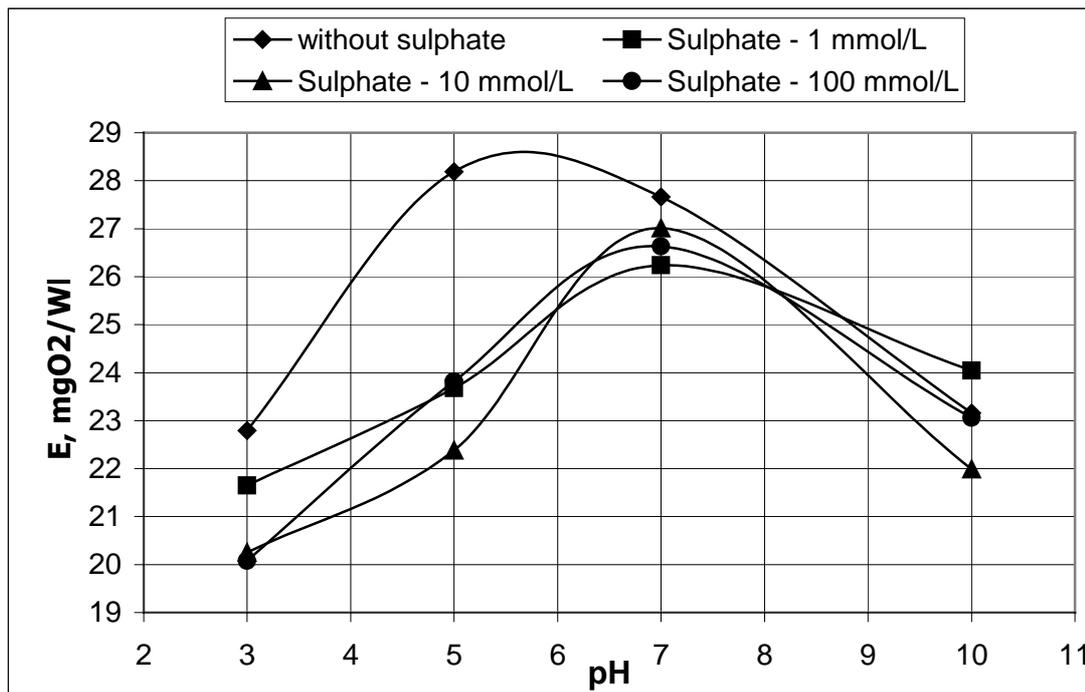


Figure 4.3.5. Dependence of 2-ethoxyethanol ($C_{in}=100$ mg/L) PCO efficiency on pH at different concentrations of sulphate ion for 12-h treatment

The dependence of 2-ethoxyethanol degradation rate on SO_4^{2-} ions addition can be seen on Fig. 4.3.5. The addition of sulphate ion was found to affect the process negatively at pH 3 and pH 5. The highest detrimental effect was established at pH 5 – at the concentration of sulphate ions 10 mM/L the PCO efficiency decreased for 20%. These results confirm that the influence of anions is dependent on pH of aqueous solution (Wang et al., 2000). The inhibitive effect was larger under acidic conditions. The main explanation is the acid/base properties of TiO_2 Degussa surface – strong adsorption with $TiOH_2^+$ at low pH and repulsion of SO_4^{2-} ion by TiO^- at basic pH.

At the same time the insignificant influence of SO_4^{2-} ions addition – lesser than 5 % - was detected at pH 7 and pH 10. It can be explained by the fact that $Ti-O^-$ is predominant at pH 7 and pH 10 for Degussa P25 TiO_2 , so the adsorption of sulphate can be neglected (Wang et al., 2000).

The obtained results of the anions' influence on 2-ethoxyethanol are comparable with the literature survey and can be explained logically. However, the obtained results with ethylene glycol cannot find an explanation in present paper. Moreover, the

difference between the sulphate influence on ethylene glycol and 2-ethoxyethanol may be attributed to the inaccuracy of the experiments.

The result showed that in case of different substances the dependence of PCO efficiency on the presence of mineral additives is also different. This fact makes the installation of PCO as a practical treatment method very complicated: every contaminated water system needs its particular research and should be tested individually experimentally.

5 CONCLUSIONS

De-icing agents and jet fuel aqueous solution readily yield to PCO over UV-irradiated titanium dioxide. The experiments confirmed that neutral medium is preferable for the oxidation. The efficiency of PCO depends on the initial concentrations of 2-ethoxyethanol. Under conditions of present study the process efficiency steadily increases with the increasing of 2-ethoxyethanol concentration. The decreasing point of the efficiency was not achieved within the studied concentration range, even with initial concentration of pollutant 2000 mg/L.

The addition of tert-butanol as a radical scavenger resulted in reduction of PCO efficiency of 2-ethoxyethanol mostly in alkaline medium, which indicated that the radical mechanism plays certain, although not dramatic, role in PCO of de-icing agents.

The investigations of the energy saving PCO showed that the decrease in PCO efficiency of 2-ethoxyethanol due to reduced mixing appeared to be independent on pH. The results of the research showed 50 % loss in jet fuel aqueous extract PCO efficiency in case of oxidation without mixing compared to constant mixing. However, for 2-ethoxyethanol solutions the losses in PCO efficiency contained 35 %. Results showed that UV-transparent de-icing agents may be effectively removed from the solution by PCO with reduced or even no stirring of TiO₂ slurries. Application of

buoyant photocatalyst appeared to be justified in the treatment of jet fuel aqueous extract due to its UV screening properties.

Visual observations during the investigations of PCO of de-icing agents showed, that the most stable form of TiO_2 suspension was in neutral medium both in pure water and in aqueous solution of pollutants. At the same time, the highest sedimentation was observed in acidic medium.

The TiO_2 suspension fractional composition was found to be dependent on pH and the presence of organic admixtures. The maximum percentage of the finest TiO_2 particles was established for acidic medium, where efficiency of de-icing agents' PCO was the poorest. On other hand, neutral medium, beneficial for PCO efficiency, was favourable for particles agglomeration, which indicates minor role of the photocatalyst particles size in PCO efficiency: the effect of pH is attributed to adsorption issues.

Reducing mixing during the PCO also influenced the particle size distribution. Within the constant mixing agglomeration of particles occurred as PCO of 2-ethoxyethanol proceeded. Fraction composition of TiO_2 suspension during the PCO without mixing seems analogous, compare to the constant mixing. However, periodical mixing 15 min/h did not allow particles to agglomerate, episodically crashing the coarse fractions.

The PCO efficiency of de-icing agents was found to be dependent on the presence of mineral admixtures. Ferric, ferrous and manganese ions inhibited the oxidation rate. The effect of sulphate presence was found to be complex: its influence on PCO efficiency depends on pH and concentration of sulphate. However, the present research confirms the findings of previously published reports that the influence of mineral additives on PCO rate of different substances is also different. Therefore every particular water system requires an individual experimental research of mineral additives' effect.

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