



Tatjana Karpova

**AQUEOUS PHOTOCATALYTIC OXIDATION OF
STEROID ESTROGENS**

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ABSTRACT

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Concerns have increased regarding the detection of endocrine-disrupting compounds in the effluents of sewage treatment plants (STPs). These compounds are able to disrupt normal function of the endocrine system of living organisms even at trace concentrations. Natural and synthetic steroid estrogens (SEs) are believed to be responsible for the majority of the endocrine-disrupting effects. Municipal sewage, the main source of SEs in the environment, is a complex mixture of a wide range of pollutants at concentrations much higher than those of SEs. Low concentrations of SEs in the presence of co-pollutants thus make their removal problematic.

The main objectives of the present work were to study the potential of photocatalytic oxidation (PCO) to effectively treat SE-containing aqueous solutions and to identify the optimum conditions for such treatment. The results showed that SEs can be effectively degraded photocatalytically. Due to the adsorption properties of SEs on the TiO₂ photocatalyst surface alkaline medium was found to be beneficial for SE oxidation despite the presence of co-pollutants in concentrations characteristic for the sanitary fraction of municipal sewage.

The potential of PCO to selectively oxidise SEs was examined in the presence of co-pollutants of the sanitary fraction of sewage - urea, saccharose and human urine. The impact of ethanol, often used as a solvent in the preparation of SE stock solutions, was also studied and the results indicated the need to use organic solvent-free solutions for the study of SE behaviour. Photocatalytic oxidation of SEs appeared to be indifferent towards the presence of urea in concentrations commonly found in domestic sewage. The effect of other co-pollutants under consideration was far weaker than could be expected from their concentrations, which are from one hundred to a few thousands times higher than those of the SEs. Although higher concentrations can dramatically slow down the PCO of SEs, realistic concentrations of co-pollutants characteristic for the sanitary fraction of domestic sewage allowed selective removal of SEs. This indicates the potential of PCO to be a selective oxidation method for SE removal from the separate sanitary fraction of municipal sewage.

Keywords: β -estradiol (E2); 17 α -ethynylestradiol (EE2); sucrose; starch; wastewater; photocatalysis; titanium dioxide; advanced oxidation processes; environmental pollution

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Lappeenranta, July 2007

Tatjana Karpova

TABLE OF CONTENTS

| | |
|---|-----------|
| ABSTRACT..... | 3 |
| ACKNOWLEDGEMENTS..... | 5 |
| TABLE OF CONTENTS..... | 7 |
| LIST OF PUBLICATIONS | 9 |
| LIST OF ABBREVIATIONS AND SYMBOLS | 11 |
| 1 INTRODUCTION..... | 13 |
| 2 ENVIRONMENTAL CONTAMINATION WITH STEROID ESTROGENS... 16 | 16 |
| 2.1 ENDOCRINE SYSTEM AND STEROID ESTROGENS | 16 |
| 2.1.1 <i>Nature of steroid estrogens.....</i> | <i>17</i> |
| 2.1.2 <i>Mechanism of endocrine disruption.....</i> | <i>19</i> |
| 2.1.3 <i>Occurrence of SEs in aquatic environment</i> | <i>21</i> |
| 2.1.4 <i>Health effects</i> | <i>22</i> |
| 2.2 CONVENTIONAL SEWAGE TREATMENT PLANT AND ITS ROLE IN AQUATIC CONTAMINATION WITH STEROID ESTROGENS | 23 |
| 2.2.1 <i>Sewage and its treatment</i> | <i>23</i> |
| 2.2.2 <i>Removal of trace pollutants in STP</i> | <i>24</i> |
| 2.2.3 <i>Fate of steroid estrogens in STP.....</i> | <i>25</i> |
| 2.2.4 <i>Environmental potencies of aquatic steroid estrogens.....</i> | <i>26</i> |
| 2.2.5 <i>Removal rates of steroid estrogens in conventional STP.....</i> | <i>28</i> |
| 2.2.6 <i>Steroid estrogens in surface waters</i> | <i>29</i> |
| 2.2.7 <i>Proposals for steroid estrogens elimination improvement in STP</i> | <i>30</i> |
| 2.3 POTENTIAL TREATMENT STRATEGIES FOR EFFECTIVE STEROID ESTROGEN REMOVAL..... | 31 |
| 2.3.1 <i>Biodegradation and separation technology.....</i> | <i>31</i> |
| 2.3.2 <i>Advanced oxidation processes</i> | <i>31</i> |
| 2.3.3 <i>Treatment costs</i> | <i>35</i> |
| 3 AQUEOUS PHOTOCATALYTIC OXIDATION..... 36 | 36 |
| 3.1 MECHANISM OF OXIDATION..... | 36 |
| 3.2 PHOTOCATALYTIC PROPERTIES OF TITANIUM DIOXIDE | 41 |
| 3.3 PARAMETERS INFLUENCING PCO | 42 |
| 3.3.1 <i>Effect of pH and adsorption.....</i> | <i>43</i> |
| 3.3.2 <i>Initial concentration of contaminant</i> | <i>44</i> |
| 3.3.3 <i>Catalyst application mode and amount</i> | <i>45</i> |
| 3.3.4 <i>Other factors</i> | <i>46</i> |
| 3.4 REACTION KINETICS..... | 47 |
| 3.5 ADVANTAGES AND DISADVANTAGES OF PCO | 48 |
| 4 PHOTOCATALYTIC OXIDATION OF STEROID ESTROGENS: AN OVERVIEW | 50 |
| 5 PRESENT RESEARCH OBJECTIVES AND STRATEGY..... 53 | 53 |
| 6 EXPERIMENTAL..... 54 | 54 |

| | | |
|------------|--|-----------|
| 6.1 | MATERIALS | 54 |
| | 6.1.1 <i>Target compounds</i> | 54 |
| | 6.1.2 <i>Co-pollutants</i> | 55 |
| | 6.1.3 <i>Photocatalyst</i> | 56 |
| 6.2 | METHODS | 57 |
| 6.3 | ANALYSIS | 58 |
| 7 | RESULTS AND DISCUSSION | 60 |
| 7.1 | PCO OF STEROID ESTROGENS IN THE PRESENCE OF ETHANOL | 60 |
| | 7.1.1 <i>Photocatalyst concentration</i> | 61 |
| | 7.1.2 <i>Influence of pH</i> | 62 |
| | 7.1.3 <i>Influence of urea</i> | 64 |
| | 7.1.4 <i>Influence of saccharose</i> | 65 |
| 7.2 | INFLUENCE OF ETHANOL | 66 |
| 7.3 | PCO OF STEROID ESTROGENS WITHOUT ETHANOL | 67 |
| | 7.3.1 <i>Influence of urea</i> | 69 |
| | 7.3.2 <i>Influence of saccharose</i> | 69 |
| | 7.3.3 <i>Influence of urine</i> | 69 |
| | 7.3.4 <i>Kinetic studies</i> | 70 |
| | CONCLUSIONS | 73 |
| | REFERENCES | 75 |
| | APPENDICES | 87 |

LIST OF PUBLICATIONS

The thesis includes the following scientific publications, referred to in the text as Appendices 1-5.

1. T. Malygina, S. Preis and J. Kallas (2005) The role of pH in aqueous photocatalytic oxidation of β -estradiol, *International Journal of Photoenergy*, **7**, 187-191
2. T. Malygina, S. Preis and J. Kallas (2006) Photocatalytic oxidation and adsorption of natural and synthetic steroid estrogens on TiO₂ in aqueous solutions at different pH, In: W. Höflinger, Ed., *Chemical Industry and Environment V*, Inst. Chem. Eng., Vienna Univ. Technol., **1**, 339-347 (Communications of the 5th European Meeting on Chemical Industry and Environment, Vienna, May 3-5, 2006)
3. T. Karpova (previously T. Malygina), S. Preis and J. Kallas (2007) Selective photocatalytic oxidation of steroid estrogens in water treatment: urea as co-pollutant, *Journal of Hazardous Materials*, **146**, 465-471
4. T. Karpova, A. L. Barros Torres, S. Preis and J. Kallas (2007) Selective photocatalytic oxidation of steroid estrogens in presence of saccharose and ethanol as co-pollutants, *Environmental Chemistry Letters*, in press
5. T. Karpova, S. Preis and J. Kallas (2007) Selective photocatalytic oxidation of steroid estrogens in the presence of copollutants in the sanitary fraction of domestic sewage, *International Journal of Photoenergy*, **2007**, Article ID 53853, 8 p.

The author's contribution to the content of the publications is as follows:

All experimental work presented in this thesis has been carried out by the author, except for a small part of the adsorption of synthetic estrogen and a part of the adsorption and PCO of saccharose, performed by two undergraduate students under supervision of the author.

1. The author initiated the idea of the application of photocatalytic oxidation to the treatment of wastewater contaminated with steroid estrogens. The author carried out all the experiments and made all the necessary calculations. She interpreted the results and wrote the paper together with the co-authors.
2. The author planned and performed the experimental work, and supervised the work of the undergraduate student. The author made all the calculations, interpreted the results and prepared the manuscript for publication.
3. The author carried out all the experimental and calculation work. She wrote the paper based on the obtained results.
4. The author performed the experimental work, planned and supervised the work of the undergraduate student, who contributed part of the data of saccharose adsorption and PCO. The author interpreted the results and wrote the paper together with the co-authors.
5. All the experiments and calculations were made by the author. The paper was written by the author together with the co-authors.

LIST OF ABBREVIATIONS AND SYMBOLS*Abbreviations*

| | |
|--------|---|
| AOP | Advanced Oxidation Process |
| COD | Chemical Oxygen Demand |
| EDC | Endocrine-Disrupting Compound |
| E1 | Estrone |
| E2 | 17 β -Estradiol |
| E3 | Estriol |
| EE2 | 17 α -Ethinylestradiol |
| EPA | Environmental Protection Agency |
| HR | Hormone Receptor |
| HRE | Hormone Response Elements |
| HRT | Hydraulic Retention Time |
| HRTh | Hormone Replacement Therapy |
| hsp | heat shock proteins |
| MeEE2 | Mestranol |
| mRNA | messenger RNA |
| PCO | Photocatalytic Oxidation |
| Pol II | Polymerase 11 |
| eq. | equation |
| REACH | Registration, Evaluation and Authorisation of Chemicals |
| RNA | Ribonucleic Acid |
| SE | Steroid Estrogen |
| SRT | Sludge Retention Time |
| STP | Sewage Treatment Plant |
| TOC | Total Organic Carbon |
| UV | Ultraviolet |
| VTG | Vitellogenin |

Symbols

| | |
|--------|---|
| A, B | reactant or reagent |
| Ac | acceptor |
| Cat | catalyst |
| D | donor |
| c | concentration of reactant [$\mu\text{g L}^{-1}$] |
| c_0 | initial concentration of reactant [$\mu\text{g L}^{-1}$] |
| e^- | electron |
| E | PCO efficiency [$\text{mg W}^{-1} \text{h}^{-1}$ per $\text{g L}^{-1} \text{TiO}_2$] |
| h^+ | positively charged hole |
| $h\nu$ | photonic energy |
| I | irradiation intensity [mW cm^{-2}] |
| k | apparent reaction rate constant [min^{-1}] |
| K | Langmuir adsorption coefficient of reactant [$\text{L } \mu\text{g}^{-1}$] |
| m | concentration of TiO_2 [g L^{-1}] |
| q | equilibrium surface concentration [$\text{mg g}^{-1} \text{TiO}_2$] |
| r | PCO reaction rate [$\mu\text{g L}^{-1} \text{min}^{-1}$ or $\mu\text{mol dm}^{-3} \text{min}^{-1}$] |
| R^2 | correlation coefficient |
| s | solution irradiated surface area [cm^2] |
| t | time [h] |
| V | volume [L] |

1 INTRODUCTION

In recent years various international and local regulations have become stricter concerning the amounts of pollutants in wastewaters and the quality of the treated effluents discharged into the aquatic environment. However, many natural and synthetic pollutants are not generally monitored and controlled, although they are known or suspected to cause harmful ecological effects and can be deleterious to human health.

Such contaminants are usually present in trace concentrations, posing an environmental problem at microgram or even nanogram per litre levels. They are only partially removed and can resist in conventional water treatment processes. Widespread concerns are being raised due to the increasing number of cases when such contaminants are detected in surface water bodies, and due to their potential to affect the development, reproduction and health of wildlife, livestock and even humans. Evidence has emerged that these contaminants are able to interact with and disrupt the endocrine systems of living organisms and, thus, such pollutants have been labelled endocrine-disrupting compounds (EDCs). The growing group of substances under consideration includes industrial chemicals (phthalates, phenolics, polychlorinated biphenyls, organochlorine pesticides, etc.), synthetic pharmaceuticals and some natural steroid estrogens (SEs).

Of the recognized EDCs, natural and synthetic SEs are believed to be responsible for the majority of endocrine-disrupting effects on living organisms. SEs have high estrogenic activity as they are potent already at the fraction of ng L^{-1} concentrations, while most other EDCs are active at $\mu\text{g L}^{-1}$ level (Purdom et al., 1994; Pettersson et al., 2006). These compounds have been detected in different concentrations in surface waters all over the world, however only few abatement strategies have been proposed.

Extensive literature analysis indicates that the detection of EDCs is a topic of great interest in environmental water contamination. Concern over the potential consequences of exposure to EDCs has attracted increasing attention of national and international organisations like the European Commission, the European Parliament, the US

Environmental Protection Agency (EPA), the World Health Organisation, the International Programme on Chemical Safety, non-governmental organizations, and the chemical industry (Mendes, 2002; Matthiessen and Johnson, 2007). The European Commission defined an EDC as “an exogenous compound that causes adverse health effects in an intact organism, or its progeny, consequent to changes in endocrine function” (European Commission, 1997). Several major research projects on EDCs have been carried out: the European Union’s Poseidon and Repharmawater projects, the US EPA projects, and the Australian Water Conservation and Reuse Research Program (Ternes et al., 2004; Ternes et al., 2005; Ying et al., 2004).

New European legislation for the Registration, Evaluation and Authorisation of Chemicals (REACH) was proposed by the European Commission in 2003. The aim of this regulation is better and earlier identification of the properties of chemical substances in order to improve protection of the environment and human health. The REACH Regulation was adopted in the end of 2006 by the Council of Environment Ministers and the European Parliament and came into force on 1 June 2007. A European Chemicals Agency was established to control the implementation of REACH regulations (Official Journal of the EU, 2006; Matthiessen and Johnson, 2007).

In anticipation of future stricter regulations the development of new techniques which are able to eliminate such pollutants is essential. Such techniques should not replace the traditional treatment system, but act as a supplement to improve the quality of discharge waters.

Along with a number of other techniques for water treatment, advanced oxidation processes (AOPs) are widely studied. These processes utilise powerful oxidising species to degrade various organic pollutants in contaminated water and air. The chemical reactions involved are basically similar to those that occur in the environment, but the reaction rate is much faster.

Photocatalytic oxidation (PCO), an AOP, is considered a prospective technology for elimination of organic pollutants under mild conditions of pressure and temperature. This

promising method offers many advantages over conventional and some advanced abatement strategies. There is considerable research in this area throughout the world and the results are highly promising (Blake et al., 1991). Thus research in the application of PCO to the elimination of the pollutants of contemporary environmental concerns is very attractive.

The scope of the present dissertation work was study of the applicability of PCO to the elimination of SEs from wastewaters, analysis of optimum process conditions, and approximation of the research conditions to real ones.

2 ENVIRONMENTAL CONTAMINATION WITH STEROID ESTROGENS

2.1 Endocrine system and steroid estrogens

An endocrine system is a network of glands, hormones and receptors. Along with the nervous system, it maintains and regulates the body's growth, development, immunity, reproduction and other functions and responses. Ductless glands produce, store and secrete directly into the blood stream a number of hormones. The endocrine system includes the adrenal, pituitary, thyroid, parathyroid glands, pancreas and gonads (testes in males and ovaries in females). The pineal and thymus glands and kidneys are also sometimes included in the endocrine system. Nearly all animals, including mammals, non-mammalian vertebrates (birds, fish, reptiles, amphibians) and invertebrates (insects, snails, etc) have an endocrine system (Ying et al., 2004).

A hormone is a biochemical, the production of which causes a specific biological change or activity in another cell or tissue located elsewhere in the body. Hormones operate as chemical messengers and interact with specific receptors to generate normal responses and biological functions. Generally, there are four main types of hormones: proteins, amino acid derivatives, eicosanoids and steroids (Lister and van der Kraak, 2001).

Steroid hormones are one of a group of biologically active organic compounds that are secreted by the adrenal cortex, testis, ovary, and placenta. They are synthesized from cholesterol and are characterised by the presence of a cyclopentane-o-perhydrophenanthrene ring (Figure 1). Estrogens are a group of steroid hormones that regulate and sustain the female sexual development and reproductive function (Dictionary of Science and Technology, 1992).

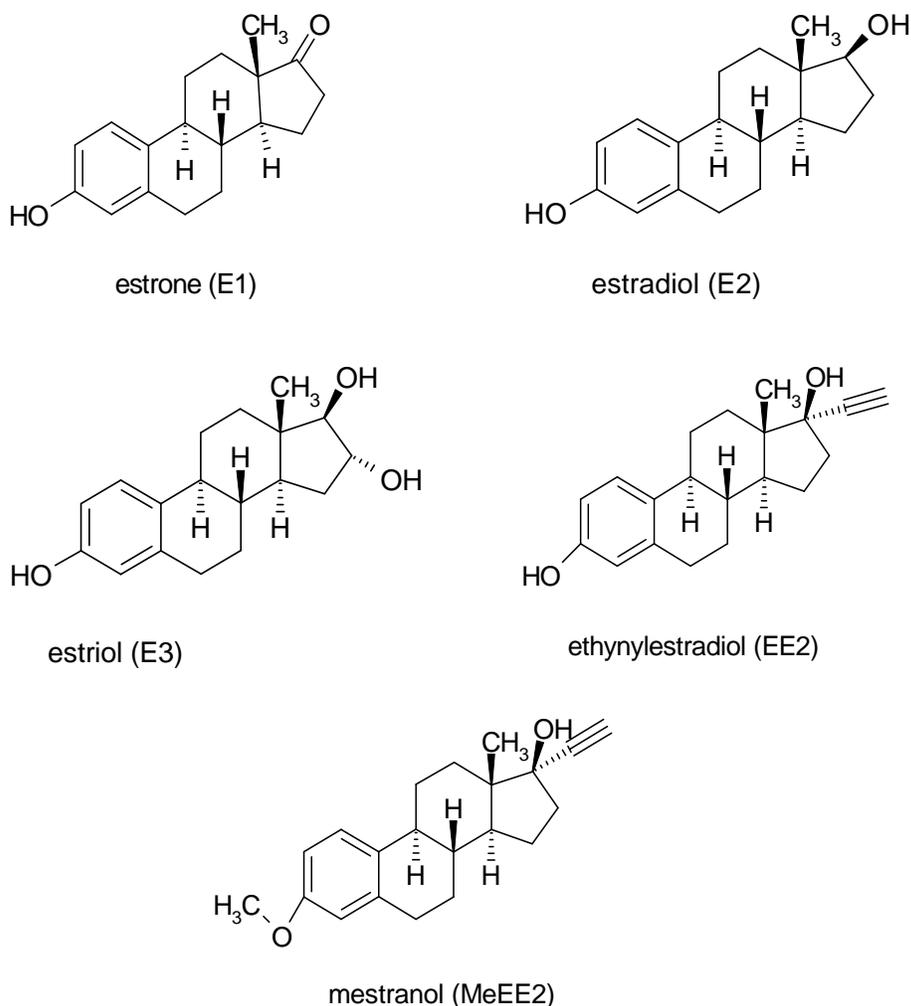


Figure 1. Molecular structures of SEs

2.1.1 Nature of steroid estrogens

Natural estrogens

Although natural SEs are present in both male and female organisms, they are usually present at considerably higher levels in females of reproductive age. SEs play an important role in growth, development and puberty, and influence many body parts (skin, bones, arteries, brain) (Hess et al., 1997). In females, SEs are involved in the development of secondary sex characteristics and in regulating the menstrual cycle and pregnancy. In males, the purpose of estrogen is to control certain functions of the

reproductive system (maturation of sperm); it is also required for healthy libido (Stryer, 2000).

The amounts of natural SEs vary depending on species, age, sex or reproductive stage. The three major naturally occurring estrogens in women are estrone (E1), 17 β -estradiol (E2), and estriol (E3). E2, referred to as a “female” hormone but present in both females and males, is a most important estrogen in humans. It not only has a vital impact on reproductive and sexual functions, but also affects other organs. In a female organism E2 is secreted by the ovaries and it is the primary estrogen until menopause. E2 levels vary through the menstrual cycle, with levels highest just before ovulation. E1 is formed from E2 and represents a weaker estrogen; it is predominant in postmenopausal women. Weak estrogen E3 is produced in large amounts during pregnancy and is a breakdown product of E2 (Dictionary of Science and Technology, 1992).

There is also a group of compounds called phytoestrogens, natural plant chemicals generally found in food, which can have "estrogen like" effects in the body (Dictionary of Science and Technology, 1992).

Synthetic estrogens

Synthetically produced SEs are used in pharmaceuticals as part of birth control pills and other contraceptives, in hormone replacement therapy (HRTh), and in some countries also for cattle hormonal growth promotion in farming.

17 α -ethinylestradiol (EE2), a synthetic form of E2, is a main active component of hormonal contraceptives to prevent ovulation and, thus, pregnancy. Oral contraceptives contain between 30 and 50 μ g of EE2 per pill (Desbrow et al., 1998).

Hormone replacement therapy (HRTh) is a system of medical treatment for menopausal, perimenopausal and postmenopausal women to prevent discomfort and health problems caused by reduced hormone levels. A series of drugs intended to artificially boost hormone levels are applied in this treatment. HRTh is also used by transgender or

transsexual people to attain the secondary sex characteristics of their desired sex. Synthetic SEs are among the major types of hormones involved in HRTh (Handbook of Chemistry and Physics, 1976).

Hormonal animal growth promotion is widespread in those countries where it is licensed. In general, most growth promotion implants for cattle contain a combination of up to 20 mg of estrogens and 200 mg of androgens or progesterone (Dictionary of Science and Technology, 1992).

Physico-chemical properties

From the physico-chemical properties in Table 1, one can see that SEs are hydrophobic organic compounds. The solubilities of natural SEs are approximately 13 mg L^{-1} , while synthetic EE2 and mestranol (MeEE2) has much lower solubility of 4.8 mg L^{-1} and 0.3 mg L^{-1} respectively. The low vapour pressures indicate low volatility of SEs.

Table 1. Physico-chemical properties of SEs (Lai et al., 2000)

| Name of SE | Molecular weight | Water solubility (mg L^{-1} at 20°C) | Vapour pressure (mm Hg) |
|------------|------------------|---|-------------------------|
| E1 | 270.4 | 13 | $2.3 \cdot 10^{-10}$ |
| E2 | 272.4 | 13 | $2.3 \cdot 10^{-10}$ |
| E3 | 288.4 | 13 | $6.7 \cdot 10^{-10}$ |
| EE2 | 296.4 | 4.8 | $4.5 \cdot 10^{-10}$ |
| MeEE2 | 310.4 | 0.3 | $7.5 \cdot 10^{-10}$ |

2.1.2 Mechanism of endocrine disruption

Some compounds can interfere with the endocrine system, disturbing the homeostatic mechanisms of the body or initiate processes at wrong times of the life cycle. Human and wildlife are exposed to phytoestrogens daily. The lack of harmful effects of

phytoestrogens on health may be explained by slow adaptation during the co-evolution of plants and mammals (Sonnenschein and Soto, 1998). However, sudden exposure of organisms to SEs, which are foreign to their natural ecosystems, and even changes in the amount of native SEs may result in negative effects on health.

Generally, hormones are bound to sex hormone binding globulins and in this form they are transported through the blood. Free hormones readily diffuse across cell membranes and bind to inactive hormone receptors (HRs). HRs are specific intracellular molecules that are present in the nucleus and cytoplasm and are activated by the binding of specific steroid hormones, mediating their biological effects. HRs are found in many tissues, including reproductive organs and secondary sex organs, bones, liver and brain. (Dictionary Science and Technology, 1992). The interaction of a hormone with its HR initiates the biological activity that leads to the countless effects associated with the particular hormone (Mendes, 2002).

Inactive HRs are associated with heat shock proteins (hsp) (Figure 2). With binding of SE to a HR, the hsp disassociate and provoke a conformational change that activates the receptor. Activated dimers then bind to hormone response elements (HRE) of genes in the nucleus. This process stabilises the binding of transcription factors involved in gene activation and transcription (Figure 2). Transcriptional factors (B, D, E, F) and ribonucleic acid (RNA) polymerase II (Pol II) are recruited for transcription. Following transcription, messenger RNA (mRNA) is translated into protein by ribosomes. Consequently, by producing new proteins that alter cellular functions, foreign hormones can interfere with cell function and physiology (Ing and O'Malley, 1995).

Summarising, there are several mechanisms for foreign SEs which interfere with the endocrine system: (a) mimicking the effects of natural hormones via binding to the receptor; (b) binding to the receptor without its activation and preventing the binding of natural hormones; (c) reacting directly or indirectly with hormone structure and thus altering it; (d) interfering with synthesis and metabolism of natural hormones; (e) binding to transport proteins altering the levels of natural hormones in the blood circulation (Baker, 2001).

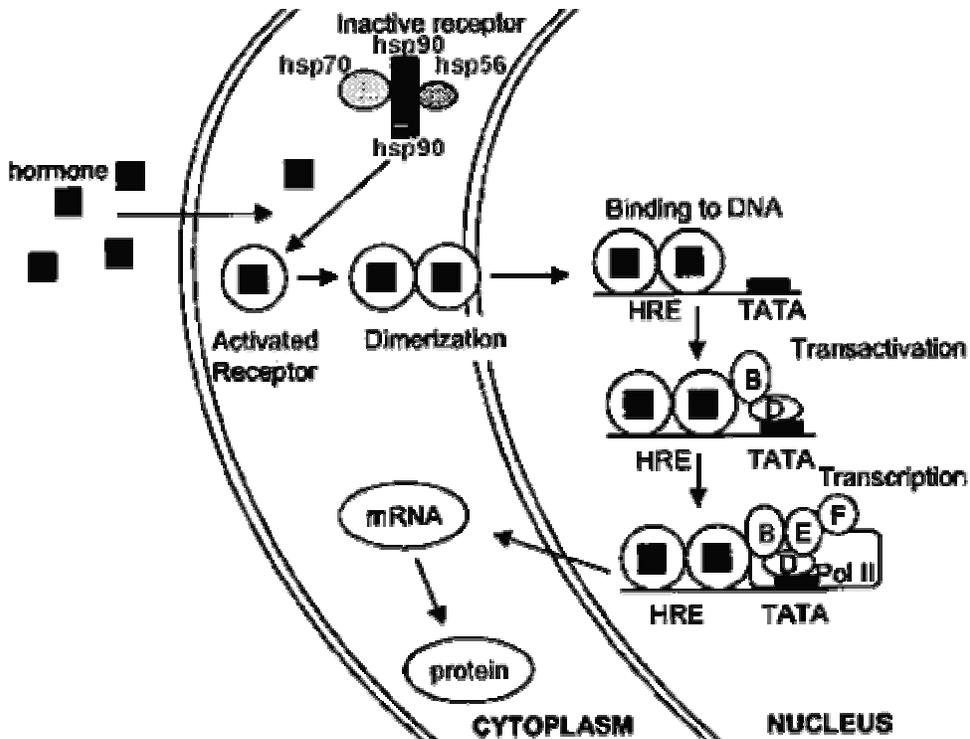


Figure 2. The mechanism of steroid hormone receptor action in the cell (Ing and O'Malley 1995)

2.1.3 Occurrence of SEs in aquatic environment

There are several sources and pathways for the exposure of SEs to the environment, for example, wastewaters from production of synthetic SEs in pharmaceutical industry and runoff waters from agriculture. Intensive farming with both natural and synthetic SEs in its runoff waters also acts as a SE contributor to environmental contamination with SEs. However, the most important source of SEs in the environment is domestic sewage. Natural SEs together with the residues of synthetic ones, originating from contraceptives and other pharmaceuticals, are excreted by humans mainly through urine. Table 2 represents the approximated daily amounts of human excreted SEs. The increasing amount of SEs in domestic sewage is due to the growing world population and the increasing urbanisation and consequently consumption of synthetic SEs.

Table 2. Daily excretion (μg) of SEs in humans (Johnson et al., 2000)

| Category | E1 | E2 | E3 | EE2 |
|-----------------------|-----|-----|------|-----|
| Males | 3.9 | 1.6 | 1.5 | |
| Menstruating females | 8 | 3.5 | 4.8 | |
| Menopausal females | 4 | 2.3 | 1 | |
| Pregnant women | 600 | 259 | 6000 | |
| Women (contraceptive) | | | | 35 |

2.1.4 Health effects

The effects of SEs on the endocrine system can result in health changes of the organism itself or might not be seen until the next generation. The development of embryos and foetuses are especially sensitive to disruption. Although trace amounts of SEs do not affect adults, they can have a crucial impact on the developing embryo. The time of exposure is assumed to be more important than the dose (Ying et al., 2004).

The observed impacts of SEs on wildlife include hermaphrodite fish and polar bears, reproductive failure in birds and abnormalities in the reproductive organs of reptiles, amphibians and non-vertebrates (Jobling et al., 1998; Ahmed, 2000). The health effects on humans include reproductive abnormalities, effects on male to female ratio, decreased sperm counts and quality, both male and female fertility problems (reproductive function, miscarriage, ectopic pregnancy, stillbirth, premature birth), and an increase in certain types of male and female cancers (testicular cancer, prostate cancer, breast cancer), effects on brain and behaviour (Ahmed, 2000; Mendes, 2002; Ferguson, 2002). The studies on the impact of SEs on health of living organisms are still being carried out.

2.2 Conventional sewage treatment plant and its role in aquatic contamination with steroid estrogens

2.2.1 Sewage and its treatment

Sewage, defined correctly, is a type of wastewater that is contaminated with urine and faeces, but the term is often used to mean any wastewater. "Sewage" or wastewater includes human-produced liquid waste from domestic residences, institutions, and in many areas also from business properties and industry, and usually discharged via a pipe or sewer or similar structure. Residential sewage is a mixture of two fractions of wastewater: household or greywater (from baths, showers, sinks, dishwashers, kitchen, etc.) and sanitary or blackwater (from toilets) (Boeije et al., 1998). Frequently, one can use the term "sewage" meaning the municipal wastewater that consists of a broad range of contaminants resulting from the combination of wastewaters from various sources. Occasionally, this combination may also include storm water runoff. Sources of industrial wastewater often require special treatment processes.

Sewage treatment, or domestic wastewater treatment, is a process for removing pollutants from sewage and consists of physical, chemical and biological processes to produce effluent and solid waste (sludge) appropriate to be released back into the environment or reused. However, both effluent and sludge often remain contaminated with toxic organic and inorganic compounds.

The treatment process of sewage is performed in sewage treatment plants (STPs). It generally involves three stages: primary, secondary and tertiary treatment. First, the separation of solids from the stream takes place. Subsequently, dissolved biological matter is converted into sludge using water-borne micro organisms. Finally, the sludge is neutralised and disposed off or re-used, and the treated water can be disinfected. The final effluent is released into a receiving water body.

Sewage systems capable of treating storm water are known as combined systems. Such systems are avoided as they reduce the efficiency of STPs and can overflow the treatment

system during storms. These combined systems are no longer permitted in European countries. Instead storm water is treated separately.

2.2.2 Removal of trace pollutants in STP

Most conventional STPs are not designed to remove trace contaminants and relatively high amounts of these pollutants and their metabolites can be released into the aquatic environment via effluents. The degree of the removal of trace pollutants in STPs essentially depends on the biological treatment stage. Biodegradation or biotransformation of trace contaminants may take place only if a primary organic substrate is available for the bacteria to grow on. Thus, co-degradation probably occurs, in which case the bacteria break down or partially convert the trace pollutant and do not use it as a carbon source. In another possible scenario, mixed-substrate growth takes place and the bacteria use the trace pollutant as a carbon and energy source and may mineralise it totally (Ternes et al., 2004).

The biodegradation of some trace pollutants depends on the age of the activated sludge. When considering for instance SEs, significant decomposition of EE2 was observed only when the sludge age was at least eight days. However, average STPs in Europe and the US do not satisfy these requirements. There are two possible mechanisms explaining the dependence of removal rates of some contaminants on activated sludge age. With increasing sludge age, i.e. extending residence time of micro organisms, the population of bacteria may become more diverse. Alternatively, responding to the lower sludge loading and, thus, lower organic substrate available the bacteria may also diversify their metabolic activity (Ternes et al., 2004).

The redox conditions also affect the degradation activity of bacteria. Joss et al. (2004) reported that the degradation rate of E1 increases in the transition from anaerobic to anoxic as well as between anoxic and aerobic. E2 decomposes at a high rate under all redox conditions, whereas synthetic EE2 degrades only under aerobic conditions.

2.2.3 Fate of steroid estrogens in STP

SEs, both natural and synthetic, are excreted mainly in estrogenically less active conjugated forms of glucuronides or sulphates (Desbrow et al., 1998) and enter municipal STPs with domestic sewage. However, not only metabolites but also biologically active original SEs have been detected in effluent waters of various STPs around the world. Thus, inevitably many of these estrogenic compounds find their way into receiving aquatic ecosystems through the discharge waters.

SEs have been widely identified and reported in STPs discharge waters. The estrogenicity of effluents demonstrates the inefficiency of conventional STPs processes to completely eliminate SEs. Moreover, the STPs are believed to act as a chemical reactor converting part of the inactive forms of estrogen metabolites back to more potentially harmful active ones (Baronti et al., 2000). According to some researchers (Johnson and Sumpter, 2001; D'Ascenzo et al., 2003) this transformation occurs due to the enzymes being synthesized by faecal bacteria *Escherichia Coli* present in sewage.

Ying et al. (2002) reported detected SEs at concentrations ranging up to 70 ng L⁻¹ for E1, 64 ng L⁻¹ for E2, 18 ng L⁻¹ for E3 and 42 ng L⁻¹ for EE2 in STP effluents of different countries (Table 3).

Recently, Johnson et al. (2005) compared SE content in the effluents of 17 European STPs with various treatment approaches and presented quantitative results. The total hydraulic retention time (HRT) ranged between 4 and 120 h and sludge retention time (SRT) between 3 and 30 days. The highest SE amounts (13 ng L⁻¹ of E2 and 35 mg L⁻¹ of E1) were detected in the effluents of STPs with only primary treatment. For the 16 STPs with secondary treatment the median concentration of E1 was 3 ng L⁻¹ and E2 (0.7-5.7 ng L⁻¹) was only found in six of them. EE2 at the level of 0.8-2.8 ng L⁻¹ was detected in two of them.

Table 3. Concentration of steroid estrogens in the effluents of STPs (Ying et al., 2002)

| Location | Concentration, ng L ⁻¹ * | | | |
|-------------|-------------------------------------|---|---------------|------------------|
| | E1 | E2 | E3 | EE2 |
| Italy | 2.5-82.1 (9.3) | 0.44-3.3 (1.0) | 0.43-18 (1.3) | <LOD-1.7 (0.45) |
| Netherlands | <0.4-47 (4.5) | <0.1-5.0 (<LOD) | - | <0.2-7.5 (<LOD) |
| Germany | <0.1-18 (1.5) | <0.15-5.2 (0.4) | - | <0.1-8.9 (0.7) |
| Canada | <LOD-48 (3) | <LOD-64 (6) | - | <LOD-42 (9) |
| UK | 1.4-76 (9.9) | 2.7-48 (6.9) | - | <LOD-7 (<LOD) |
| Japan | - | 3.2-55 (14) ^a <LOD-43 (13) ^b 0.3-30 (14) ^c | - | - |
| USA | - | 0.48-3.66 (0.9) | - | <LOD-0.76 (0.25) |

* Concentration range and median in parenthesis

LOD – limit of detection

^a summer sampling, ^b autumn sampling, ^c winter sampling

2.2.4 Environmental potencies of aquatic steroid estrogens

To compare SEs on the basis of estrogenic potency, several research groups have conducted experiments in vitro and in vivo, measuring the content of vitellogenin (VTG) in blood plasma of male fish. VTG is a protein usually found only in female fish. In male fish SEs induce VTG synthesis, which makes it a very sensitive biomarker for the detection of estrogenic effects. Johnson and Sumpter (2001) summarised the data of various researchers using the estrogenic potency of E2 as equivalent to one unit (Table 4).

Table 4. Relating SEs concentrations in STPs effluent to potential impacts on wildlife (Johnson and Sumpter, 2001)

| Compound | In vitro E2 equiv. | Typical effluent conc., (ng L ⁻¹) | Typical predicted E2 equiv. (in vitro) | In vivo VTG response in trout, E2 equiv. | Typical predicted E2 equiv. (in vivo) | Judgement |
|----------|--------------------|---|--|--|---------------------------------------|------------------|
| E1 | 0.5 | 5 | 2.5 | 0.5 | 2.5 | concern |
| E2 | 1 | 1.5 | 1.5 | 1 | 1.5 | concern |
| E3 | 0.005; 0.04 | 20 | 0.1 | 0.001 | 0.02 | little concern |
| EE2 | 1-2 | 0.5 | 0.5-1 | 25 | 12 | greatest concern |

By relating the potencies with the amounts of SEs in STP effluents, the following assessments of the environmental impact of each SE have been made by Johnson and Sumpter (2001):

E1. Although it may have just half the potency of E2, it is frequently found in STP effluents at concentrations twice those of E2. STPs appear to be less effective at removing E1 than other SEs.

E2. Although it has the greatest potency among natural SEs, based on typical effluent concentrations its overall impact on estrogenicity would appear to be less than E1. Many STPs show relatively good removal performance for this compound.

E3. Although high concentrations in effluents have been reported, its relatively low potency as compared to other SEs makes E3 of less concern.

EE2. In vitro results of combined potency and effluents concentration of *EE2* would not place the compound as the most dangerous. However, in terms of the environment, in vivo potency should have a greater weightage, measured using real effluent waters, and indicating *EE2* as undoubtedly the most potent SE. Therefore, the elimination of *EE2* could have the largest single impact on the estrogenicity of the effluents. At the same time *EE2* is difficult to evaluate in the effluents, as its low concentration are close to the measuring limits of currently available analytical techniques.

More recent results of Thorpe et al. (2003) demonstrated in vivo the following order of estrogenic activities of SEs: $EE2 \gg E2 > E1$. *EE2* was found to be 11 to 27 times more potent than *E2* and 33 to 66 times more potent than *E1*.

2.2.5 Removal rates of steroid estrogens in conventional STP

Large differences in SEs elimination rates have been reported for each individual STP: 19-98% for *E1*, 62-98% for *E2*, 76-90% for *EE2*. Despite this, different research groups agree on average elimination rates of SEs in STPs of around 80% for *E2* and *EE2* and 65% for *E1*. The lower removal rates of *E1* result in its higher levels in effluents. Occasionally, the levels of *E1* in effluent were higher than in the influent. This anomaly may be explained by partial conversion of *E2* to *E1*, as *E1* is the first by-product of *E2* biodegradation (Johnson and Sumpter, 2001) and deconjugation of estrogenic metabolites during the STP process.

Summarized research data on SEs removal by various types of STP showed the following results:

- Primary treatment, i.e. sedimentation or sedimentation with chemical precipitation, is unable to eliminate SEs (Desbrow et al., 1998; Johnson et al., 2005);

- Secondary treatment with activated sludge with longer hydraulic and sludge retention times has a very good, up to 90%, SE elimination rate (Johnson et al., 2007; Hashimoto et al., 2007) ;
- Membrane bioreactors (microfiltration plates, ultrafiltration hollow-fiber type) exhibited good performance in removal of natural SEs but were less effective against synthetic ones (Joss et al., 2004; Clara et al., 2004; Kreuzinger et al., 2004);
- Biological aerated filters as secondary treatment perform worse than any other biological sewage treatment (Johnson et al., 2007);
- Additional tertiary biological treatment can improve biological filter plant performance in SEs removal (Johnson et al., 2007). However, there is no specific assurance on this count.

2.2.6 Steroid estrogens in surface waters

The levels of SEs in effluent-receiving surface waters across Europe vary a lot, with the largest concentration detected downstream of STPs. The levels are dependent on the type of STP process used, density of population in the area and various other factors. In Europe, available dilution of receiving waters also plays a key role for a large number of big cities, especially during the summer months.

Belfroid et al. (1999) reported up to 6 ng L⁻¹ of SEs in surface waters in the Netherlands. In France, estrogens have been detected in the range from 1.0 to 3.2 ng L⁻¹ with no considerable difference between natural and synthetic SEs (Cargouet et al., 2004). The coastal surface waters of the German Baltic Sea have been shown to contain SEs at levels between 0.10 (E1) and 17 (EE2) ng L⁻¹ (Beck et al., 2005).

Moreover, Kuch and Ballschmiter (2001) found E2 and EE2 in concentrations up to 2.1 and 0.5 ng L⁻¹ respectively even in tap water samples. These data indicate the inadequate elimination of SEs in conventional STPs and their presumable persistence and accumulation potential in the ecosystem, which in turn can lead to the penetration of

these contaminants into potable water. Therefore, an effective and economically reasonable treatment technique able to eliminate SEs from municipal sewage is clearly needed.

2.2.7 Proposals for steroid estrogens elimination improvement in STP

The reported data indicate the ability of biological treatment to remove SEs. However, despite the reportedly good elimination rates, discharge waters containing low levels of SEs may still provoke estrogenic effects in living organisms. Thus, the rate of SE elimination in conventional STP is unacceptably slow. Several suggestions have been made to improve STP performance in SE elimination. According to Johnson et al. (2005) increased HRT and SRT can result in an increase in SE removal. To achieve this, the treatment tanks should be doubled or trebled in size to enhance biodegradation of SEs. However, due to the limited land availability in many urban European cities this solution seems to be impractical. Suggestions to enhance the SE removal rates with increased activated sludge concentration also did not provide the solution for the problem as sorption was found to be not as effective as biodegradation (Andersen et al., 2005).

Municipal sewage is a very complex mixture of a wide range of contaminants with unknown exact concentrations. The presence of pollutants with much higher concentration makes the removal rates of SEs doubtful. Therefore, the differences in sewage composition at each individual site do not allow the development of a universal strategy for SEs elimination. However, the separation of the SE-containing sanitary fraction will make the composition of this part of sewage more predictable. This offers a possibility to develop a common approach for effective SE removal and monitoring. Thus, separate treatment of sanitary sewage may appear beneficial compared to the treatment of large volumes of biologically treated municipal sewage.

2.3 Potential treatment strategies for effective steroid estrogen removal

Since SEs can only be partially removed from aqueous media with conventional STPs, there is a need for an additional treatment process. These pollutants may potentially be removed by various technologies including biological treatment, adsorption on a porous media, membrane separation, advanced oxidation processes, and ultraviolet (UV) degradation. Several treatment strategies were overviewed, although all of them appear to have drawbacks.

2.3.1 Biodegradation and separation technology

Biodegradation and sorption on an organic-rich solid phase were found to be principal mechanisms of SE elimination in biological treatment (Johnson and Sumpter, 2001). This technology, widely used in conventional STPs and described in details before, can only inadequately remove SEs without additional process improvements. The adsorption of trace contaminants in the presence of concentration-predominant organic pollutants can occur only to some extent as they will compete for the adsorption sites. A few studies concerning adsorption and membrane separation as possible treatment methods for SEs removal have been published (Chang et al., 2004; de Rudder et al., 2004; Nghiem et al., 2002). However, techniques that provide a simple redistribution of pollutants between aqueous and solid phases do not allow safe and complete removal of SEs. In addition, further safe handling of SEs accumulated on the separation media would be required (Nghiem et al., 2002).

2.3.2 Advanced oxidation processes

AOPs developed for aqueous wastes treatment include ozonation, UV radiation, Fenton processes, hydrogen peroxide (H₂O₂) and catalysts such as titanium dioxide (TiO₂). These methods can be applied separately, in combinations or even sequentially. They have proven to effectively oxidise a broad variety of organic pollutants at both low and

high concentrations and they are promising in the ultimate removal of SEs. AOPs are treatment technologies that produce and use powerful oxidising intermediates, for instance the hydroxyl radical ($\bullet\text{OH}$), to oxidise target organic contaminants from water and air. The chemical reactions involved are essentially the same as if the pollutants were slowly oxidised in the environment, but the oxidation rate is billions of times faster (Bolton, 2001). AOPs lead not only to the decomposition of target pollutants, but also to complete mineralization if the treatment time is sufficient, although it is often not necessary to operate the processes to this level of treatment and therefore the target pollutants are usually degraded to biodegradable intermediates. AOPs are particularly appropriate for effluents containing refractory, toxic or non-biodegradable materials.

Ozone (O_3) is a powerful oxidant and can oxidize pollutants either directly or by generating $\bullet\text{OH}$ radicals that then react with other species. These two pathways compete for the substrates to be oxidized. The direct oxidation of organic substances with aqueous ozone has a much larger activation barrier than the oxidation with $\bullet\text{OH}$ radicals. However, the molecular ozone concentration is much larger than that of the radicals. The production of hydroxyl radicals mainly occurs at high pH, thus the radical oxidation pathway dominates under alkaline conditions, while direct oxidation with molecular ozone predominates under acidic ones. The formation of $\bullet\text{OH}$ radicals from O_3 can be enhanced by exposure of the solution to UV light, addition of H_2O_2 , or other actions. Ozonation showed a positive effect for SE elimination, although residual estrogenic activity of oxidation by-products at doses of ozone normally applied in potable water treatment has been detected. To effectively reduce the estrogenicity, the ozone doses used for drinking water disinfection are needed (Ried et al., 2002; Huber et al., 2004; Alum et al., 2004). Moreover, Huber et al. (2004) reported the slow reappearance of EE2 after ozonation making the complete elimination of estrogenic activity impossible even at ozone doses applied for disinfection of drinking water. This unexpected behaviour was explained by the side reaction of a small fraction of EE2 with ozone hindering the cleavage of the phenolic ring, which is crucial for binding to the estrogen receptor and, thus, responsible for estrogenicity.

Many AOPs use H_2O_2 , the oxidising strength of which is relatively weak. However, the addition of UV light increases the rate and potency of oxidation through generation of $\bullet\text{OH}$ radicals. H_2O_2 in low concentrations may also be applied to enhance the rate of other AOPs, as the molecule easily splits into two $\bullet\text{OH}$ radicals. Fenton reagent has also proven to be very efficient in the treatment of some organics. However, this treatment alone was not effective for SE elimination even under drinking water treatment conditions due to scavenging of the oxidising agents (Ternes et al., 2005).

The application of direct photolysis would require relatively clean sewage as the UV light can be scattered by particles present in the aqueous stream. It is well known that turbidity causes quenching of the radiation (Pareek et al., 2003; Pujara et al., 2007; Saien and Soleymani, 2007). It has also been reported that direct photolysis is much less efficient in SE removal than when combined with other techniques (Rosenfeldt and Linden, 2004; Coleman et al., 2004).

The choice of the most suitable AOP approach has to be made on the basis of the chemical properties of the effluent and sometimes a combination of various techniques can be more efficient. Some AOP combinations applied to sewage treatment are presented in Table 5 (Bolton, 2001).

SE removal in STP effluent using several combinations of AOPs has been studied by Onari et al. (2002). They observed O_3/UV and $\text{O}_3/\text{TiO}_2/\text{UV}$ to be the best combinations, where the decomposition of SEs occurs through carboxylic acids. The average removal rate was, however, only 85% for both strategies.

Photocatalysis has also been studied for SE removal. The publications of several research groups have indicated that this treatment strategy can be very effective in degradation of the target compounds without formation of estrogenic intermediates (Ohko et al., 2002; Coleman et al., 2004). Therefore, photocatalysis is considered as a potential alternative for efficient SEs elimination from aqueous wastes and this alternative is the subject of the present research.

Table 5. Combinations of AOPs for sewage treatment

| Strategies | Process fundamentals | Main chemical reactions |
|---|---|---|
| O ₃ / UV | Photolysis of O ₃ through a complex chain of reactions, generating •OH radicals. Increase in pH enhances radical formation. H ₂ O ₂ can enhance the process. | $O_3+h\nu+H_2O \rightarrow 2 \bullet OH+O_2$ |
| O ₃ / H ₂ O ₂ or hydroxide | Alkaline conditions are able to produce •OH radicals. With H ₂ O ₂ reaction rate is increased ten thousand times. UV can enhance the process. | $O_3+H_2O_2 \rightarrow 2 \bullet OH+3 O_2$ |
| UV / H ₂ O ₂ | Direct photolysis of H ₂ O ₂ – reaction of direct cleavage of central O-O bond. Stoichiometric amount of H ₂ O ₂ must be added. | $H_2O_2+ h\nu \rightarrow 2 \bullet OH$ |
| Fenton reagent / H ₂ O ₂ | Fenton reagent contains Fe ²⁺ , which acts as a catalyst. UV can enhance the process. | $Fe^{2+}+ H_2O_2 \rightarrow Fe^{3+}+OH^-+\bullet OH$ |
| TiO ₂ / UV photocatalysis | Process reaction involves excitation of electrons via absorption of high energy photons: production of electron holes and •OH radicals. Addition of O ₃ , O ₂ or H ₂ O ₂ can enhance reaction rate. | To be explained in details in chapter 3.1 |

In real sewage conditions SEs are present as trace pollutants together with bulk organics of undefined composition. The bulk organics can be expected to be eliminated in preference due to much higher concentration. Therefore, for AOPs to be effective in SE removal the sewage needs to be first separated from the bulk organics or the

SE-containing sanitary fraction has to be separated from the main sewage stream before treatment. The selectivity of the treatment processes towards the SEs in the presence of additional pollutants thus has to be studied.

2.3.3 Treatment costs

AOPs often involve higher capital and operating costs compared with biological treatment and, thus, more research for a cost effective process is essential. Ried et al. (2004) estimated the approximate costs of some treatment methods (Figure 3).

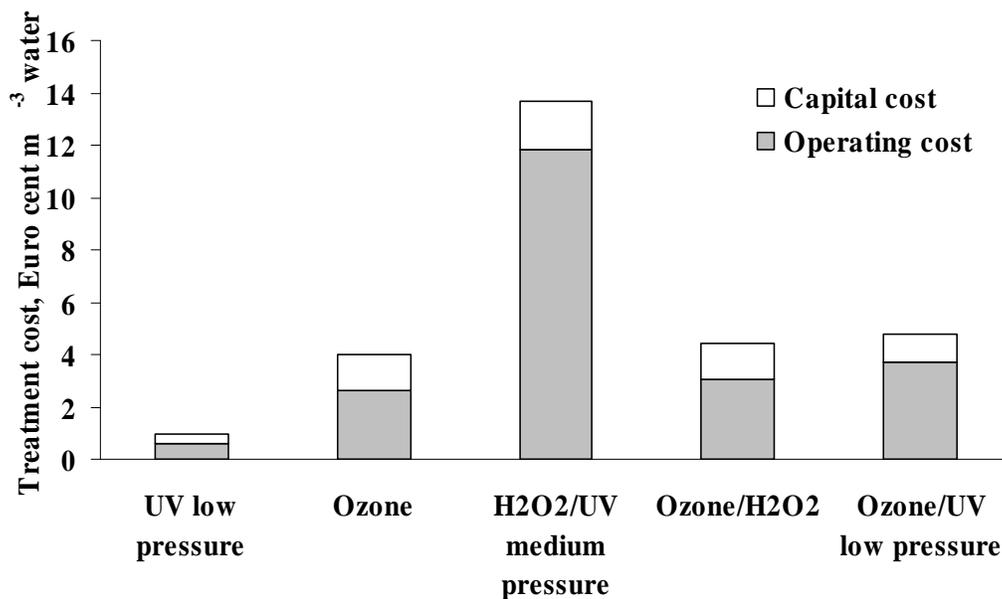


Figure 3. Comparison of operating and capital costs of various treatment technologies (Ried et al., 2004)

The treatment costs of other AOPs depend on various conditions: composition of water to be treated, process design, water quality to be obtained, etc. The prediction of exact expenses can be complicated. However, in comparison with membrane techniques with capital costs around 20 euro cents m⁻³ the costs for AOPs are significantly lower.

3 AQUEOUS PHOTOCATALYTIC OXIDATION

Photocatalytic oxidation has gained much attention in the area of polluted water treatment, since this process has exhibited the ability to convert to non-toxic biodegradable intermediates or even completely mineralise various kinds of toxic and hazardous organic contaminants such as organochloride compounds, pesticides, herbicides, surfactants, dyes and other harmful pollutants at mild temperature and pressure conditions (Hoffmann et al., 1995; Bhatkhande et al., 2002). The successful application of PCO for the removal of low-level organic pollutants has been also demonstrated (Chen and Jenq, 1998; Le-Clech et al., 2006). This method attracts attention also because of the possibility of direct use of solar energy.

3.1 Mechanism of oxidation

For a chemical reaction (eq. 1) a corresponding catalytic reaction may exist (eq. 2):



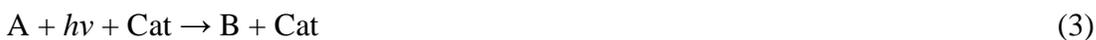
Catalysis occurs when the addition of a catalyst (Cat) changes the rate of establishing an equilibrium state of the reaction (2) as compared to the equilibrium state of the reaction (1). The catalyst interacts with the reactant(s) and through a lower energy pathway accelerates a thermodynamically favoured but kinetically slow reaction (Serpone and Emeline, 2002). After completion of the reaction the catalyst remains unaltered and can be separated in the original state and quantity.

The catalysis can be homogeneous (occurs in a homogeneous phase) and heterogeneous (takes place at the interfacial boundary between two phases). The present work deals with aqueous heterogeneous photocatalysis.

The overall process of traditional heterogeneous catalysis involves five independent steps (Herrmann, 1999):

- 1) Transfer of the reactant(s) in the fluid phase to the catalyst surface,
- 2) Adsorption of at least one of the reactants,
- 3) Reaction in the adsorbed phase,
- 4) Desorption of the products,
- 5) Removal of the products from the interface region.

The photocatalytic reaction happens when the catalytic reaction is induced by absorption of photonic energy ($h\nu$) by the reagent (eq. 3). Consequently, the only difference from conventional catalysis is the way of catalyst activation: thermal activation is replaced by photonic. Both artificial UV-irradiation and solar radiation can be applied for the catalyst excitation.



In other words, photocatalysis is the acceleration of a photochemical transformation by the action of a photocatalyst. Most photocatalysts are semiconductor metal oxides, which possess band gap – a void region that extends from the top of the electron-filled valence band to the vacant conduction band. Absorption of photonic energy higher than the band gap produces electron excitation in the photocatalyst, and electrons (e^-) gain sufficient energy to change levels from the valence to the conduction band. Simultaneously, an electron vacancy or hole (h^+) is created in the valence band (Dalrymple et al., 2007).

Various potential photocatalysts have been studied: oxides such as TiO_2 , ZnO , ZrO_2 , CeO_2 , etc. and sulphides such as CdS , ZnS , etc. The best photocatalytic performance with maximum quantum yield has been observed with titanium dioxide (Herrmann, 1999). The basics of the PCO can be illustrated as follows:



A photocatalytic reaction occurs in the adsorbed phase. Thus, the adsorption of the reactant on the catalyst surface is a prerequisite for successful decomposition. The electron-hole pair migrates to the catalyst surface, where it either recombines or participates in redox reactions with reactants adsorbed on the photocatalyst: holes act as oxidants and electrons are good reductants (Figure 4). The reactive radical species, thus, attack the reactant molecule and cause its hydroxylation, oxidation and, finally, mineralization to carbon dioxide and water.

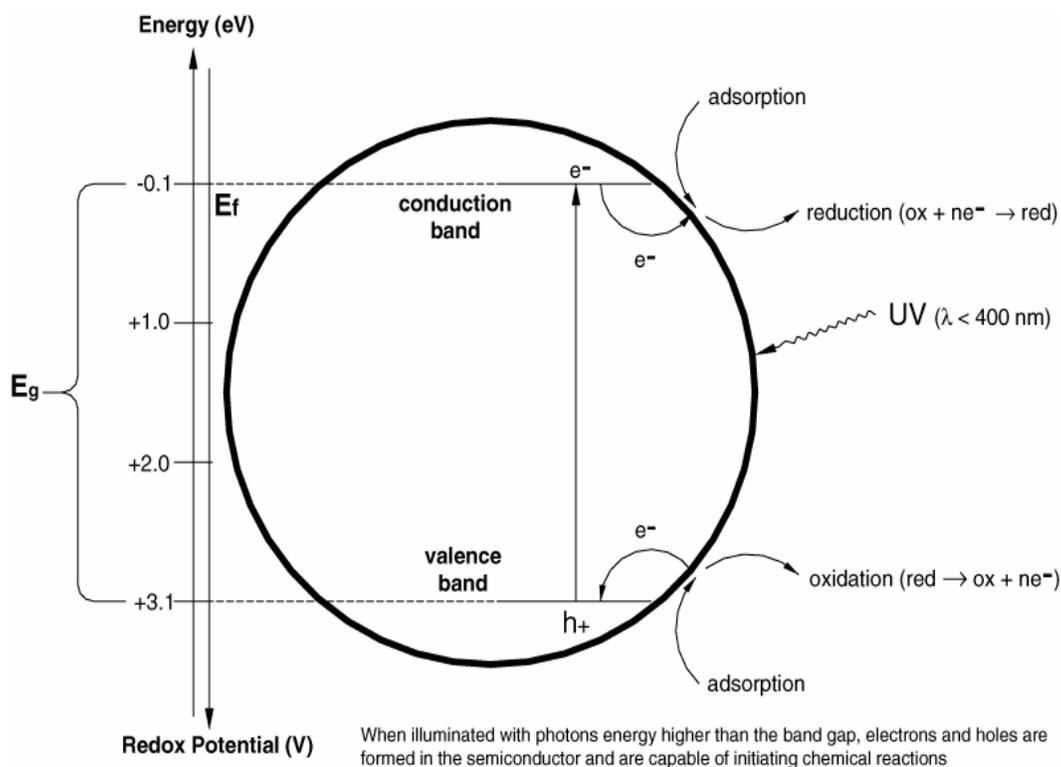
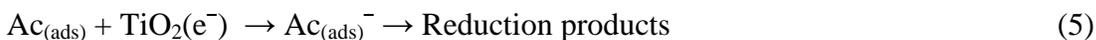


Figure 4. Scheme of PCO process over TiO_2 catalyst surface (Dalrymple et al., 2007)

Transfer of electrons across the interface is dependent on the relative energy levels of the hole and electron traps on the solid surface and of the energy levels of electron donors and acceptors in the fluid phase (Carey, 1992). In the presence of a fluid phase, a spontaneous adsorption happens and based on the redox potential of each adsorbate, an electron transfer proceeds towards acceptor molecules (Ac), while positive holes are

transferred to donor molecules (D) (this corresponds to the transfer of an electron from the donor to the solid) (Herrmann, 1999):



Each ion formed subsequently reacts to form the intermediates and final products.

The most common electron acceptor in aqueous solutions is adsorbed or dissolved molecular oxygen. The reaction produces a superoxide ion ($O_2^{\bullet-}$), which is readily protonated and disproportionated to give hydrogen peroxide and oxygen (Hoffmann et al., 1995):



Hydrogen peroxide acts as an oxidant, but also as an electron scavenger as an alternative to dissolved molecular oxygen. $H_2O_2^{\bullet}$ dissociates to an extremely reactive hydroxyl radical and the hydroxide ion even easier than H_2O_2 does, due to the extra electron (Hoffmann et al., 1995; Baird, 1997):



Thus, the efficiency of the PCO can be enhanced by the addition of H_2O_2 . On the other hand, H_2O_2 can also react with a hole and the efficiency of the PCO process can decrease at hydrogen peroxide excessive concentrations - excess H_2O_2 can act as a hydroxyl radical scavenger and form a much weaker oxidant hydroperoxyl radical (Balcioglu and Inel, 1996; Sun et al., 1997; Carp et al., 2004):



The hole produced by irradiation of the catalyst reacts with water or surface-bound hydroxyl ion producing the hydroxyl radical (Baird, 1997):



The oxidation potentials of the oxidising species can be seen in Table 6 with a higher value indicating a higher reactivity. Holes possess an extremely high oxidation potential (3.2 V) (Matthews, 1986) and thus should be capable of oxidizing almost all chemicals. Even one-electron oxidation of water resulting in the generation of hydroxyl radicals should be energetically feasible (eq. 12).

Table 6 Oxidation potential of several oxidising species (Carey, 1992)

| Oxidant | Oxidation potential (V) |
|---|-------------------------|
| Positively charged hole h^+ on TiO_2 | 3.20 |
| Hydroxyl radical $\bullet\text{OH}$ | 2.80 |
| Ozone | 2.07 |
| Hydrogen peroxide | 1.77 |
| Permanganate ion | 1.67 |
| Chlorine | 1.36 |

The hydroxyl radical is a powerful, non-selective chemical oxidant, which reacts rapidly with most organic pollutants. The produced hydroxyl radical remains adsorbed at the interface, as shown experimentally by Carey (1992). Therefore, for the hydroxyl radical to react with organic compounds, these probably also need to be adsorbed or in the vicinity of the catalyst surface at the time of the excitation. For very dilute solutions the reaction rate is likely limited by the rate of mass transfer of the substrate to the surface.

Consequently, PCO may proceed via the following mechanism (Linsebigler et al., 1995; Bahnemann, 2004): (1) direct oxidation with positively charged holes - adsorption of

reactant on the catalyst surface, followed by a direct subtraction of the pollutant's electrons; (2) oxidation with hydroxyl radicals that takes place at the catalyst surface (i.e. a trapped hole at the particle surface) or in its vicinity. Both reactions may proceed simultaneously, although positively charged holes have an oxidation potential about 1.15 times bigger than a hydroxyl radical (Table 6). Which mechanism dominates in the PCO process is largely determined by the chemical and adsorption properties of the reactant and the chemical reaction conditions.

In addition, the electrons and holes may recombine together without electron donors or acceptors within a few nanoseconds (frequency of about 10^8 Hz) (Park et al., 1999) and this recombination determines the PCO quantum yield and, thus, its rate. Both holes and electrons have to be efficiently scavenged to avoid their accumulation and, thus, recombination according to equation (14):



3.2 Photocatalytic properties of titanium dioxide

Titanium dioxide is one of the most widely used metal oxides in industry. It is applied as a catalyst support and as a catalyst. It is also used as a pigment material, as its high refractive index in the visible range allows preparation of thin films.

Titanium dioxide generally exhibits the highest photocatalytic activity of the photocatalysts. Other semiconductors that can be used as photocatalysts are ZnO, CeO₂, CdS, ZnS, WO₃, etc. However, these semiconductors are not as attractive for PCO as TiO₂: it is biologically and chemically inert, inexpensive and resistant to photocorrosion and chemical corrosion (Carp et al., 2004). Only ZnO has shown comparable activity (Bahnemann et al., 1991). For this reason the use of other semiconductors in environmental studies is rather limited (Hoffmann et al., 1995).

The photocatalytic efficiency of TiO₂ is dependent on crystal structure, particle size and surface area. There are three forms of TiO₂: anatase, rutile and brookite. In most cases, anatase is the most active crystal form – it is thermodynamically less stable than rutile, but its formation is kinetically favoured at lower temperatures (<600°C). The lower temperature of crystallization of TiO₂ may explain its higher surface area and a higher surface density of active sites for adsorption and catalysis (Herrmann, 1999). PCO process effectiveness is governed by the catalyst lifetime and recombination probability of the electron-hole pair. Therefore, anatase is often mixed with rutile, a less catalytically active form, to reduce the rate of recombination of the electron-hole pair (Bhatkhande et al., 2002; Dalrymple et al., 2007). The band gap of anatase is 3.2 eV and it absorbs photons within the near UV range (~380 nm) of the electromagnetic spectrum. However, solar radiation starts at a wavelength of about 300 nm at ground level. Thus, 4-5% of the solar energy reaching the surface can be utilized in PCO with TiO₂ as the photocatalyst (Zhang et al., 1994).

Of the wide range of various mixtures of TiO₂, Degussa P25 has been most widely applied. It consists of ca. 75% of anatase and 25% of rutile, has an average individual particle size of 20-30 nm and a high surface area of 50 m² g⁻¹. The small size of the particles can provide high efficiency of surface trapping of photon-generated electrons and holes, thus increasing the probability of PCO on the catalyst surface (Dalrymple et al., 2007).

3.3 Parameters influencing PCO

The identification of optimal process parameters is essential for effective PCO. However, various pollutants undergo PCO via different chemistry, and thus, the effect of process parameters is dependent on the pollutant type: some contaminants degrade better under alkaline media conditions, in other cases neutral or acidic media can be beneficial, etc. Therefore, a particular PCO system requires substantial research to establish the most efficient treatment conditions and the effects of most important operating factors are

generally studied for each individual type of contaminant (Parent et al., 1996; Bhatkhande et al., 2002).

3.3.1 Effect of pH and adsorption

The pH of the solution has a complex effect on the PCO rate, which is dependent on the type of contaminant, surface state of the catalyst and the electrostatic interaction between the reactant and the catalyst surface.

The impact of pH can be observed on the electric surface charge of the metal catalyst. The electric charge of the particle is represented by its zeta potentials. For instance, in TiO₂ aqueous dispersions the zeta potential was found to decrease linearly with the pH of the solution. “Titanol” (TiOH), TiO₂ primary hydrated surface functionality, is a neutral surface state (Dalrymple et al., 2007). The zero point charge reported for TiO₂ dispersion without additional solutes varies from pH 4.0 to 6.8. Therefore, the TiO₂ surface is positively charged (TiOH⁺) in acidic solutions and attracts anions. In alkaline media the TiO₂ surface becomes deprotonated and has negative charge (TiO⁻) and, thus, repels negative ions (Halmann, 1996).

An important factor in heterogeneous PCO is the adsorption of the pollutant on the catalyst surface as it is a necessary step in the heterogeneous catalytic process. The pH has significant effect on adsorption by affecting not only the catalyst surface charge, but also the ionic state of the reactant. Generally, the adsorption of the reactant and, therefore, the degradation rate are at maximum near the zero point charge of the catalyst (Chen and Ray, 1998; Subramanian et al., 2000; Bhatkhande et al., 2002). For some weakly acidic reactants the PCO rate increases at lower pH due to the increased adsorption under acidic conditions (Subramanian et al., 2000). Other contaminants undergo decomposition at certain pH range and the PCO rate can increase with elevated pH. However, even with poor reactant adsorption, PCO can occur in alkaline media, presumably due to the oxidation with hydroxyl radicals.

PCO also shown complicated behaviour dependent on pH in terms of mineralization of pollutants: beneficial for hydroxylation and oxidation of functional groups, high pH may be observed as less effective for mineralization, i.e. reduction in TOC of organic compounds (Tanaka and Saha, 1994; Bhatkhande et al., 2002). This may be explained by the stronger oxidative potential of positively charged electron holes compared to the one of OH-radicals.

The influence of pH and adsorption on the PCO process cannot be generalised and the optimum conditions have to be determined experimentally in each particular case (Parent et al., 1996). However, adsorption has been reported to play a significant role when water-insoluble organics are oxidised (Hidaka et al., 1992); confirmation of this statement can also to be found in the results of the present work.

3.3.2 Initial concentration of contaminant

Nature and concentration of the contaminant are both important factors for the PCO process. The reaction rate as well as the surface adsorption rate is highly dependent on the concentration of the reactant: the process reaction rate increases with high reactant concentrations. However, often one can observe the maximum rate followed by a decrease. This can be explained by the UV-screening effect of the reactant and/or deactivation of the catalyst. Thus, highly concentrated waters need to be diluted or pre-treated to undergo successful degradation (Robert and Malato, 2002). The decreasing rate is also attributed to the decrease in reactant concentration during the reaction.

PCO is able to effectively eliminate micropollutants. However, micropollutants undergo PCO with much lower degradation rates compared to the competing reactions with co-pollutants at much higher concentrations. Therefore, the system, examined in the present research, was exposed to a risk of low efficiency in the removal of target contaminants due to their trace concentrations. Thus the objective to study PCO of SEs in the presence of co-pollutants with much higher concentrations was set up.

3.3.3 *Catalyst application mode and amount*

Use of the optimum photocatalyst concentration is essential for the PCO process as excess catalyst can reduce the amount of energy being transferred in the medium as the solution opacity increases due to increased light scattering of TiO₂ particles. The optimum concentration of the catalyst is dependent on the type and concentration of the contaminant, and the rate of generation of free radicals depends itself on the operation conditions of the reactor (Kamble et al., 2003A; Kamble et al., 2003B).

In principle, catalysts can be employed either as finely divided powders suspended (slurried) in the aqueous media or immobilized on a suitable support material. When a suspended catalyst is applied, its type, dosage and preparation method have to be taken into consideration. For a supported catalyst several parameters have to be considered: support material (quartz sand, glass, silica gel, optical fibers, alumina clays, ceramics), particle size of the support, type of catalyst, amount of catalyst on the support, immobilization method, calcination temperature. The choice of proper catalyst is clearly connected with the reactor design.

The present work deals with the special case of micro-concentrations of pollutant SEs, which makes the photocatalyst concentration factor essential for the research purpose: high concentrations of the photocatalyst around 1 g L⁻¹, usually reported to be optimum, resulted in complete adsorption of SEs without a chance to follow the changes on the PCO course. Therefore, in this work a suitable concentration of suspended Degussa P25 was established to trace the changes in SE concentration in the solution in the PCO experiments.

3.3.4 Other factors

Irradiation intensity

Incident radiation intensity (irradiance) is usually measured in Einstein s^{-1} (moles of photons s^{-1}) or power per area units (W m^{-2}). When solar radiation is applied the term “suns” is widely used as a measure of irradiance. One “sun” is equivalent to irradiance of one solar constant - the sun irradiance on the outer atmosphere when the sun and earth are spaced at the mean earth/sun distance of 149 597 890 km. Presently accepted value of one sun constant is about 1360 W m^{-2} .

The reaction rate is directly proportional to the radiation intensity. At low radiation fluxes (less than 1 sun) a linear dependence of the reaction rate on the illumination intensity is expected. Beyond this radiation flux the reaction rate shows a square root dependence on the intensity and often the yields of reaction products increase. The square root law is valid in an intermediate regime. The square root dependency between reaction rate and light intensity has been explained by competition between the oxidation of the reactant molecule and the combination of charge carriers generated by the subsequent absorption of two photons by a single semiconductor particle. At very high fluxes (more than 100 suns) the reaction rate will remain constant upon further increase of the illumination intensity due to transport limitation (Bahnemann et al., 1991; Bhatkhande et al., 2002).

Reactor design

Depending on the type of catalyst applied, the reactors can be fixed-bed or suspended batch mechanically stirred. In suspended catalyst reactors the reaction rate is predominantly determined by the light intensity on the surface, the quantum efficiency of the catalyst and the adsorption properties of the reacting and non-reacting compounds in the solution. However, the use of suspensions requires the separation and recycling of the catalyst from the treated liquid, which can be inconvenient, time-consuming and expensive process. The application of sintered metal candle filters working under the pressure of titanium dioxide suspension column with the cake discharge mechanism

offers a possibility to technically solve these problems, making the use of suspended catalyst more effective (Kamble et al., 2004; Pujara et al., 2007).

In fixed-bed reactors with an immobilized catalyst the active surface area is much smaller, which can lead to lower PCO rates. Immobilization of the catalyst on the support generates another problem – the reaction occurs on the liquid-solid interface and mass transfer from the liquid bulk to the catalyst surface may play a significant role in the PCO rate (Ray and Beenackers, 1998; Kamble et al., 2004).

3.4 Reaction kinetics

Good data fit to the Langmuir adsorption isotherm is commonly observed and the monomolecular Langmuir-Hinshelwood kinetic model is generally applied to formally describe the process and to find the reaction rate constant:

$$r = -\frac{dc}{dt} = \frac{k \cdot K \cdot c}{1 + K \cdot c} \quad (15)$$

where r is process reaction rate, k is apparent reaction rate constant, K – the Langmuir adsorption coefficient of the reactant and c is its concentration at time t .

This equation usually shows a good data fit to the linear dependence of the reciprocal reaction rate on the reciprocal initial concentration of the pollutant:

$$\frac{1}{r} = f\left(\frac{1}{c}\right) \quad (16)$$

If the concentration of the reactant is very low, i.e. $K \cdot c \ll 1$ and the denominator approximates unity, which is precisely the case in the present study. In this case the Langmuir-Hinshelwood model can be simplified to a pseudo first order kinetic reaction:

$$r = -\frac{dc}{dt} = k' \cdot c \quad (17)$$

where $k' = k \cdot K$, the apparent reaction rate constant.

The pseudo first order rate constant can often be determined by observed reactant relative concentration changes as a function of time. The integration of the differential equation (17) results in satisfactory data fit to the logarithmic dependence of the pollutant's concentration on treatment time.

3.5 Advantages and disadvantages of PCO

The overall picture of PCO potential for successful application can be understood after considering both advantages and disadvantages of this process (Herrmann, 1999; Bhatkhande et al., 2002; Kamble et al., 2004). The summarized advantages offered by PCO are as follows:

- Process operation at ambient temperature and pressure conditions;
- Possibility for natural resources utilisation, i.e. solar radiation, which should result in considerable economic savings;
- Chemical stability of TiO_2 in aqueous media and at a wide range of pH ($0 \leq \text{pH} \leq 14$);
- Relatively low cost of TiO_2 ;
- Good deposition capacity for noble metal recovery;
- No additives required (only oxygen from air);
- Process applicable at low pollutant concentrations;
- Total mineralization achieved for many organic pollutants;
- Efficient with halogenated compounds even very toxic for bacteria in biological water treatment;
- Possible combination with other water treatment methods.

However, there several drawbacks that hamper successful PCO application on an industrial scale for wastewater treatment:

- Necessity for treated water to be transparent at the spectral region, where the catalyst absorbs UV light;
- Engineering design and operation strategies need to be developed for the industrial scale: solution to achieve uniform catalyst irradiation with the same incident intensity, minimisation of incident light losses due to light scattering, opacity, absorption by liquid, etc;
- Need for an effective and economically feasible separation technique for suspended catalyst reactors; the immobilised catalyst reactors have a much lower PCO rate than suspended ones;
- Relatively slow complete mineralization of heteroatoms at their reduced state;
- Presence of radical scavengers lowering the PCO rate (a subject of the present research);
- Competitive adsorption/oxidation of non-target co-pollutants (a subject of the present research);
- Fouling of the catalyst.

Most of the research on PCO has been done in laboratory-scale experiments. However, despite the reported drawbacks, several pilot plants have been built and successfully studied for the PCO of water contaminated with various pollutants, and some photocatalytic devices have already been commercialised (Alfano et al., 2000; Malato et al., 2002; Bahnemann, 2004; Kositzi et al., 2004; Lee and Mills, 2004).

4 PHOTOCATALYTIC OXIDATION OF STEROID ESTROGENS: AN OVERVIEW

During the last decade several academic groups have dedicated their research efforts to PCO of SE. Coleman et al. (2000) studied PCO using TiO₂ immobilised on Ti-6Al-4V alloy with E2 as a target pollutant. E2 was found to be readily eliminated by PCO in the presence of oxygen. 50% degradation of E2 was obtained in 40 min and 98% degraded in 3.5 h. The group also reported occurring of some direct photolysis. The initial rate data fitted the pseudo-first order kinetic reaction and the rate constant was calculated to be 0.016 min⁻¹ under the conditions employed. The dependence of the process rate on pH was found to be similar to phenol behaviour, yielding a maximum rate at pH 12.

The photocatalytic degradation of E2 using immobilised TiO₂ was also investigated by Nakashima et al. (2002). These researchers compared the results from two reactors: an immobilised catalyst system and a system with a rotating immobilised porous catalyst. Black-light fluorescent lamps, illumination intensity of 0.24 mW cm⁻², were used in the study. The authors did not observe any photolysis in the process; however, they observed E2 adsorption onto the immobilised catalyst in the dark. 98% degradation of E2 was obtained after 1 h of PCO using first type of reactor and the first-order rate constant was calculated to be 0.033 min⁻¹. The second reactor showed 90% degradation of E2 in 20 min; the rate constant was 0.050 min⁻¹. This indicated that the apparent mass-transfer rate of E2 on the TiO₂ could be improved by rotation of the immobilised catalyst.

The authors modified the second reactor for a larger volume of treated water (Nakashima et al., 2003). The UV light intensity was 1.2 mW cm⁻². The authors examined the degradation of E1 and E2 with initial concentration of 250 µg L⁻¹ and the calculated first-order rate constants were 0.12 and 0.15 min⁻¹ respectively. Study of temperature dependence showed an increase of the process rate with the increased temperature. This effect was explained by better mass transfer of the SEs to the catalyst surface. The PCO rate of discharged water samples from the STP was consistent with the rate obtained with

model solutions. The catalyst showed reproducibility of the results in E1 oxidation for at least four times in batch experiments.

Ohko et al. (2002) examined the PCO of E2 using suspended TiO_2 at a concentration of 1 g L^{-1} and evaluated the estrogenic activity during the reaction. The target compound exhibited total mineralization in 3 h. The intermediate products were elucidated to be 10ϵ - 17β -dihydroxy- $1,4$ -estradien- 3 -one and testosterone-like species. The suggested mechanisms of E2 degradation were discussed theoretically and experimentally confirmed. The phenol moiety of the E2 molecule, one of the essential groups interacting with estrogen receptors, was proposed to be the starting point of the degradation, making the loss of the estrogenic activity almost concurrent with the initiation of the PCO. The estrogenic activities of intermediates were found to be negligible.

Mitamura et al. (2004) investigated the PCO of SEs and their conjugates. TiO_2 catalyst immobilised on glass beads was used. Glass beads (13.6 g) were spread to cover the bottom of a glass Petri dish and the SE solution ($1 \mu\text{M}$, 15 ml) was added. The Petri dish was placed in a light shielded box and irradiated by black light lamp for 6.5 h. E2, its 17-glucoronide and E1, having an unconjugated phenolic hydroxyl group at C-3 position, were completely eliminated in 4-h PCO. However, 20-25% of E2- and E1-3-glucoronide and 90% of E1 sulphate, conjugated at the 3-hydroxy group, were not degraded after 6.5 h of PCO. These data supported the suggestion of Ohko et al. (2002) that the PCO of SEs was started from the phenolic hydroxy group.

The loss of estrogenicity of E1, E2 and EE2 by UVA photolysis and PCO using immobilised TiO_2 has been studied by Coleman et al. (2004). Both processes were found to be capable of eliminating SEs. The data indicated 50% reduction in estrogenicity after 10 min of PCO and 100% reduction within 1 h for all three SEs. The degradation of SEs by photolysis was several times slower than by PCO: 9 times for E2, 6 times for E1 and 2.5 times for EE2. The calculated pseudo-first rate constants for PCO of the three SEs were 0.086 - 0.106 min^{-1} , whereas for photolysis the numbers were 0.11 - 0.035 min^{-1} . This indicated that the PCO process is much more efficient than UVA photolysis in SE elimination. Two mechanisms of SE degradation were suggested as follows: via

extraction of benzylic hydrogen to form the $\text{CH}\cdot$ radical, which combines with oxygen, or via attack of hydroxyl group and formation of quinone.

The initial SE concentration and UV light intensity effects were also studied (Coleman et al., 2005A). A linear relationship between the PCO rate and SE initial concentrations has been observed. The process rate was reported to be proportional to the square root of UV light intensity for the PCO. The quartz coil reactor coated internally with TiO_2 that was used in this research was found to be much more effective than the one used in the first study of this research group (Coleman et al., 2000): the rate constant for E2 was 0.174 min^{-1} compared to the previously obtained 0.016 min^{-1} . This was attributed to the increased surface area of the immobilised catalyst. The calculated rate constants for E1 and EE2 were 0.156 and 0.231 min^{-1} respectively. The much faster EE2 degradation was explained by the presence of the triple bond in the ethynyl group, which easily absorbs UV light.

The influence of presence of Ag and Pt deposited on the TiO_2 catalyst on the PCO rate of SEs has been tested using immobilised catalyst (Coleman et al., 2005B). The addition of metals showed no effect on the PCO at the metal concentration levels found in water. The low concentrations of SEs compared with high concentration of hydroxyl radicals and holes in the process explained the absence of positive effect on the process rate. Thus, evidently there is no need for addition of expensive metals to the photocatalytic degradation of low levels of pollutants.

5 PRESENT RESEARCH OBJECTIVES AND STRATEGY

Since preliminary studies showed relatively efficient elimination of SEs by means of PCO, treatment of the SE-containing sanitary fraction of domestic wastewater with PCO seems to be theoretically possible. However, one of the main issues of the practical application of this strategy, the effect of co-pollutants at concentrations many times exceeding those of SEs on PCO efficiency of SEs, has remained practically unstudied. The approach seems, however, to be justified since co-pollutants inevitably accompany SEs in domestic wastewater and cannot be easily removed or separated. The research therefore targets the co-pollutants issue to answer the question of selectivity in SEs removal.

An experimental study was therefore undertaken to elucidate the effects of key process parameters such as pH on the PCO of SEs and their adsorption on the TiO₂ surface. The influence of the presence of co-pollutants characteristic for the sanitary fraction of domestic wastewater, including urea, saccharose and urine, was also studied. In the course of the research the impact of ethanol often used as a solvent in preparation of SE stock solutions was also clarified.

6 EXPERIMENTAL

6.1 Materials

6.1.1 Target compounds

Natural β -estradiol and synthetic 17α -ethynylestradiol (Sigma-Aldrich) were used as target SEs. These compounds are of the greatest environmental concern: E2 and EE2 are found to be the most potent of the SEs (Johnson and Sumpter, 2001; Thorpe et al., 2003). The molecules of these SEs differ only in that the ethynyl group in EE2 is connected to the tertiary carbon atom with the alcohol moiety (Figure 1).

An aqueous solution of SEs is usually prepared by dissolving first in an organic solvent due to their hydrophobic character and extremely low solubility in water (Table 1). The use of organic solvents when making SE aqueous solutions is widespread practice (Alum et al., 2004; Coleman et al., 2004; Huber et al., 2004; Coleman et al., 2005). Initially, in the present research, the author used ethanol (Altia Oy, Finland) as an organic solvent for the preparation of the stock solution of SEs. The target SEs were first dissolved using 99.5%-ethanol followed by gradual dilution with Milli-Q water to prepare the stock aqueous solution of 10 mg L^{-1} . The stock solution was kept in an ultrasonic bath for 30 min for complete dissolution of SE colloids. This solution was constantly stirred at room temperature in a hermetically sealed flask to avoid re-crystallisation of the SEs. The solutions with the required concentrations for the experiments were prepared by dilution of the stock solution with Milli-Q water under stirring for 30 min. These solutions contained approximately 4 g L^{-1} of ethanol.

In further studies ethanol was found to interfere with the PCO of the SEs. Therefore, the SEs, the molecules of which contain phenolic moieties, were successfully dissolved in water with a strongly alkaline reaction (pH 12.4) making the stock solutions free of the organic solvent. The preparation of ethanol-free stock solution was conducted in a similar

manner to the ethanol-containing one. The initial concentration of SEs in the PCO-treated solutions prior to suspending the photocatalyst was $500 \mu\text{g L}^{-1}$.

6.1.2 Co-pollutants

Boejie et al. (1998) have reconstituted a synthetic sanitary fraction of domestic sewage based on an extensive literature analysis, indicating urea and potato starch as the most common co-pollutants. However, chromatographic analysis, the only available analytic technique for SEs, in the presence of potato starch may be problematic due to clogging of chromatography columns. Starch consists mainly of poorly water-soluble amylose and insoluble amylopectin, polymers containing chains of mono- and disaccharide units. Therefore disaccharide saccharose was chosen as a completely water-soluble starch replacement with a similar molecular structure (Figure 5).

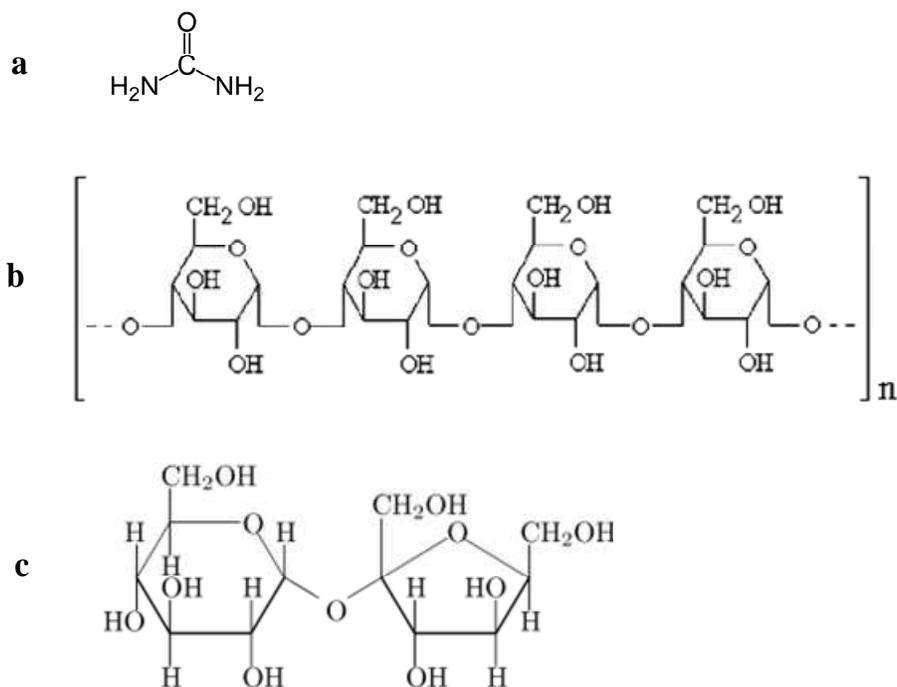


Figure 5. Molecular structures of urea (a), potato starch (b) and saccharose (c)

The co-pollutants were added to the solutions to be treated simultaneously with the SEs. Urea and saccharose were first dried at 105° C. The medium concentration of urea of 75 mg L⁻¹ usually found in municipal wastewater (Boeije et al., 1998) was used in the experiments. The adsorption and PCO of urea were also studied.

The stock solution of saccharose of 1 g L⁻¹ was made with Milli-Q water and then used in the preparation of the SE-containing samples to be treated. A concentration of saccharose of 50 mg L⁻¹ was used as equivalent to the medium potato starch concentration in domestic sewage (Boeije et al. 1998). The PCO degradation of saccharose itself was also studied in solutions with an initial concentration of saccharose of 150 mg L⁻¹.

To simulate conditions prevailing in real sanitary effluents, the PCO of SEs was studied in the presence of human urine. The urine-water ratio was chosen from the average human excretion of 0.06 to 0.27 L of urine per each use of a dual flush system toilet utility of 3 to 6 L of water per flush. Both the maximum of 90 mL L⁻¹ (concentrated) and minimum of 10 mL L⁻¹ (diluted) concentrations of urine in water were tested for SEs removal. Diluted urine did not show a noticeable UV-absorption at 365 nm; concentrated samples exhibited minor absorbance at this wavelength.

6.1.3 Photocatalyst

Titanium dioxide (Degussa P25, surface area 50 g m⁻²) was selected as the photocatalyst. The source of photons was near-UV irradiation (365 nm). The issue of photocatalyst concentration was an important aspect studied in the present work. The commonly used TiO₂ concentration of around 1 g L⁻¹ (Wei and Wan, 1991; Dalrymple et al., 2007) was excessive for the microgram concentration of SEs: after suspending of 1 g L⁻¹ of TiO₂ to the solution containing 500 µg L⁻¹ of the SEs, the bulk concentration of target pollutants decreased below its detection limit in two minutes of PCO. An appropriate concentration of the photocatalyst was carefully selected, aiming the bulk concentration of SEs to be around 200 µg L⁻¹ after adsorption of SEs on the TiO₂ surface from the initial 500 µg L⁻¹ in the solution (Appendices 1/pp. 188-189 and 2/p. 343). A TiO₂ concentration of

10 mg L⁻¹ was found to meet the stated requirement and was used in further PCO experiments unless specified otherwise.

Higher concentrations of TiO₂ were used in experiments with saccharose; experiments with saccharose required higher catalyst concentration due to its slow oxidation (refer to Appendix 4/ The PCO and adsorption of saccharose).

Synthetic syringe filters with a pore size 0.45 µm were initially used to separate the catalyst from the solution at the sampling stage. However, partial adsorption of E2 by the filter material affecting the measured results was observed. Consequently, centrifugation at 10,000 rev min⁻¹ was used to separate TiO₂ from the samples before analysis.

6.2 Methods

The PCO experiments were performed in 0.25-L capacity thermostatted batch glass reactors with an inner diameter of 100 mm, provided with a magnetic stirrer (Figure 6). The agitation intensity was maintained with a standard 25-mm Teflon stirrer at 300 rpm. A 365-nm UV-lamp (Sylvania F15W) was positioned horizontally over the reactor; the irradiance was about 1.1 mW cm⁻² measured by UVX Radiometer (UVX, USA). All PCO experiments were compared with reference samples, treated under identical conditions except UV-radiation.

The adsorption experiments with the SEs and urea under various pH conditions were performed in 0.50-L capacity flasks, where the solutions were mixed with TiO₂ at a stirring frequency of 900 rpm for 24 h at 25 °C. Each flask was handled separately as a single-point sample. The adsorption experiments were repeated three times. The equilibrium concentration of compounds adsorbed on the surface of the catalyst q , mg g⁻¹ TiO₂, was calculated from the mass balance of the SEs in the liquid phase. The experiments determining the adsorption properties of saccharose from the solution containing 250 mg L⁻¹ of saccharose on 1 g L⁻¹ of TiO₂ were performed for 1 h in a similar manner.

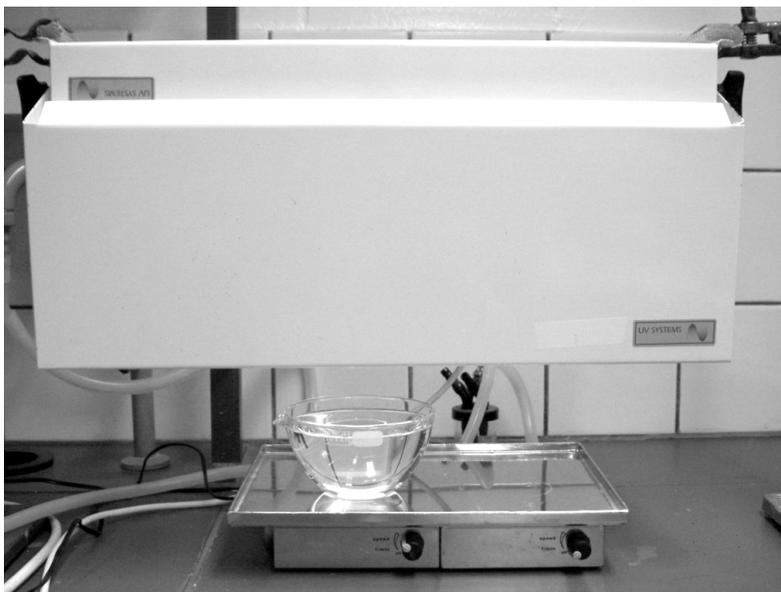


Figure 6. Experimental facility: UV-lamp, reactor, thermostat, magnetic stirrer

6.3 Analysis

The concentrations of SEs were measured by means of HPLC with a UV-detector using a 150-mm ZORBAX Eclipse XDB-C18 column (Agilent) at the wavelength 278 nm; the mobile phase was acetonitrile-water (1:1) at a flow rate of 1.0 mL min^{-1} . The detection limit of the UV detector was $10\text{-}20 \mu\text{g L}^{-1}$, smaller SE concentrations could not be reliably analysed.

The urea concentrations were measured according to the method developed by Mulvenna and Savidge (1991) and Goeyens et al. (1998), and adapted for the present research. The 10-mL test tubes were filled with 3.5 mL of the 35-fold diluted sample, 0.25 mL of the reagent A and stirred. Reagent B in an amount of 0.8 mL was then immediately added and stirred. The test tubes were stored at room temperature for 72 h in the dark. The light absorbance was then measured at 520 nm. Reagent A was made of 8.5 g diacetylmonoxime in 250 mL of water together with 10 mL of a solution containing 0.95 g of thiosemicarbazide in 100 mL of water (all chemicals Sigma-Aldrich). Reagent

B was prepared by dissolving 300 mL of concentrated sulphuric acid in 535 mL of water with the addition of 0.5 mL of a solution containing 0.15 g of ferric chloride in 10 mL of water.

Chemical oxygen demand (COD), measured by a standard procedure (Greenberg, 1995), and total organic carbon (TOC) were determined in PCO and adsorption experiments with saccharose. COD was also measured to observe the changes in the concentration in the urine samples. The TOC analyses were carried out using the Shimadzu 5050-A TOC analyser.

7 RESULTS AND DISCUSSION

The PCO was characterized by the process efficiency relative to the TiO₂ concentration, calculated as the decrease in the concentration of the SE divided by the amount of energy reaching the surface of the sample and by the concentration of the catalyst used:

$$E = \frac{\Delta c \cdot V \cdot 1000}{I \cdot s \cdot t \cdot m} \quad (18)$$

E (mg W⁻¹ h⁻¹ per g L⁻¹ TiO₂) represents the PCO efficiency relative to the catalyst concentration; Δc (μg L⁻¹) – decrease in the target compound concentration; V (L) - volume of treated sample; I (mW cm⁻²) - irradiation intensity; s (cm²) - solution irradiated surface area; t (h) - treatment time; m (g L⁻¹) – concentration of TiO₂.

7.1 PCO of steroid estrogens in the presence of ethanol

Preliminary results indicated that the natural SE E2 readily yields to the PCO over UV-irradiated TiO₂. An alkaline medium was found to be the most efficient for the process. Since the effective TiO₂ concentration most often used in PCO is between 1 and 3 g L⁻¹ (Wei and Wan, 1991), concentration of photocatalyst of 1 g L⁻¹ was initially used in the preliminary study to be able to compare the experimentally obtained data with previously published work (Ohko et al., 2002). The results showed that the process efficiency increased with the increasing initial concentration of E2 within the initial concentration range from 350 to 780 μg L⁻¹. The optimum E2 concentration was not observed within the concentration range studied in the present research.

However, at such a high photocatalyst concentration a sharp decrease in E2 concentration in the bulk solution was noticed as a result of the introduction of TiO₂: the disappearance of E2 was observed within the first two minutes of the experiment. This was explained by the large excess of adsorbent TiO₂ as compared to the concentration of the target

compound; E2 was apparently completely adsorbed by the catalyst. Thus, the commonly used concentration of TiO_2 of 1 g L^{-1} was found to be excessive for the microgram concentration of SEs. Therefore, the search for a more appropriate TiO_2 concentration was undertaken.

7.1.1 Photocatalyst concentration

The concentrations of TiO_2 in suspensions for the PCO experiments were carefully selected for both SEs separately, so that the target compound's concentration decreased due to adsorption on the catalyst from initial 500 to equilibrium $200 \mu\text{g L}^{-1}$ in 24 h. The selection procedure was carried out for different pH values (Appendices 1/pp. 188-189 and 2/p. 343) consuming a great deal of time. The results are shown in Figure 7.

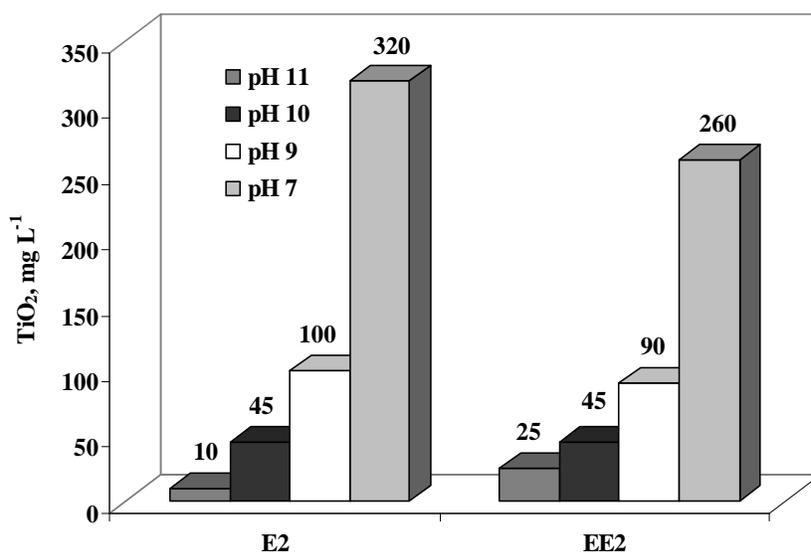


Figure 7. The TiO_2 catalyst concentrations sufficient for the adsorption of E2 and EE2 from initial 500 to equilibrium $200 \mu\text{g L}^{-1}$ in 24-h experiments vs. pH

The smallest TiO_2 concentration of 10 mg L^{-1} was used in further PCO experiments unless specified otherwise. This concentration of photocatalyst allows observation of the adsorption and oxidation results within the measurable SE concentration range: higher

concentrations of TiO_2 result in adsorption and rapid elimination of SEs from the solution.

7.1.2 Influence of pH

Adsorption isotherms

The adsorption characteristics of the SEs on the TiO_2 surface were carefully studied for various pH values (Figure 8). The results indicate that the adsorption of both natural and synthetic SEs increases with increasing pH. In fact, a practically linear logarithmic increase of the surface concentration q versus the increase of pH was observed. This corresponds to a linear dependence of the SEs adsorption on the concentration of OH-ions in the solution (Appendix 2/ Figure 3).

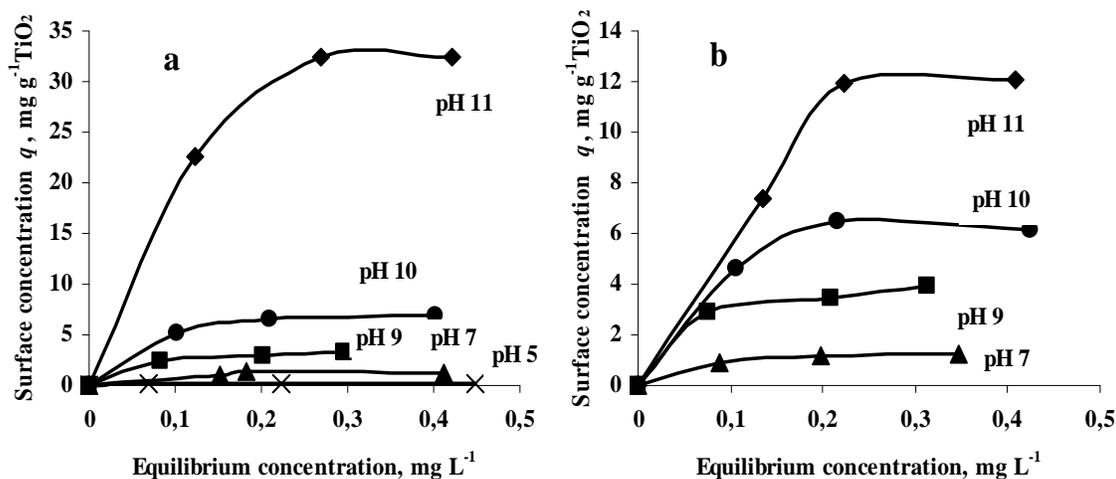


Figure 8. Adsorption isotherms for E2 (a) and EE2 (b) on TiO_2 catalyst surface at different pH values in the presence of ethanol

The fact that both SEs are adsorbed well in a strongly alkaline medium in combination with the knowledge about poor adsorption of phenolic compounds under similar conditions (Robert et al., 2000) indirectly indicates that the adsorption takes place at the site, where the alcohol group is attached to the SE molecule and not at the phenolic

moiety.

In addition, the adsorption of E2 at pH 11 was noticeably better than that of EE2, although at lower pH the surface concentration values for both SEs were almost identical. The difference can be explained presumably by the presence of the ethynyl group in the EE2 molecule (Figure 1) and the poor adsorption of phenolic groups in alkaline media: the position of the non-polar ethynyl group next to the alcohol one possibly geometrically hinders the adsorption from this molecule side; hence it is most likely not involved in the adsorption. E2, however, is adsorbed on the catalyst by its alcohol group with no obstacles. This observed difference in the adsorption of the two SEs due to the difference in the molecular structure indicates the key role played by the alcohol group in adsorption under alkaline media conditions.

PCO experiments

The experimental results showed that the PCO efficiency of both SEs increased with increasing pH (Appendix 2/p. 345). The strongly alkaline medium was observed to be the most efficient for the PCO process. It can be seen that the efficiency decreases with treatment time, the reason for which can be the decreasing concentration of the SEs and, thus, the decreasing adsorption and reaction rate (Figure 9).

Both adsorption (Figure 8) and PCO efficiency (Figure 9) consistently improve with increasing pH. Additionally, at pH 11 the PCO of E2 proceeds with higher efficiency than that of EE2, which is also in agreement with the data for adsorption of SEs. These facts indicate that the PCO rate is determined by the adsorption properties of the SEs on the TiO₂ surface.

It was also found that both the adsorption of SEs and the PCO efficiency increased practically linearly with increasing concentration of OH⁻ions. This may be attributed to direct oxidation with the positively charged holes or oxidation with OH⁻radicals in the vicinity of the semiconductor surface.

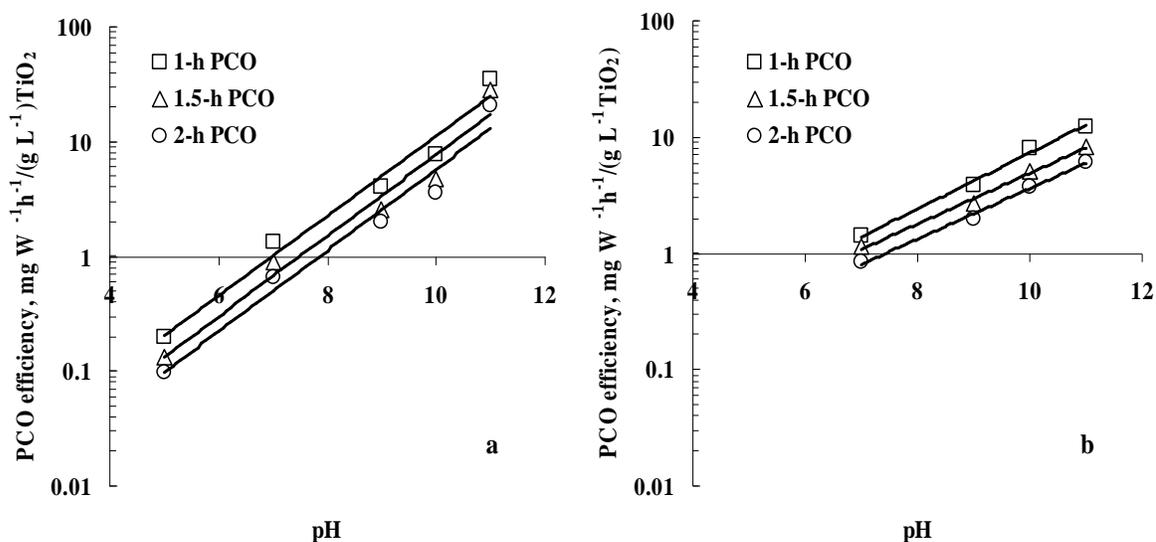


Figure 9. Dependence of PCO efficiency on pH of E2 (a) and EE2 (b) solutions at different treatment times in the presence of ethanol

7.1.3 Influence of urea

Urea itself did not show any detectable PCO degradation in 2 h at the TiO_2 concentration of 10 mg L^{-1} at any of the pH values tested (Appendix 3/p. 467). The photocatalyst concentration was then increased to 1 g L^{-1} and this concentration was tested in adsorption and PCO experiments with urea. Regardless of the 100-fold increase in TiO_2 concentration, no change in urea concentration was observed within 2-h PCO. This may be explained as due to poor urea adsorption on the TiO_2 surface: the series of adsorption experiments showed no adsorption of urea within the limits of precision of measurements in the range of pH under consideration.

Both adsorption behaviour and PCO of SEs were studied in the presence of urea (Appendix 3/pp. 467-469). No influence of urea was detected when ethanol was also present in the solution: the character of the dependence of SE adsorption on pH remains similar to the one observed in the absence of urea; also no particular difference on the PCO efficiency was observed when compared to the PCO without urea. The observed independence of the PCO of SEs on urea presence may be explained by the poor adsorption of urea at the TiO_2 surface.

7.1.4 Influence of saccharose

The experimental results in the presence of saccharose showed that the pattern of pH dependence remained similar to that previously obtained in the presence of ethanol only. However, a decrease in the PCO efficiency was observed in the presence of saccharose and ethanol compared to that when only ethanol was present (Figure 10; also see Appendix 4/ Figure 1). This indicates that saccharose is a powerful competitor for the SEs: a concentration of ethanol as great as 4 g L⁻¹ was not able to mask the effect of saccharose in a concentration of only 50 mg L⁻¹.

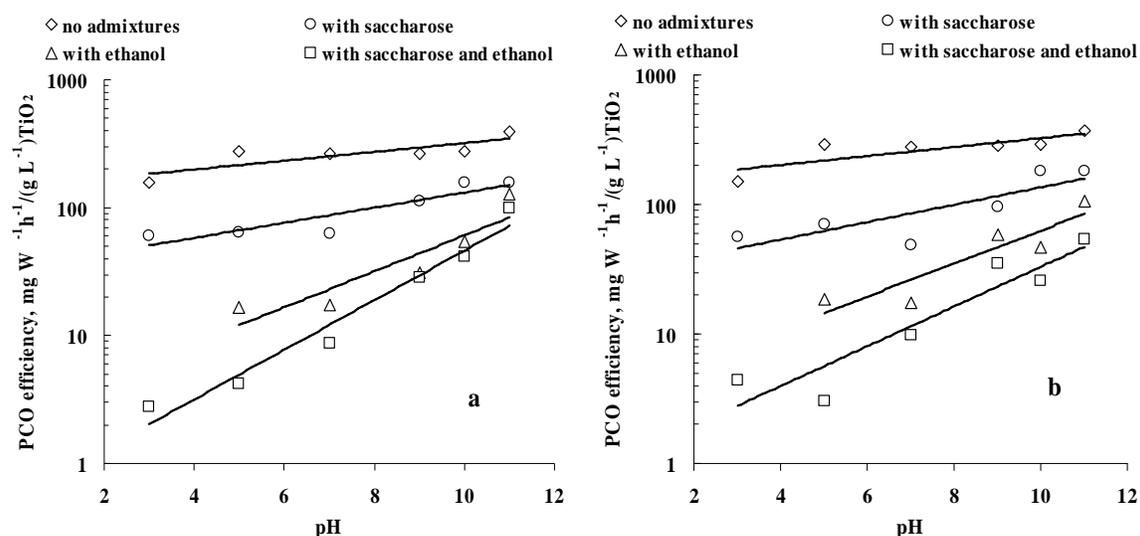


Figure 10. The dependence of PCO efficiency E on pH for E2 (a) and EE2 (b) solutions in the presence of admixtures at 15 min of treatment

In order to have a better understanding of the interactions between the SEs and saccharose, the PCO of saccharose was tested under similar experimental conditions as for the SEs. Initial experiments with 50 mg L⁻¹ of saccharose and 10 mg L⁻¹ of TiO₂ showed no valuable results: no visible degradation of COD or TOC was observed within 4 h. After several experimental approximations towards increased concentrations of the catalyst with various concentrations of the pollutant, the TiO₂ concentration of 500 mg L⁻¹ and the saccharose concentration of 150 mg L⁻¹ were selected (Appendix 4/ The PCO and adsorption of saccharose). Under the conditions of increased

concentrations, the results of 2-h PCO showed some saccharose oxidation, about 10%, in strongly alkaline medium. This is in an agreement with the observations of Vamathevan et al. (2001, 2002), who reported that the PCO rate of saccharose is relatively slow, when compared to other organic molecules. This relatively slow degradation of saccharose indicated that competitive oxidation of saccharose may not be a reason for the deterioration of the PCO efficiency of SEs in the presence of saccharose.

The adsorption of saccharose on TiO_2 was also studied and showed relatively poor results compared to the adsorption of SEs (Appendix 4/ The PCO and adsorption of saccharose). Consequently, the poor adsorption of saccharose and, thus, its poor PCO appears to be the reason for its minor, although noticeable, influence on the PCO of SEs under the experimental conditions.

7.2 Influence of ethanol

Experimental studies indicated that ethanol, present in the SE solutions as a solvent in an amount of 4 g L^{-1} , appears to be the most competitive substance interfering with the adsorption and thus the PCO of SEs (Appendices 3/pp. 468-470 and 4/ The influence of ethanol). Both the PCO (Figure 10 (“no admixtures” and “with ethanol”)) and adsorption (Figure 11) of SEs proceeded much better in absence of ethanol – this was attributed to the competitive adsorption of ethanol at the active sites of TiO_2 and the possible OH-radical scavenging known for alcohols. However, the dependence on pH repeated the previously observed pattern: increasing pH enhanced the adsorption and PCO efficiency.

Proof of the OH-radical scavenging effect of ethanol was found in the fact that the presence of ethanol affected the PCO of SEs to a greater extent than adsorption of SEs, particularly under strongly alkaline media conditions. Thus, under moderately alkaline pH from 9 to 10 the PCO efficiency deterioration in the presence of ethanol was consistent with the deterioration of adsorption, then at pH 11 the PCO efficiency decreased by about 2.3 times more than the adsorption (Figures 10 and 11). This could be

explained by the role of OH-radicals in oxidation: radicals may be scavenged by ethanol molecules thus decreasing the PCO rate of SEs.

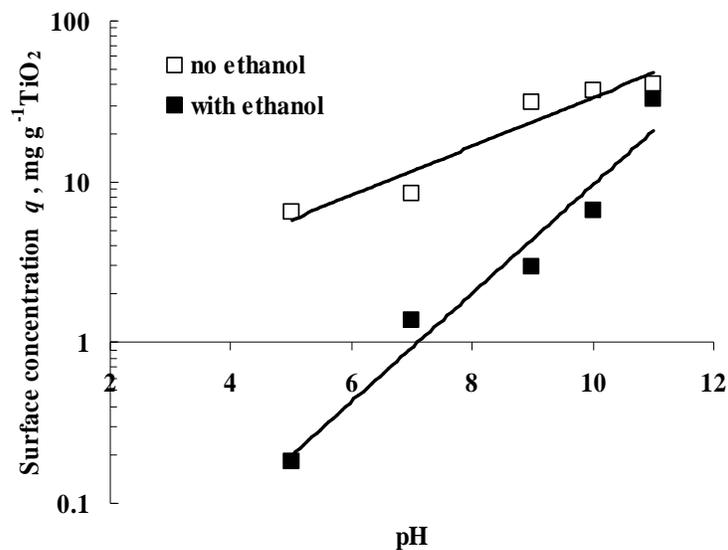


Figure 11. The E2 surface concentration on TiO₂ vs. pH with and without ethanol

7.3 PCO of steroid estrogens without ethanol

The dependence of the PCO efficiency of the SEs on pH with and without co-pollutants in the absence of ethanol as a solvent can be seen in Figure 12. It can be seen that the strongly alkaline medium was the most efficient for the PCO of both natural and synthetic SEs. This pattern remained the governing one for both natural and synthetic SEs despite the presence of admixtures.

The adsorption characteristics of the SEs on TiO₂ were also carefully studied for various pH values (Figure 13). The results indicate that the adsorption of SEs increases with increasing pH.

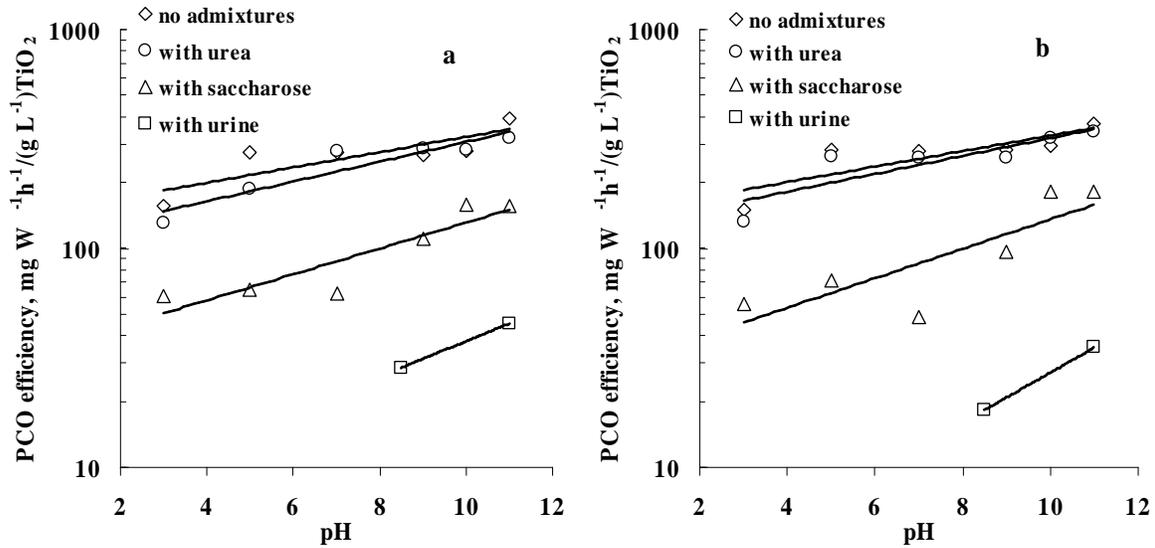


Figure 12. The dependence of the PCO efficiency of E2 (a) and EE2 (b) on pH: treatment time 15 min and 10 mg L^{-1} TiO_2 except urine - 120 min and 1 g L^{-1} respectively

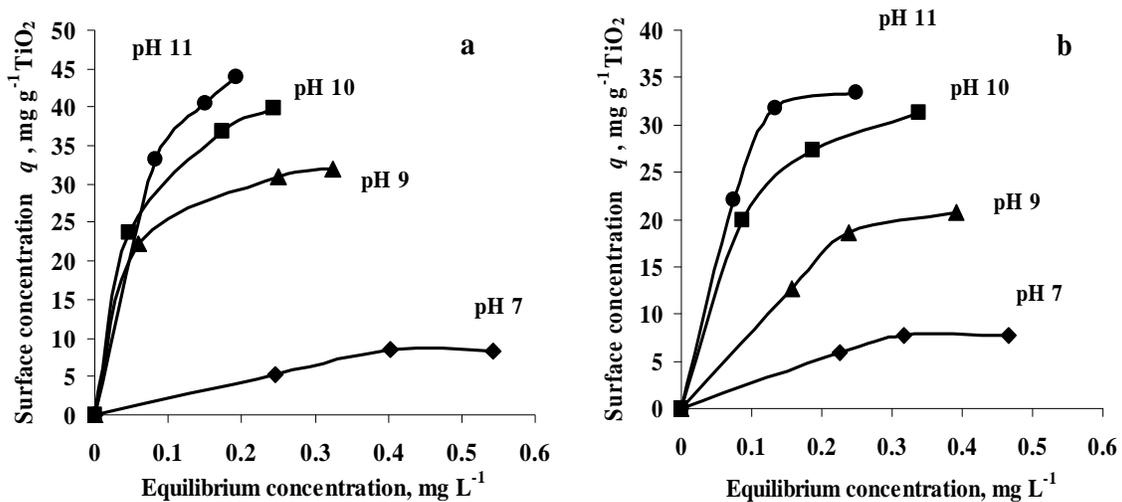


Figure 13. Adsorption isotherms for E2 (a) and EE2 (b) on TiO_2 catalyst surface at different pH without co-pollutants

The PCO efficiency and adsorption consistently improve with the increasing pH confirming previously declared statement, that the PCO rate is determined by the adsorption properties of the SEs on the TiO_2 surface.

7.3.1 Influence of urea

The presence of urea at a concentration of 75 mg L^{-1} , commonly observed for municipal wastewaters, showed negligible effect on the EE2 adsorption on the photocatalyst. The effect of urea on E2 adsorption was more pronounced; the adsorption deteriorated at all pH values except pH 7, although it was of the same order of magnitude as without the co-pollutant (Appendices 3/pp. 469-471 and 5/pp. 3-4). The difference in behaviour of the two substances may be explained by the difference in the hydrophilic properties of the two molecules: the presence of urea as an additional pollutant may have a stronger effect on adsorption of the more hydrophilic E2 molecule than of EE2, having a more hydrophobic character.

The presence of urea had negligible effect on the PCO of SEs, although the influence on E2 was a little more evident (Figure 12).

7.3.2 Influence of saccharose

The presence of saccharose essentially hindered the PCO efficiency of SEs for the entire pH range (Figure 12; see also Appendices 4/ The influence of saccharose and 5/pp. 4-5). This indicates that saccharose is a more powerful competitor for the PCO of SEs than urea. Therefore, the ability of the PCO to oxidise SEs in a selective manner should be verified in agreement with the experimental conditions; greater concentrations of co-pollutant may effectively slow down the PCO of the SEs.

7.3.3 Influence of urine

The effect of urine as a co-pollutant on the PCO of SEs was studied under two pH conditions: pH 11 (the most beneficial for the process) and pH 8.5 (natural pH of urine diluted with the Milli-Q water) (Appendix 5/p. 5). The photocatalyst concentration used was 1 g L^{-1} . The substances did not undergo significant oxidation under the experimental

conditions: the COD of the urine solution obtained from 100-fold dilution of the urine sample was initially around $200 \text{ mg O}_2 \text{ L}^{-1}$ and decreased by only 10 to 20 % at pH 8.5 and at pH 11 remained practically unchanged over a period of 2 h. A more concentrated urine solution with initial COD of $1400 \text{ mg O}_2 \text{ L}^{-1}$ remained essentially unaltered with PCO under the same conditions.

Initially, a concentrated urine solution was used in the experiments. Besides the negligible decrease in COD, no significant oxidation of SEs was observed within 2 h of the PCO. Presumably, the constituent compounds of urine, being resistant towards the PCO, occupied the adsorption sites of the photocatalyst and did not allow the SEs to adsorb and oxidise under competitive adsorption conditions. On the other hand, the PCO degradation of SEs was clearly exhibited with the diluted urine concentration; the target compounds were eliminated dependent on pH as in Figure 12. Complete oxidation of E2 and 95% oxidation of EE2 were observed at pH 11 in the 2-h PCO; around 75% of both SEs were oxidised under natural pH conditions. This result was observed with a negligible decrease in COD, which indicates that the SEs can be degraded in a selective manner by PCO in a strongly alkaline medium. Greater concentrations of co-pollutants in urine may, however, dramatically slow down the PCO of the SEs.

7.3.4 Kinetic studies

The reaction kinetics was elucidated as presented in paragraph 2.4 for the pseudo first order kinetic reaction (eq. 17) (Appendix 5/ pp. 5-6). The results of the PCO experiments of the SEs solutions with and without co-pollutants were plotted as $\ln(c/c_0)$ against time in minutes, where c_0 represents the initial concentration of the SEs. The best fit line was drawn and the equation and correlation coefficient, R^2 , were obtained. The plots demonstrated that the PCO of the SEs exhibited satisfactory fit to the pseudo first order equations, which is consistent with previously published results (Ohko et al., 2002; Coleman et al., 2005A). The rate constant k' was obtained from the slope and the initial rate was calculated by multiplying k' by c_0 . The half-life was then calculated. The results are presented in Table 7.

Table 7. Kinetic parameter value for PCO of SEs with and without co-pollutants

| Substance | pH | k' (min^{-1}) | Rate ($\mu\text{mol dm}^{-3}$ min^{-1}) | Half- life (min) | R^2 | Substance | pH | k' (min^{-1}) | Rate ($\mu\text{mol dm}^{-3}$ min^{-1}) | Half- life (min) | R^2 |
|-----------------------|-----|-------------------------------|--|------------------------|-------|------------------------|-----|-------------------------------|--|------------------------|-------|
| E2 | 11 | 0.254 | 0.528 | 2.8 | 0.995 | EE2 | 11 | 0.295 | 0.519 | 2.4 | 1.000 |
| | 10 | 0.091 | 0.190 | 7.4 | 0.995 | | 10 | 0.116 | 0.205 | 5.9 | 0.999 |
| | 9 | 0.070 | 0.140 | 9.7 | 0.988 | | 9 | 0.107 | 0.188 | 6.5 | 1.000 |
| | 7 | 0.068 | 0.132 | 10.4 | 0.984 | | 7 | 0.110 | 0.191 | 6.2 | 0.999 |
| | 5 | 0.072 | 0.148 | 9.6 | 0.990 | | 5 | 0.107 | 0.184 | 6.5 | 0.999 |
| | 3 | 0.034 | 0.070 | 20.2 | 0.998 | | 3 | 0.042 | 0.070 | 16.6 | 0.997 |
| E2 with urea | 11 | 0.263 | 0.441 | 2.6 | 1.000 | EE2 with urea | 11 | 0.293 | 0.458 | 2.4 | 1.000 |
| | 10 | 0.183 | 0.290 | 3.7 | 0.986 | | 10 | 0.241 | 0.378 | 2.9 | 1.000 |
| | 9 | 0.176 | 0.290 | 3.9 | 0.990 | | 9 | 0.100 | 0.159 | 6.6 | 0.917 |
| | 7 | 0.175 | 0.278 | 3.9 | 0.993 | | 7 | 0.094 | 0.138 | 7.2 | 0.978 |
| | 5 | 0.068 | 0.116 | 10.1 | 0.987 | | 5 | 0.088 | 0.141 | 7.8 | 0.989 |
| | 3 | 0.036 | 0.058 | 19.0 | 0.996 | | 3 | 0.032 | 0.048 | 21.2 | 0.997 |
| E2 with saccharose | 11 | 0.049 | 0.083 | 13.7 | 0.992 | EE2 with saccharose | 11 | 0.058 | 0.091 | 11.8 | 0.996 |
| | 10 | 0.036 | 0.061 | 19.0 | 0.984 | | 10 | 0.050 | 0.076 | 13.7 | 0.997 |
| | 9 | 0.022 | 0.036 | 30.9 | 0.975 | | 9 | 0.018 | 0.031 | 36.3 | 0.975 |
| | 7 | 0.011 | 0.019 | 58.8 | 0.989 | | 7 | 0.009 | 0.015 | 72.6 | 0.984 |
| | 5 | 0.010 | 0.017 | 63.2 | 0.969 | | 5 | 0.011 | 0.017 | 60.1 | 0.983 |
| | 3 | 0.016 | 0.027 | 42.2 | 0.997 | | 3 | 0.015 | 0.022 | 48.0 | 0.995 |
| E2 with urine | 11 | 0.021 | 0.039 | 31.8 | 0.883 | EE2 with urine | 11 | 0.022 | 0.035 | 29.0 | 0.850 |
| | 8.5 | 0.011 | 0.019 | 62.5 | 0.967 | | 8.5 | 0.012 | 0.019 | 60.3 | 0.979 |

The data reveal that in the absence of co-pollutants, the PCO of EE2 proceeded relatively faster than that of E2, except at pH 11 and pH 3, where the rates are almost equal. This result is in agreement with the data of other authors (Coleman et al., 2005A). Although their data differ from the results given in Table 7 due to the significantly higher UV-light intensity used, it is of the same order of magnitude.

In the presence of urea and saccharose, however, the rate of PCO of E2 was faster in neutral and strongly acidic media. No noticeable difference in the PCO rates of the SEs

could be seen when urine was present as a co-pollutant. The results clearly indicate that despite the presence of co-pollutants, the PCO of the SEs exhibited the highest rate under strongly alkaline media conditions.

The impact of co-pollutants is once again illustrated in Figure 14, where the degradation curves of SEs are plotted for pH 11, the most beneficial pH for the PCO, in the absence and presence of the admixtures under consideration. The interference of the co-pollutants was, nevertheless, far weaker in respect to the PCO of the SEs than could be expected from the hundred to thousands times higher concentration of the admixtures. This indicates the potential of PCO to be a selective oxidation method for the removal of SEs from wastewaters.

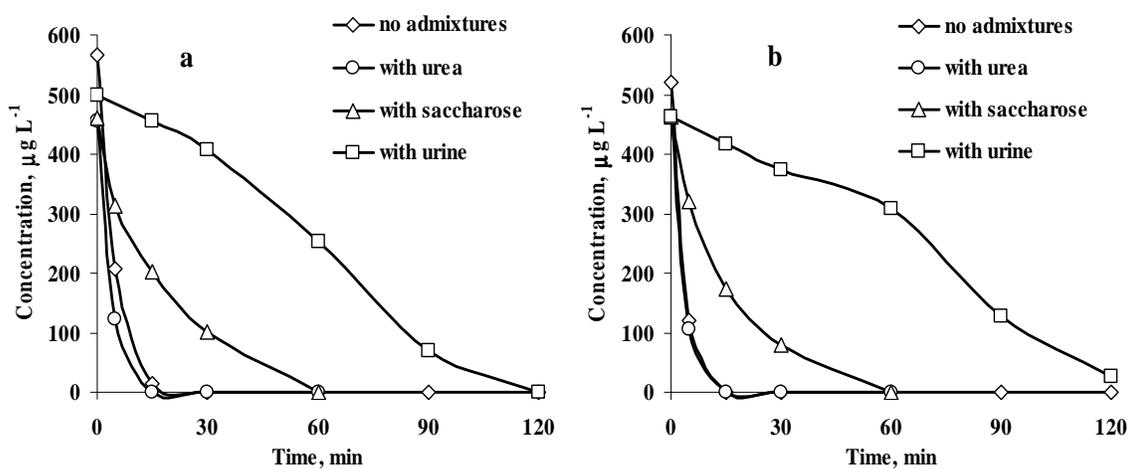


Figure 14. The rate of PCO of E2 (a) and EE2 (b) at pH 11 under different admixture conditions: 75 mg L⁻¹ of urea, 50 mg L⁻¹ of saccharose, 10 mL L⁻¹ of urine

CONCLUSIONS

The results of the present research showed that both natural and synthetic SEs can be photocatalytically degraded on UV-irradiated TiO₂ surface at very small (10 mg L⁻¹) concentrations of the photocatalyst. Alkaline conditions were observed to be the most beneficial for the PCO of both SEs regardless of the presence of the co-pollutants under consideration. The beneficial character of alkaline media was found to be determined by the adsorption properties of SEs on the TiO₂ surface: the target pollutants were observed to adsorb to a greater extent under alkaline media conditions. The difference in the molecular structure of the studied SEs resulted in a slight difference in the adsorption and also the PCO rate of the SEs.

The inhibiting effect of ethanol, often used in preparation of stock solutions of SEs, on the PCO rate of the SEs was found to be strong. This indicates the necessity to use organic solvent-free dissolution techniques for the study of SE behaviour.

The PCO of SEs was observed to be independent of the presence of urea in concentrations commonly found in domestic sewage. Saccharose appears to be a more powerful competitor in PCO reactions than ethanol. It interferes with the PCO of the target compounds hindering the oxidation rate of SEs: saccharose, poorly adsorbed and oxidised photocatalytically itself, most likely acts as an OH-radical scavenger. Urine significantly decreased the PCO rate of SEs at concentrations above 1:100. Nevertheless, the effect of the co-pollutants on the PCO of SEs is far weaker than could be expected from the concentrations of the admixtures, which are from one hundred to a few thousand times higher than that of the SEs.

Although higher concentrations of co-pollutants can dramatically slow down the PCO of SEs, realistic concentrations of urea and saccharose, characteristic for the sanitary fraction of domestic sewage, allowed selective removal of SEs. Thus, the potential of the PCO to be a selective oxidation method for SE removal from wastewaters was clearly demonstrated. Though the distance between establishing of PCO selectivity towards SEs

and the practical application may be long, the application of PCO in separate treatment of sanitary fraction of domestic sewage appears to be more promising for the maximum concentration of SEs and minimum volume to be treated.

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APPENDICES

APPENDIX 1

The role of pH in aqueous photocatalytic oxidation of β -estradiol

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The role of pH in aqueous photocatalytic oxidation of β -estradiol

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ABSTRACT. Experimental studies of aqueous photocatalytic oxidation (PCO) of β -estradiol in TiO₂ suspensions were undertaken. The dependence of PCO efficiency and adsorption of β -estradiol on pH was studied. It was found that both the adsorption of β -estradiol and the PCO efficiency increased practically linearly with increasing concentration of OH⁻ ions. The predominant role of direct β -estradiol oxidation with positively charged holes was thus indirectly confirmed.

1. INTRODUCTION

Recently, it has been suggested that several types of chemical present in the aquatic environment, even in nanogram concentrations, affect the reproduction of wildlife, livestock and even humans [1]. Owing to their steroid-like structures, it is assumed that these chemicals disrupt normal endocrine functions through interaction with steroid hormone receptors [2]. They are believed to have severe toxicity, high accumulation potential in the body, and persistence in the environment [3]. A growing number of industrial chemicals (phenolics, phthalates, polychlorinated biphenyls and organochlorine pesticides), some natural estrogens, and synthetic pharmaceuticals have been found to be most potent endocrine-disrupting compounds (EDCs). Municipal and industrial wastewaters together with runoff from agricultural production are considered important sources of EDCs in water. Farming plays a further significant role as a source of synthetic estrogens used for hormonal growth promotion [4].

Endocrine-disrupting compounds are difficult to remove totally from wastewaters by traditional primary and secondary treatment [5]. Moreover, the activated sludge process, which is commonly used for treating sewage at wastewater treatment plants (WTPs), is now assumed to act as a chemical reactor producing free estrogens. For example, commonly found estrogenic alkylphenols and steroidal estrogens are the products of incomplete breakdown of their respective parent compounds [6]. As a result EDCs have been detected in discharge water from various sewage WTPs. Domestic effluents have been reported to contain levels of EDCs between 1 and 50 ng L⁻¹, concentrations that are enough to influence the reproduction of male fish [7].

The penetration of EDCs into the water environment has consequently become a subject of worldwide growing concern. An effective water and wastewater treatment method able to eliminate EDCs is thus

needed. Recent interest in the removal of steroidal estrogens has resulted in publications concerning biological treatment [5, 6, 8], membrane separation [9], adsorption [10] and various advanced oxidation processes (AOPs). Although some publications show safe oxidation of steroidal estrogens in nitrification-denitrification stage of wastewater biological treatment at WTPs [8], a certain risk of EDC discharge to the environment remains [6, 11]. Attributable to separation methods, simple redistribution of pollutants does not allow safe and complete elimination of contaminants. In addition, the release of pollutants accumulated at the membrane surface presents a further risk [9]. Advanced oxidation methods are promising in EDC removal, although a certain risk of residual estrogenic activity at ozone doses commonly applied in potable water treatment has been pointed out [12]. Photocatalytic oxidation (PCO) strategies, however, have exhibited effective mineralisation of EDCs without formation of estrogenic intermediates [13–15]. Despite the clear potential of PCO, there is a lack of information concerning the mechanism of EDC elimination. For example, Coleman et al. [13] indicated an alkaline aqueous medium to be preferable in β -estradiol PCO; however, no explanation for such behaviour has been given.

The PCO may proceed via a dual mechanism [16]: (1) adsorption of the pollutant by the surface of the titanium dioxide, which is followed by a direct subtraction of the pollutant's electrons, i.e. oxidation, with positively charged holes; (2) oxidation with hydroxyl radicals at the catalyst surface or in its vicinity. Both reactions may proceed simultaneously, although positively charged holes have an oxidation potential about 1.25 times bigger than a hydroxyl radical [17]. Which mechanism dominates in PCO depends on the chemical and adsorption properties of the pollutant.

β -Estradiol is one of the basic natural estrogens, exhibiting the highest estrogenic activity and persistence in waters [6]. This study examined the dependence of PCO efficiency and adsorption of β -estradiol

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on pH and in particular a possible connection between the PCO performance and the β -estradiol adsorption on the TiO₂ surface.

2. MATERIALS AND METHODS

The aqueous solution of β -estradiol was prepared according to the recommendations of Nakashima [18]. Due to the hydrophobic character of β -estradiol, its solubility in water is low, which makes its dissolution even in microgram amounts difficult. β -Estradiol in the amount of 10,000 μg (Sigma-Aldrich) was dissolved in 100 ml of 99.5%-ethanol (Altia Oy, Finland). Following this, the alcoholic stock solution was gradually diluted in an ultrasonic bath with Milli-Q water to prepare 1 L of initial aqueous solution for complete dissolution of β -estradiol colloids. The initial aqueous solution was constantly stirred at room temperature in a hermetically sealed flask to avoid re-crystallisation of β -estradiol. The chromatographic analysis of the solution showed satisfactory stability of the target pollutant in the flask for at least two weeks. The sample solutions with the required concentrations for the experiments were prepared by dilution of the initial aqueous solution with Milli-Q water under stirring for 30 min. The initial concentration of the sample solutions was 500 $\mu\text{g L}^{-1}$ if not otherwise specified. All experiments were conducted at 25 ± 1 °C. The pH value was adjusted with sulphuric acid or sodium hydroxide.

Titanium dioxide (TiO₂, Degussa P25) under near-UV irradiation (365 nm) was selected as a photocatalyst. Synthetic syringe filters with a pore size 0.45 μm were initially used to separate the catalyst from the solution. However, a partial adsorption of β -estradiol by the filter material was observed. Consequently, centrifugation at 10,000 rpm was used to separate TiO₂ from the samples before the analysis.

The PCO experiments were performed in a 0.25-L capacity thermostatted batch glass reactor, having an inner diameter of 100 mm, equipped with a magnetic stirrer. The agitation intensity was maintained with a standard 25-mm Teflon stirrer at 300 rpm. A 365 nm UV-lamp was positioned horizontally over the reactor; the irradiance was about 1.1 mW/cm^2 , measured by the optical radiometer UVX (UVX, USA) at a distance corresponding to the level of the free surface of the reactor.

The concentrations of TiO₂ in the suspensions for the PCO experiments were carefully selected so that the target compound concentration decreased due to adsorption on the catalyst from an initial 500 to equilibrium 200 $\mu\text{g L}^{-1}$.

The experiments determining the adsorption isotherms were performed in 0.50-L capacity flasks, in which the β -estradiol solution was mixed with TiO₂ at a stirring frequency of 900 rpm for 24 hours. The TiO₂ concentrations in the flasks corresponded to the amounts of TiO₂ established previously for

a measurable, a few hundreds $\mu\text{g L}^{-1}$, decrease in β -estradiol aqueous concentration at different pH. Each flask was handled separately as a single-point sample, i.e. without intermediate sampling, and each experiment was repeated three times. The equilibrium concentration of β -estradiol adsorbed on the surface of the catalyst q , mg g^{-1} TiO₂, was calculated from the mass balance of the sample.

The concentration of β -estradiol was determined by means of HPLC with 150-mm ZORBAX Eclipse XDB-C18 column (Agilent), UV-detector at the wavelength 278 nm, and mobile phase acetonitrile/water 1 : 1 at a flow rate of 1 mL min^{-1} .

3. RESULTS AND DISCUSSION

The experiments showed that β -estradiol readily yields to PCO over UV-irradiated TiO₂. Since the most effective catalyst concentration is between 1 and 3 g L^{-1} [19], a concentration of TiO₂ of 1 g L^{-1} was initially used in the preliminary study. This concentration was also chosen because it was used in previous studies [15] and would make our data comparable. However, under these experimental conditions a sharp decrease in β -estradiol concentration was noticed as a result of the introduction of TiO₂. This could be attributed to the abundant presence of TiO₂ in comparison to the concentration of the target compound: β -estradiol may simply be adsorbed by the catalyst. Further PCO experiments were carried out with carefully selected TiO₂ concentrations, the choice of which was attributed to the adsorption behaviour of β -estradiol.

Adsorption isotherms. The adsorption isotherms were determined at pH 3, 5, 7, 9, and 11. The results are shown in Figure 1. One can see that β -estradiol is much better adsorbed by TiO₂ in an alkaline medium than in neutral and acidic media. In fact, a practically linear logarithmic increase of the surface concentration q versus increase of pH was observed. This corresponds with a linear dependence of β -estradiol adsorption on the concentration of OH-ions in the solution (Figure 2).

The amount of TiO₂ necessary to decrease the initial concentration of β -estradiol from 500 to 200 $\mu\text{g L}^{-1}$ is shown in Figure 3. At pH 11 a mere 10 mg L^{-1} of TiO₂ was sufficient to obtain the pre-set change in concentrations. In acidic media the proper TiO₂ concentration at pH 5 was 1750 mg L^{-1} . At pH 3 no appropriate TiO₂ concentration was found up to 12 g L^{-1} of catalyst, i.e. in strongly acidic media the adsorption is very poor.

PCO experiments. The catalyst amounts obtained for suitable decrease in β -estradiol concentrations due to adsorption were then used in the PCO experiments. Initially, the β -estradiol solution was brought to equilibrium with TiO₂ during 24-h adsorption. After this the resulting suspension was divided between two reactors: the one used for the PCO was called "active" and the other, with no UV light applied, was called "reference".

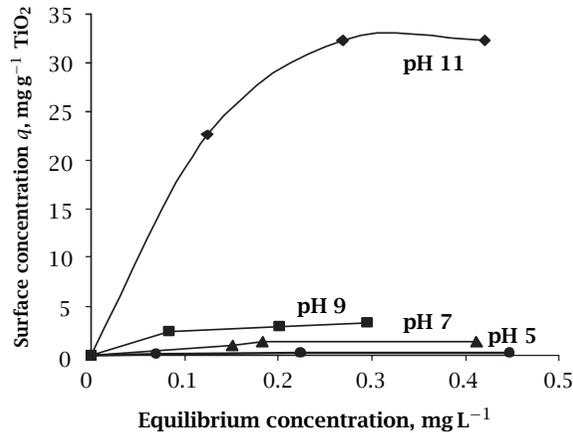


Figure 1. Adsorption isotherms for β -estradiol on TiO_2 catalyst at different pH values at 25 °C. Concentrations of TiO_2 , mg L^{-1} : pH 5-1750, pH 7-320, pH 9-100, pH 11-10.

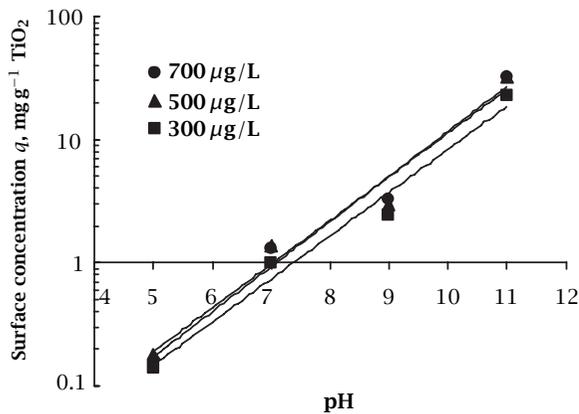


Figure 2. β -Estradiol equilibrium surface concentration on TiO_2 vs. pH at different β -estradiol initial concentrations.

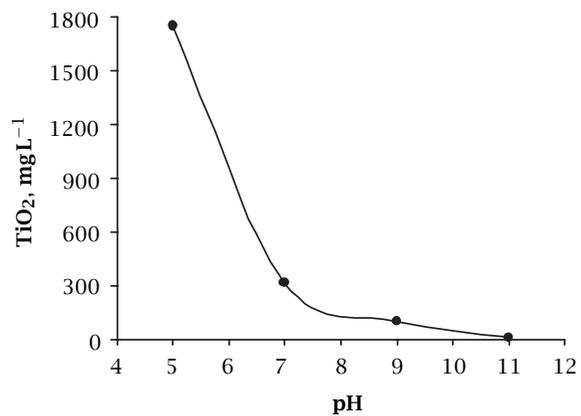


Figure 3. The TiO_2 catalyst concentration sufficient for the adsorption of β -estradiol from initial 500 to equilibrium 200 $\mu\text{g L}^{-1}$ in 24-h experiments vs. pH.

Both reactors were exposed to identical experimental conditions. The samples from the active reactor were compared to the reference samples to avoid complications caused by water evaporation. The results of the PCO experiments can be seen in Figure 4.

The results showed that the PCO of β -estradiol proceeds more slowly in a strongly alkaline medium. This could be explained by the difference in the TiO_2 concentrations used at different pH as they were obtained in the adsorption experiments (Figure 3). To bring the results to a uniform basis for assessment, the performance of PCO was characterized by the process efficiency E . The PCO efficiency relative to the catalyst concentration was calculated as the decrease in the concentration of the target compound divided by the amount of energy reaching the surface of the sample and by the concentration of the catalyst used:

$$E = \frac{\Delta c \cdot V \cdot 1000}{I \cdot s \cdot t \cdot m}$$

E —PCO process efficiency, $\mu\text{g W}^{-1} \text{h}^{-1}/(\text{g L}^{-1}) \text{TiO}_2$; Δc —decrease in the compound concentration, $\mu\text{g L}^{-1}$; V —the volume of treated sample, L; I —irradiation intensity, mW cm^{-2} ; s —solution irradiated surface area, cm^2 ; t —treatment time, h; m —concentration of TiO_2 , g L^{-1} .

The dependence of the PCO efficiency on pH can be seen in Figure 5: at pH 11 PCO proceeds with the highest efficiency. One can see that the efficiency E decreases with treatment time, which can be explained by the decreasing adsorption (Figure 1) and, thus, the reaction rate with the decreasing concentration of β -estradiol. Analysis of the obtained dependence shows a practically linear dependence of the PCO efficiency on OH-ions concentration.

Both the amount of β -estradiol adsorbed on the TiO_2 surface and the PCO efficiency follow a similar pattern: the adsorption and the PCO exhibit simple linear dependence on OH-ion concentration. The slopes

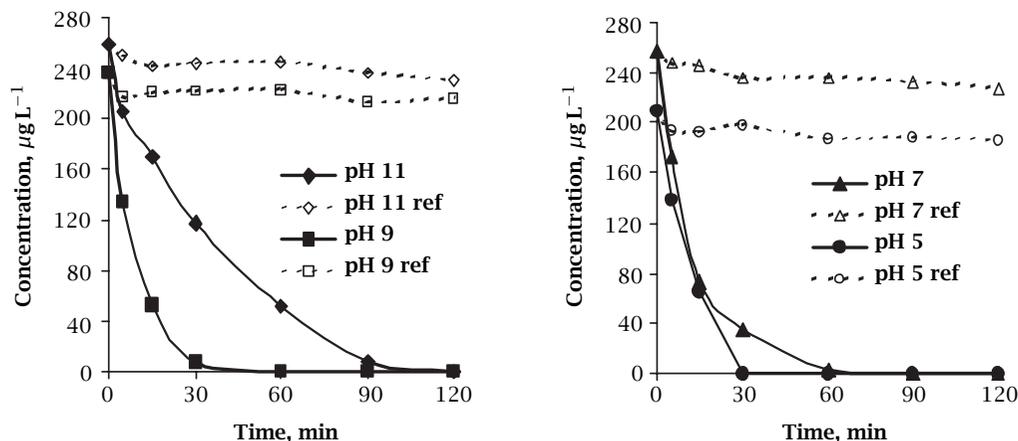


Figure 4. The rate of PCO of β -estradiol. Concentrations of TiO_2 , mg L^{-1} : pH 5-1750, pH 7-320, pH 9-100, pH 11-10.

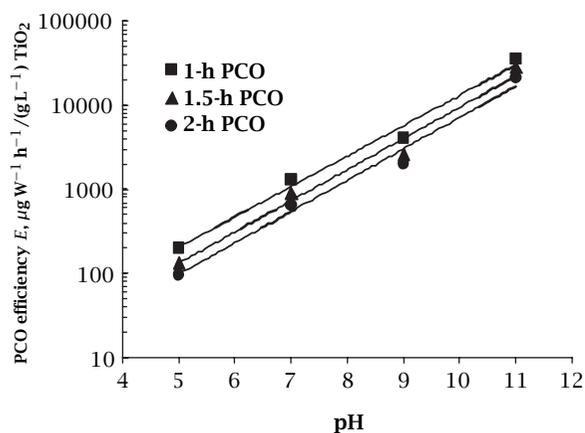


Figure 5. Dependence of PCO efficiency E on pH of β -estradiol solution at different treatment times.

of the logarithmic dependence of the PCO efficiency at different treatment times are only slightly, within 5%, bigger than the ones for adsorption (Figures 2 and 5). Perhaps, this number indicates the extent to which OH-radicals accelerate PCO. This slight difference indicates that OH-radicals may play only a minor role in PCO.

The fact that the β -estradiol molecule is adsorbed well in a strongly alkaline medium may indicate that the adsorption takes place with the molecule attached with its alcoholic group not the phenolic moiety: phenolic compounds exhibit poor adsorption by TiO_2 in alkaline media [20]. However, phenolic compounds yield better to PCO also under alkaline media conditions [21], which indicates a difference in the oxidation mechanisms of β -estradiol and phenolic compounds. This suggests the predominant transformation of the phenolic moiety in PCO shown in [15] results presumably from more complicated processes than a direct oxidation of the phenolic moiety with the positively charged holes.

4. CONCLUSIONS

The results of the research showed that β -estradiol could easily be degraded by PCO over UV-irradiated TiO_2 . The PCO of β -estradiol in TiO_2 suspension proceeds with the highest efficiency in a strongly alkaline medium. This was found to be determined by the adsorption properties of β -estradiol on the TiO_2 surface: the target pollutant was observed to adsorb to a greater extent under alkaline media conditions. Analysis of the experimentally obtained data indicates that OH-radicals may play a minor role in PCO of β -estradiol.

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APPENDIX 2

Photocatalytic oxidation and adsorption of natural and synthetic steroid estrogens on TiO₂ in aqueous solutions at different pH

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PHOTOCATALYTIC OXIDATION AND ADSORPTION OF NATURAL AND SYNTHETIC STEROID ESTROGENS ON TiO₂ IN AQUEOUS SOLUTIONS AT DIFFERENT pH

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ABSTRACT

Experimental studies of aqueous photocatalytic oxidation (PCO) and adsorption of two steroid estrogens (SEs), the natural β -estradiol (E1) and the synthetic 17 α -ethynylestradiol (EE2), in TiO₂ suspensions were undertaken. The dependence of PCO efficiency and adsorption of both SEs on pH was studied. It was found that both the adsorption of SEs and the PCO efficiency increased practically linearly with increasing concentration of OH⁻ ions. The predominant role of direct oxidation with positively charged holes was thus indirectly confirmed for both SEs. The adsorption of SEs in alkaline media was observed to be different due to the difference in molecular structures.

KEYWORDS

Endocrine disrupting compounds (EDCs), 17 α -ethynylestradiol (EE2), β -estradiol (E2), water treatment, titanium dioxide, photocatalysis

INTRODUCTION

The presence of micro-pollutants in aquatic environment originated from the effluents of wastewater treatment plants (WWTP) are of increased concern during last few decades. Pettersson et al. [1] consider natural and synthetic steroid estrogens (SEs) to be responsible for the majority of endocrine-disrupting effects on living organisms. Vethaak et al. [2] conclude that hormones, especially 17α -ethynylestradiol (EE2), are primarily responsible for the estrogenic effect. These endocrine disrupting compounds are able to interact with and disrupt natural hormonal mechanisms [3]. They are potent already at the concentrations as low as 0.1 ng L^{-1} [4, 5]. The important sources of SEs in aquatic environment are municipal and industrial wastewaters, and runoff waters from agricultural production. Recently farming was found to contribute more to the environmental contamination with SEs than it was thought before. For example, identifying the possible sources of SEs entering aquatic environment in the UK, Johnson et al. [6] predicted that the direct excretion of SEs into water courses by farm animal population is likely to be more important source of contamination than the human population.

Both natural and synthetic SEs, originated in municipal wastewaters, are excreted by humans in biologically less active conjugated forms (glucuronides or sulphates) in urine and faeces. However, they are transformed back into active forms presumably during the sewage treatment process in the presence of faecal bacteria [7-9]. The relative estrogenic activity for these SEs is as follows: $EE2 \gg \beta$ -estradiol (E2) >estrone (E1) [10]. EE2 was found to be 11 to 27 times more potent than E2 and 33 to 66 times more potent than E1 [11]. However, E1 was detected at highest concentration (20 times higher than E2) in the Swedish WWTPs' effluents [1].

The environmental impact of SEs depends on the available dilution of the effluents' receiving waters at each location. The limited dilution in Europe, especially during the summer months, results in the high loads of SEs in discharged WWTP effluents [12]. Beck et al. [13] reported the concentration of SEs in a coastal area of German Baltic Sea to be at levels between 0.1 and 17 ng L^{-1} .

In order to remove SEs from effluent, ideally European sewage treatment tanks could be doubled or trebled in size in order to prolong biodegradation of these endocrine disrupters. However, due to the limited land availability in many cases this would be impractical [12]. Also the removal of SEs with excess sludge was found to be insignificant [14]. Therefore, the addition of tertiary treatment, known to reduce micro-organic pollutants, is considered as an option [12].

Recent interest in the removal of SEs has resulted in publications concerning membrane separation [15], adsorption [16] and various advanced oxidation processes (AOPs). Attributable to separation methods, simple redistribution of pollutants does not allow safe and complete elimination of contaminants. In addition, the release of pollutants accumulated at the membrane surface presents a further risk [15]. AOPs are promising in SEs removal, although a certain risk of residual estrogenic activity at ozone doses commonly applied in potable water treatment has been pointed out [17].

Photocatalytic oxidation (PCO) was confirmed to effectively eliminate the SEs without formation of estrogenic intermediates [18-20] and is considered as a potential alternative. PCO may proceed via two mechanisms [21]: a) oxidation with positively charged holes - the adsorption of the pollutant by the surface of the TiO_2 , followed by a direct subtraction of the pollutant's electrons; b) oxidation with hydroxyl radicals that takes place at the catalyst surface or in its vicinity. What mechanism dominates in PCO depends on the chemical and adsorption properties of the target pollutant.

The present work is an extension of the previous research [22] on the mechanism of SEs PCO. We examined the influence of pH to SEs PCO efficiency and adsorption on TiO₂ for natural and synthetic SEs - E2 and EE2.

MATERIALS AND METHODS

E2 as a natural estrogen and EE2 as a synthetic one (Sigma-Aldrich) were used (Fig. 1). Due to hydrophobic character of the compounds they were first dissolved in 99.5%-ethanol (Altia Oy, Finland) and then gradually diluted with Milli-Q water to prepare the stock aqueous solution of 10 mg L⁻¹. The stock solution was constantly stirred at room temperature in a hermetically sealed flask to avoid re-crystallisation of the SEs. The solutions with required concentrations for the experiments were prepared by dilution of stock solution with Milli-Q water. The initial concentration of the solutions to be treated was 500 µg L⁻¹ if not otherwise specified. All PCO experiments were conducted at 23±2 °C. The pH value was adjusted with sulphuric acid or sodium hydroxide.

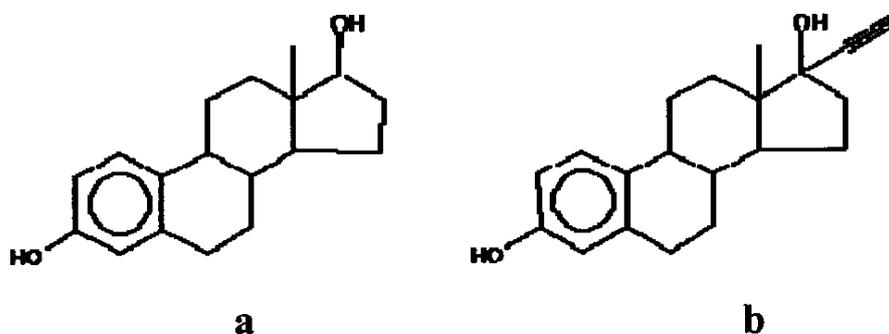


Figure 1. Molecular structures of E2 (a) and EE2 (b)

Titanium dioxide (TiO₂, Degussa P25) under near-UV irradiation (365 nm) was used as photocatalyst. Centrifugation at 10,000 rev min⁻¹ was applied to separate TiO₂ from the samples before the analysis. The PCO experiments were performed in 0.25-L capacity thermostatted batch glass reactors with an inner diameter of 100 mm, supplied with a magnetic stirrer. The agitation intensity was maintained with a standard 25-mm Teflon stirrer at 300 rpm. A 365 nm UV-lamp was positioned horizontally over the reactor; the irradiance was about 1.1 mW/cm², measured by UVX Radiometer (UVX, USA).

The concentrations of TiO₂ in suspensions for the PCO experiments were thoroughly selected for both compounds separately so that the SE's concentration decreased due to adsorption on the catalyst from initial 500 to equilibrium 200 µg L⁻¹.

The conditions of the experiments determining the adsorption isotherms were performed in 0.50-L capacity flasks, where the estrogens solutions were mixed with TiO₂ at a stirring frequency of 900 rpm for 24 hours at 25 °C. The TiO₂ concentrations in the flasks corresponded to the amounts of TiO₂ established previously for a sensible, a few hundreds µg L⁻¹, decrease in SEs' aqueous concentration at different pH. Each flask was handled separately as a single-point sample, i.e. without intermediate sampling, and each experiment was repeated three times. The equilibrium concentration of compounds adsorbed on the surface of the catalyst q , µg g⁻¹ TiO₂, was calculated from the mass balance of the sample. The concentrations of estrogens were determined by means of HPLC with 150-mm ZORBAX

Eclipse XDB-C18 column (Agilent) supplied with UV-detector at the wavelength 278 nm, mobile phase acetonitrile/water 1:1 at a flow rate of 1.0 mL min⁻¹.

RESULTS AND DISCUSSION

Adsorption isotherms The adsorption isotherms were determined at the pH from 5 to 11. The results are shown in Fig. 2. It was previously established that the adsorption of E2 in acidic media was very poor increasing with increased pH [22].

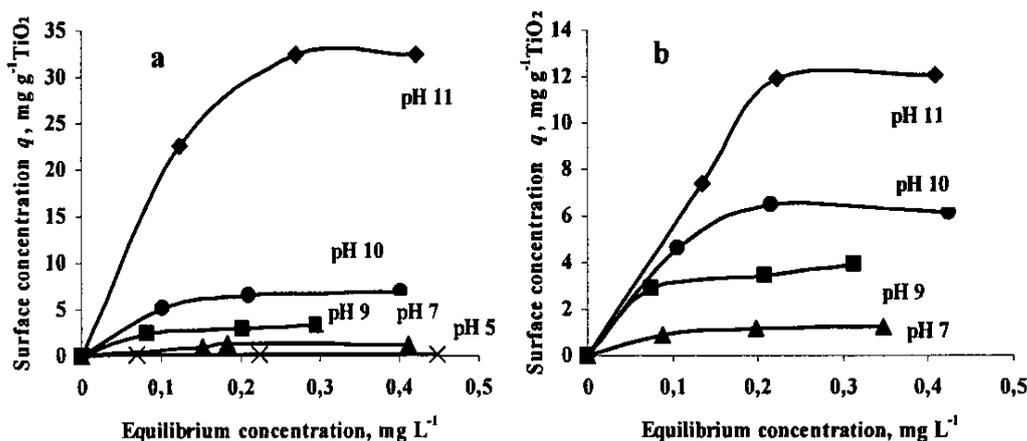


Figure 2. Adsorption isotherms for E2 (a) and EE2 (b) on TiO₂ catalyst surface at different pH values at 25°C

One can see that both E2 and EE2 are much better adsorbed by TiO₂ in strong alkaline medium than in neutral one. In fact, we observed a practically linear logarithmic increase of the surface concentration q versus the increase of pH. This corresponds to a linear dependence of the SEs' adsorption on the concentration of OH⁻ ions in the solution (Fig. 3).

The adsorption of E2 on TiO₂ catalyst surface at pH 11.0 occurred to be noticeably better than of EE2, although at lower pH values the surface concentrations of SEs under consideration were almost identical. This can be explained presumably by the presence of the acetylene group in EE2 molecule and the poor adsorption of phenolic groups in alkaline media [23]: the position of the acetylene group next to the alcohol one probably geometrically hinders the adsorption from this molecule side. The acetylene group itself is non-polar because of the small difference in electronegativity of carbon and hydrogen; hence it is most likely not involved in the adsorption. E2, however, is adsorbed on the catalyst by its alcohol group with no obstacles.

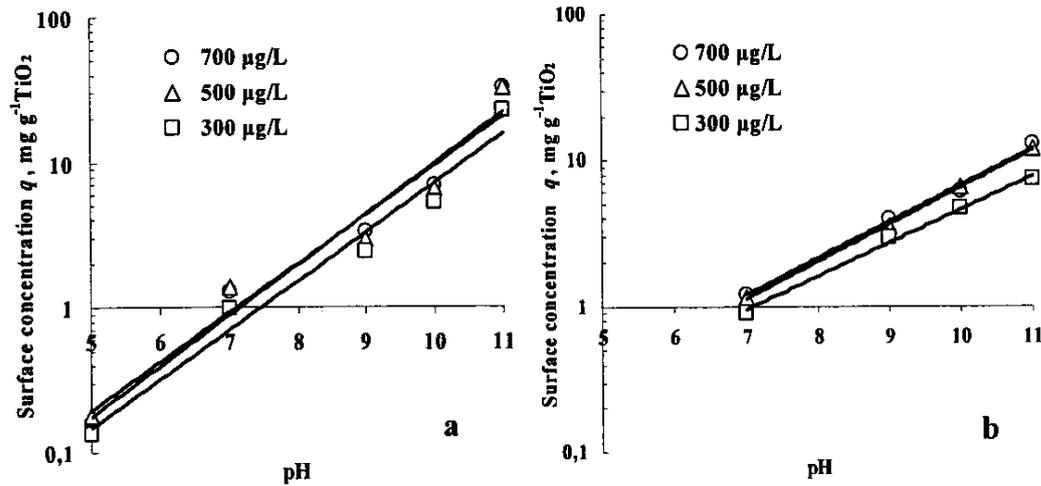


Figure 3. The E2 (a) and EE2 (b) equilibrium surface concentration q on TiO_2 vs. pH at different SEs' initial concentrations

The amount of TiO_2 necessary to decrease the initial concentration of the pollutants from 500 to 200 $\mu\text{g L}^{-1}$ is shown in Fig. 4. At pH 11 only 10 and 25 mg L^{-1} of TiO_2 for E2 and EE2 respectively were sufficient to obtain the pre-set change in concentrations. The proper TiO_2 concentration at pH 7 was several tens times higher.

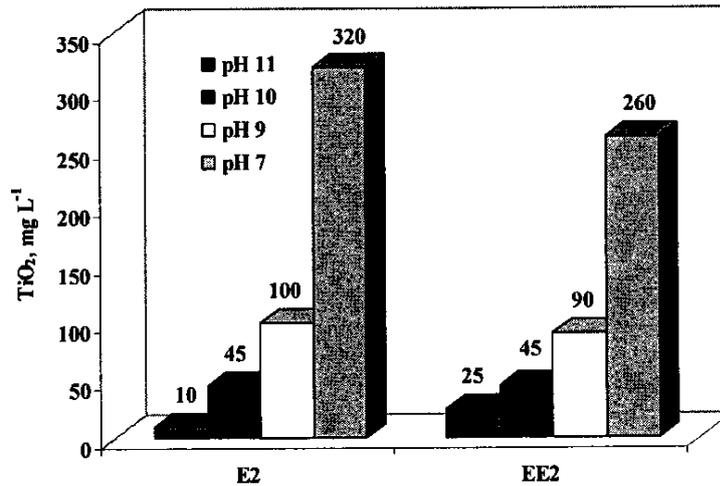


Figure 4. The TiO_2 catalyst concentrations sufficient for the adsorption of E2 and EE2 from initial 500 to equilibrium 200 $\mu\text{g L}^{-1}$ in 24-h experiments vs. pH

PCO experiments The TiO_2 amounts obtained for the suitable decrease in the SEs' concentrations due to adsorption were then used in the PCO experiments. Initially, the SEs' solutions were brought to equilibrium with TiO_2 during 24-h adsorption. After this the resulting suspension was divided to two reactors: "the active", where PCO was carried out and "the reference" with no UV light applied. Both reactors were exposed to identical experimental conditions. The samples from the active reactor were compared to the reference

ones to avoid complications caused by water evaporation. The results of PCO experiments can be seen in Fig. 5.

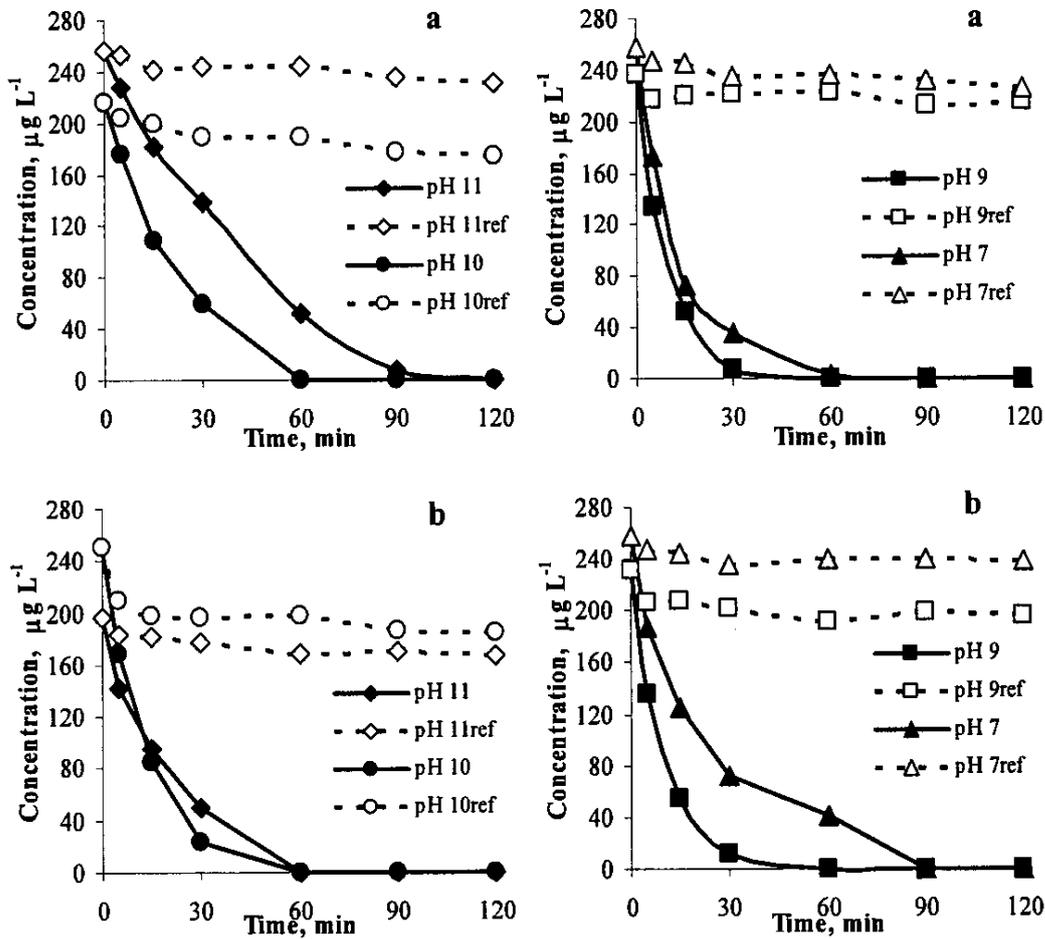


Figure 5. The rate of PCO of E2 (a) (concentrations of TiO₂, mg L⁻¹: pH 7 – 320, pH 9 – 100, pH 10 – 45, pH 11 – 10) and EE2 (b) (concentrations of TiO₂, mg L⁻¹: pH 7 – 260, pH 9 – 90, pH 10 – 45, pH 11 – 25)

One can see that the PCO of the both SEs apparently proceeds slower in strongly alkaline medium. This could be explained by the different TiO₂ concentrations obtained in the adsorption experiments (Fig. 4) used also in PCO at different pH. To compare the results on the uniform basis, the PCO performance was characterized by the process efficiency *E*. The PCO efficiency relative to the catalyst concentration was calculated as the decrease in the concentration of the target compound divided by the amount of energy reaching the surface of the sample and by the concentration of the catalyst used:

$$E = \frac{\Delta c \cdot V \cdot 1000}{I \cdot s \cdot t \cdot m}$$

where E – PCO process efficiency, $\mu\text{g W}^{-1} \text{h}^{-1}/(\text{g L}^{-1} \text{TiO}_2)$; Δc – decrease in the compound concentration, $\mu\text{g L}^{-1}$; V – the volume of treated sample, L; I – irradiation intensity, mW cm^{-2} ; s – solution irradiated surface area, cm^2 ; t – treatment time, h; m – concentration of TiO_2 , g L^{-1} .

The dependence of the PCO efficiency related to the catalyst concentration on pH can be seen in Figure 6: at pH 11 the PCO was indeed the most efficient. One can see that at pH 11 the PCO of E2 proceeds with higher efficiency than of EE2. This is in agreement with Fig. 3 for the adsorption of SEs. The results show that the efficiency E is decreasing in treatment time, which can be explained with the decreasing concentration of the SEs and, thus, the decreasing adsorption and, therefore, the reaction rate. The analysis of the results shows a practically linear dependence of the PCO efficiency on OH-ions concentration.

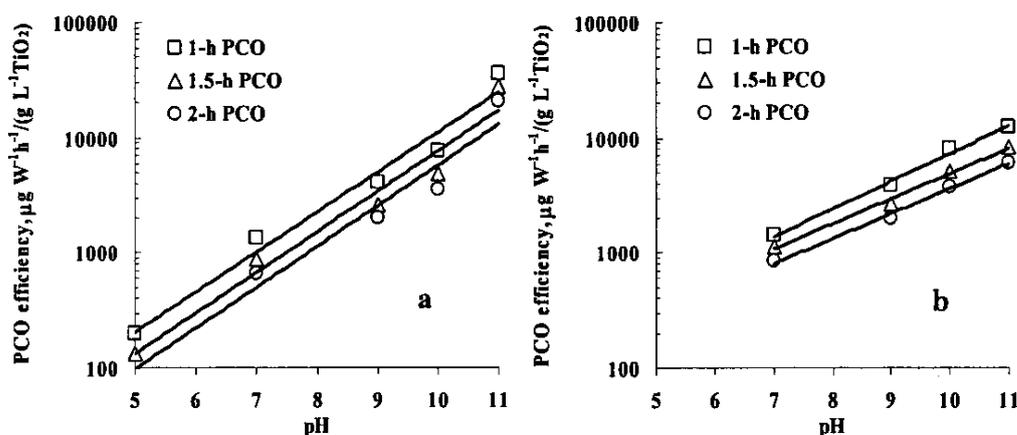


Figure 6. Dependence of PCO efficiency E on pH of E2 (a) and EE2 (b) solutions at different treatment times

An analogy in the experimental results was observed indicating that both the surface concentration of SEs on the TiO_2 and the PCO efficiency behave along the similar pattern: both the adsorption and the PCO exhibit simple linear dependence on OH-ions concentration. The slopes of the logarithmic dependence of the PCO efficiency at different treatment times are only slightly, within 5%, bigger than the ones for adsorption (Fig. 3 and 6). Perhaps, this number indicates the extent, to which increasing yields of OH-radicals formed from increasing amounts of OH-ions at higher pH accelerate PCO. This slight difference in dependences of adsorption and PCO patterns indicates a role of OH-radicals played in PCO being apparently minor.

The fact that both E2 and EE2 molecules are adsorbed well in strongly alkaline medium in combination with the knowledge about a poor adsorption of phenolic compounds under similar conditions [23] indirectly indicates that the adsorption takes place with the molecule attached with its alcohol group not the phenolic moiety. Supplementary, the observed difference in the adsorption of the two SEs due to difference in the molecular structure indicate the key role played by the alcohol group in adsorption under alkaline media conditions.

Phenolic compounds, from the other hand, yield well to PCO under alkaline media conditions [24]. This indicates the radical mechanism prevailing in their PCO. The minor role of OH-radicals observed in SEs' PCO may point to a difference in oxidation mechanisms of SEs and phenolic compounds. This, in turn, makes the predominant transformation of the phenolic moiety in PCO of E2 shown by Ohko et al. [20] resulting presumably from more

complicated process than a direct oxidation of the phenolic moiety with the positively charged holes since they should oxidize alcohol group first.

CONCLUSIONS

The results of the present research showed that both natural and synthetic SEs could be easily degraded by PCO over UV-irradiated TiO₂. The highest PCO efficiency in TiO₂ suspension was observed in strongly alkaline medium for both E2 and EE2. This was found to be determined by the adsorption properties of substances on the TiO₂ surface: the target pollutants were observed to adsorb to a greater extent under alkaline media conditions. The difference in the molecular structure resulted in a difference in the adsorption and also the PCO rate for the SEs. The analysis of the experimentally obtained data indicates a minor role of OH-radicals in PCO of SEs. The effective PCO in alkaline media may allow selective oxidation of SEs in aqueous solutions.

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APPENDIX 3

Selective photocatalytic oxidation of steroid estrogens in water treatment: urea as co-pollutant

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Selective photocatalytic oxidation of steroid estrogens in water treatment: urea as co-pollutant

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Abstract

The objective of the present research concerns the competitive photocatalytic oxidation (PCO) and adsorption of steroid estrogens (SEs) on titanium dioxide in presence of urea. The results showed the indifference of SEs towards the presence of urea in concentrations characteristic for the domestic sewage. The selective PCO of SEs appeared to be feasible in alkaline media, in which the PCO exhibited the highest efficiency. Ethanol used for hydrophobic SEs dissolution in water appeared to be interfering with the PCO.

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Keywords: 17 α -Ethinylestradiol (EE2); β -Estradiol (E2); Aqueous pollution; Endocrine disrupting compounds (EDCs); Urea

1. Introduction

The public concern over the possible consequences of exposure to endocrine-disrupting compounds (EDCs) has drawn the attention of national and international organizations due to their extreme hazard [1]. Among the other EDCs, steroid estrogens (SEs) were identified to have the highest endocrine-disrupting activity, being potent already at nanogram concentrations. The primary sources of these micropollutants are municipal wastewaters and farming. The extent of pollution with SEs is increasing due to the growing population, more intensive farming and the development of synthetic hormones (contraceptive pills, hormone replacement therapy, cattle hormonal growth promotion, etc.).

Natural and synthetic SEs, present in the sanitary fraction of wastewaters, mainly enter the wastewater treatment plants (WWTPs) in a form that is largely not estrogenic. They are excreted primarily as a variety of inactive glucuronide or sulfonide conjugates. However, during the sewage process these inactive compounds are readily transformed into ones that are potentially more harmful than original [2]. This happens presumably due to the large amounts of enzyme produced by the faecal bacteria *Escherichia coli* [3]. The inadequate removal of SEs in WWTPs results in their release to the environment. Sub-

stances that enter the water cycle via discharged wastewaters will ultimately find the way into the potable water.

Advanced oxidation processes (AOPs) are promising in the ultimate removal of SEs, although a certain risk of residual estrogenic activity at doses of ozone commonly applied in potable water treatment has been pointed out [4]. Photocatalytic oxidation (PCO) was confirmed to effectively eliminate the SEs and is considered as a potential alternative. Several publications revealed the following observations: alkaline medium was found to be beneficial for PCO [5,6], in which adsorption behaviour of the target compounds was found to play a major role [6]. The effect of initial SEs concentration and light intensity have been reported: within the solubility limits the higher the initial concentration the higher the PCO rate, which increases with increasing UV irradiance [7]. The predominant mechanism of PCO starting from the phenolic moiety of SE's molecule has been suggested [8,9]. Even several reactor designs have been suggested and tested [10–12]. The study on the estrogenicity of PCO by-products showed no formation of estrogenic intermediates [8,12]. However, the influence of other constituents of municipal wastewaters on the PCO of SEs and the selectivity of the PCO towards SEs were so far not reported. Being present in much higher concentrations, these co-pollutant substances may interfere with the PCO of SEs and presumably hinder the oxidation efficiency due to competition for the active adsorption sites.

The sanitary fraction of the municipal wastewaters is a combination of compounds present in urine and faeces. Normal urine

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is actually a highly complex aqueous solution of organic and inorganic substances. The most important organic substances are urea, uric acid and creatinine. Urea is a product formed by the liver from ammonia and carbon dioxide. Ninety-five percent of the nitrogen content of urine is in the form of this substance, the median daily load of excreted urea in urine is $17.3 \text{ g person}^{-1} \text{ day}^{-1}$ [13].

The objective of the present research was to study the selectivity of PCO of SEs in the presence of interfering compounds: the PCO of natural and synthetic SEs with and without urea as a competing substance was studied in a wide range of pH.

2. Materials and methods

The natural SE β -estradiol (E2) and synthetic 17α -ethynylestradiol (EE2) (Sigma-Aldrich) were used as target compounds (Fig. 1). These compounds are of the greatest environmental concern: E2 and EE2 are found to be the most potent among other SEs [2,14]. The molecules of these SEs differ only in the ethynyl group in EE2 connected to the tertiary carbon atom with the alcohol moiety. Due to their hydrophobic character they were first dissolved using 99.5%-ethanol (Altia Oy, Finland) as a solvent and then gradually diluted with Milli-Q water to prepare the stock aqueous solution of 10 mg L^{-1} . This solution was constantly stirred at room temperature in a hermetically sealed flask to avoid recrystallisation of the SEs. The solutions with required concentrations for the experiments were prepared by dilution of the stock solution with Milli-Q water under stirring for 30 min. The initial concentration of the solutions to be treated was $500 \text{ } \mu\text{g L}^{-1}$ if not otherwise specified. These solutions contained about 4 g L^{-1} of ethanol. All PCO experiments were conducted at room temperature of $23 \pm 2 \text{ }^\circ\text{C}$. The pH value was adjusted with sulphuric acid or sodium hydroxide. The dissolution of SEs in a stock solution without ethanol was conducted in similar manner, in which ethanol was replaced with water with strongly alkaline reaction (pH 12.4).

Urea (Merck), dried at $105 \text{ }^\circ\text{C}$, was added to the solutions to be treated simultaneously with the SEs. The medium concentration of urea of 75 mg L^{-1} attributable to the municipal wastewater [15] was used in the experiments.

Titanium dioxide (TiO_2 , Degussa P25) under near-UV irradiation (365 nm) was used as photocatalyst. Its concentrations in suspensions were 10 mg L^{-1} as was thoroughly selected in the previous study [6]. Centrifugation at 10,000 rpm was applied to separate TiO_2 from the samples before the analysis.

The PCO experiments were performed in 0.25-L capacity thermostatted batch glass reactors with an inner diameter of 100 mm, supplied with a magnetic stirrer. The agitation intensity

was maintained with a standard 25-mm Teflon stirrer at 300 rpm. A 365 nm UV-lamp was positioned horizontally over the reactor; the irradiance was about 1.1 mW cm^{-2} measured by UVX Radiometer (UVX, USA). All PCO experiments were compared with reference samples, treated under identical conditions except UV-radiation.

The adsorption experiments were performed in 0.50-L capacity flasks, where the solutions were mixed with TiO_2 at a stirring frequency of 900 rpm for 24 h at $25 \text{ }^\circ\text{C}$. Each flask was handled separately as a single-point sample, i.e. without intermediate sampling, and each experiment was repeated three times. The equilibrium concentration of compounds adsorbed on the surface of the catalyst q , $\mu\text{g g}^{-1} \text{ TiO}_2$, was calculated from the mass balance of the sample.

The concentrations of SEs were determined by means of HPLC with 150-mm ZORBAX Eclipse XDB-C18 column (Agilent) supplied with UV-detector at the wavelength 278 nm, mobile phase acetonitrile/water 1:1 at a flow rate of 1.0 mL min^{-1} . The concentrations of urea were measured according to the method of Mulvenna and Savidge [16] with modifications of Goeyens et al. [17] and the authors of the present paper. The 10-mL test tubes were filled with 3.5 mL of the 35-fold diluted sample, 0.25 mL of the reagent A and stirred. The 0.8 mL of reagent B was then immediately added with subsequent stirring. The test tubes were stored at room temperature for 72 h in the dark. The light absorbance was measured after that at 520 nm. Reagent A was made of 8.5 g diacetylmonoxime in 250 mL of water together with 10 mL of solution, containing 0.95 g of thiosemicarbazide in 100 mL of water (Sigma-Aldrich). Reagent B was prepared by dissolving 300 ml of concentrated sulphuric acid in 535 mL of water with addition of 0.5 mL of the solution, containing 0.15 g of ferric chloride in 10 mL of water.

3. Results and discussion

3.1. The PCO of SEs without urea in presence of ethanol

The results of the PCO of E2 and EE2 at different pH with the initial concentrations of $500 \text{ } \mu\text{g L}^{-1}$ can be seen in Fig. 2 (the reaction rate) and Fig. 3 (the PCO efficiency).

The PCO efficiency relative to the catalyst concentration was calculated as the decrease in the concentration of the target compound divided by the amount of energy reaching the surface of the sample and by the concentration of the catalyst used [6,18]:

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

where E is the PCO process efficiency, $\mu\text{g W}^{-1} \text{ h}^{-1} (\text{g L}^{-1} \text{ TiO}_2)^{-1}$; Δc , the decrease in the compound concentration, $\mu\text{g L}^{-1}$; V , the volume of treated sample, L; I , the irradiation intensity, mW cm^{-2} ; s , the solution irradiated surface area, cm^2 ; t , the treatment time, h; and m is the concentration of TiO_2 , g L^{-1} .

One can see that the efficiency of PCO of both natural and synthetic SEs increases with the increasing pH. The strongly alkaline medium was observed to be the most efficient for the PCO. In our previous research [6], the PCO efficiency was found

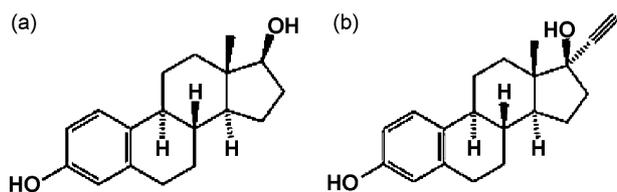


Fig. 1. Molecular structures of E2 (a) and EE2 (b).

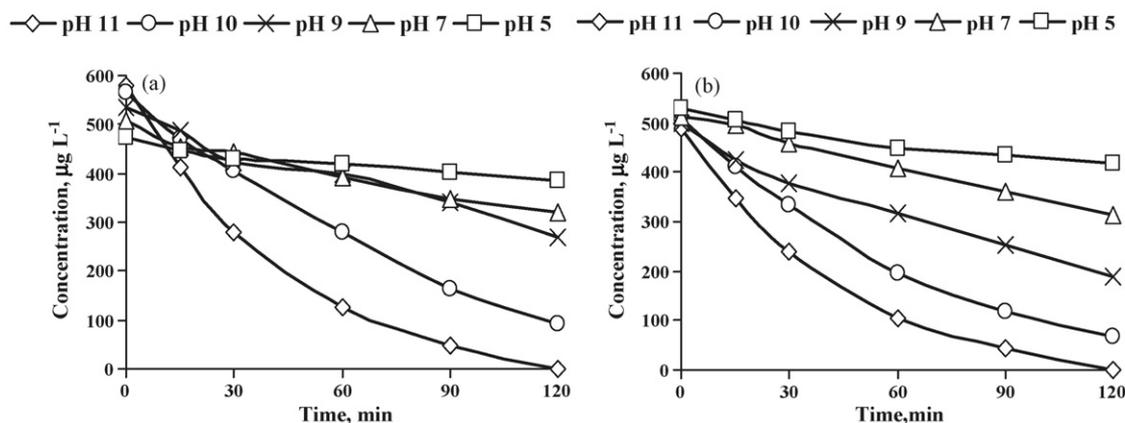


Fig. 2. The rate of PCO of E2 (a) and EE2 (b) at different pH in presence of ethanol (4 g L^{-1}).

to be determined by the adsorption properties of SEs on the TiO_2 surface: the SEs were observed to adsorb to a greater extent under alkaline media conditions. The adsorption increased practically linearly with increasing concentration of OH^- ions similar to the PCO efficiency of SEs. This could be attributed to the direct oxidation with the positively charged holes or oxidation with OH^- radicals in vicinity of the semiconductor surface.

One can see on Fig. 3 that, at pH 11, the PCO of E2 proceeds with slightly higher efficiency than of EE2. This was also due to the better adsorption properties of E2 on the TiO_2 surface established in [6]: the nonpolar ethynyl group present in EE2 molecular structure possibly hinders the adsorption of molecule with the alcohol moiety. The efficiency is decreasing in treatment time, the reason of which can be the decreasing concentration of the SEs and, thus, the decreasing adsorption and the reaction rate.

3.2. The PCO in presence of urea and ethanol

Urea did not exhibit a substantial yield to PCO under the described experimental conditions: no detectable change in urea

concentration was observed as a result of its PCO at the TiO_2 concentration of 10 mg L^{-1} at any of the pH values tested within 2 h. The photocatalyst also was tested for the PCO of urea at TiO_2 concentration as big as 1 g L^{-1} . The adsorption experiments with urea were carried out with its concentration and the concentration of TiO_2 of the same value. Regardless 100-fold increase in TiO_2 concentration, no PCO progress of urea was observed within 2 h. This may be explained by poor urea adsorption on the photocatalyst surface: the series of adsorption experiments with urea on the TiO_2 surface showed no adsorption of this substance within the limits of precision of measurements in the range of pH under consideration.

In the presence of urea, the behaviour of SEs was studied for both PCO and adsorption. The results are shown in Fig. 4 (the reaction rate) and Fig. 5 (the PCO efficiency). One can see that no particular difference in both PCO rate and the efficiency were observed when compared to the PCO of the SEs without urea. This may be explained by the weak adsorption properties of urea and thus its minor interference in PCO.

Figs. 6 and 7 also show that the adsorption of SEs is not influenced by the presence of urea in the solution when ethanol

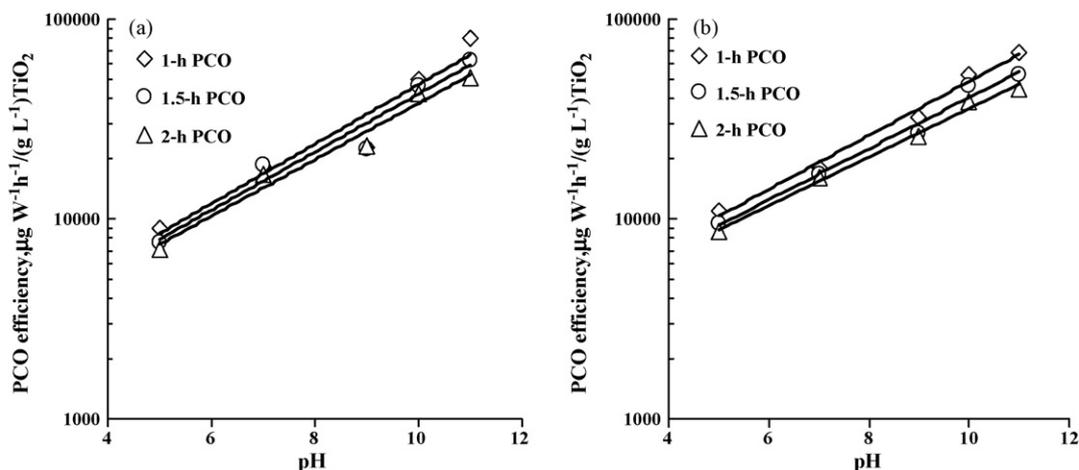


Fig. 3. The dependence of PCO efficiency E on pH for E2 (a) and EE2 (b) solutions (initial concentrations $500 \text{ } \mu\text{g L}^{-1}$) at different treatment times in presence of ethanol (4 g L^{-1}).

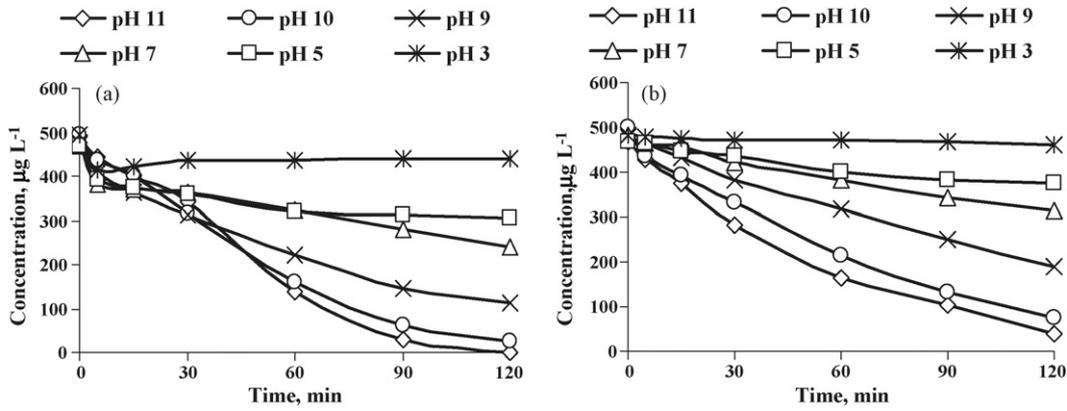


Fig. 4. The rate of PCO of E2 (a) and EE2 (b) at different pH in the presence of urea (75 mg L^{-1}) and ethanol (4 g L^{-1}).

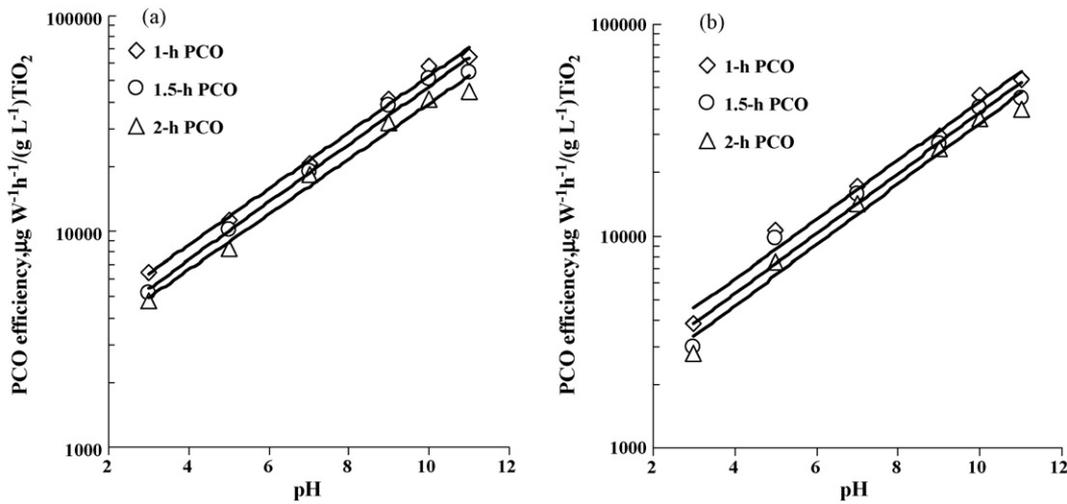


Fig. 5. Dependence of PCO efficiency E on pH of E2 (a) and EE2 (b) solutions (initial concentration $500 \text{ } \mu\text{g L}^{-1}$) in the presence of urea (75 mg L^{-1}) and ethanol (4 g L^{-1}).

is also present. The character of the dependence of the adsorption of SEs on pH remains similar to the one observed in the absence of urea: the adsorption of SEs follows the same pattern as their PCO. The selective oxidation of SEs thus could be demonstrated at higher pH.

3.3. The influence of ethanol

The observed indifference of the PCO of SEs towards the presence of urea may be explained by the poor adsorption of urea at the TiO_2 surface. However, further studies in the influence of

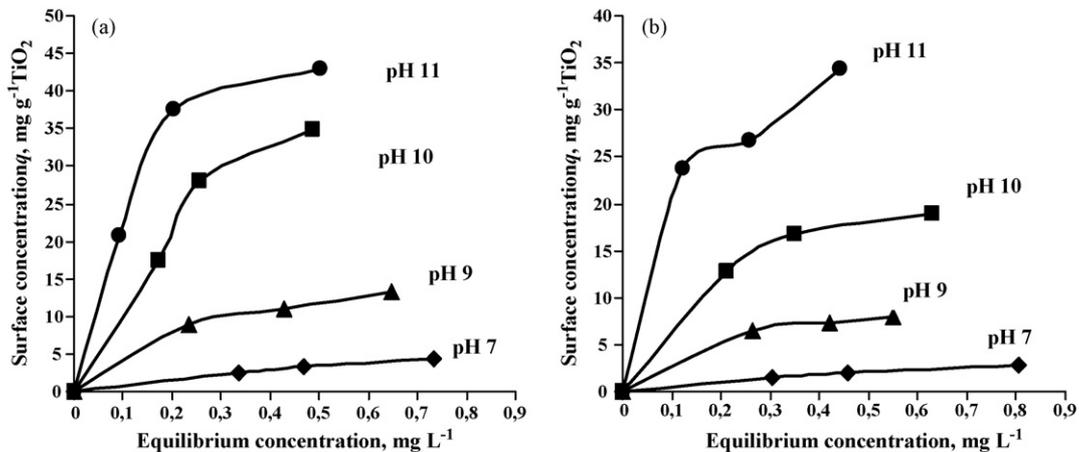


Fig. 6. Adsorption isotherms for E2 (a) and EE2 (b) on TiO_2 catalyst surface at different pH in the presence of urea (75 mg L^{-1}) and ethanol (4 g L^{-1}).

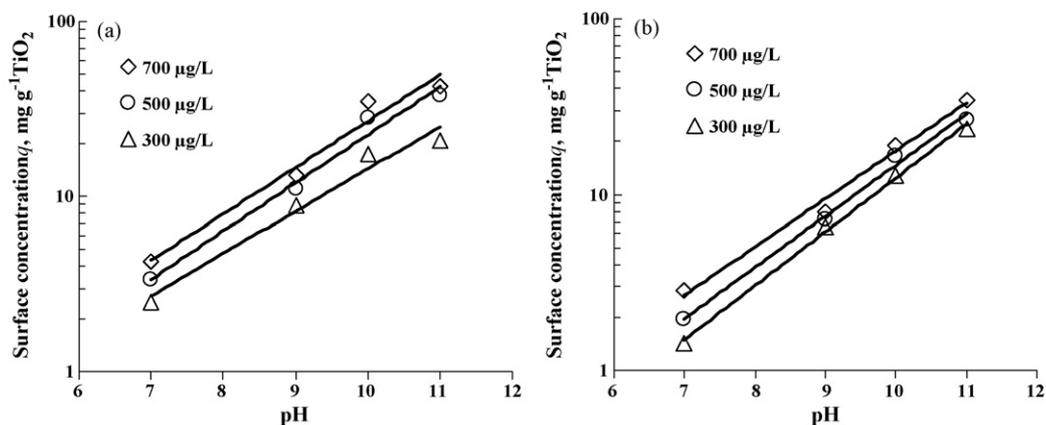


Fig. 7. The E2 (a) and EE2 (b) equilibrium surface concentration on TiO_2 vs. pH at different initial concentrations of SEs in the presence of urea (75 mg L^{-1}) and ethanol (4 g L^{-1}).

competing pollutants are needed for the reason of the inevitable presence of the solvent used for the stock solution, ethanol, in concentrations as big as 4 g L^{-1} . Practically all authors use organic solvents for SEs dissolution, making this problem of an interest for other researchers. Ethanol, for example, is the well-known OH-radical scavenger [19] and may compete for the adsorption sites.

Within the present study, the dissolution of E2 and EE2 in strongly alkaline media containing no ethanol was carried out and appeared to be successful: the stock solution of 10 mg L^{-1} was obtained with no visible precipitation. The strategy was used for the presence of phenolic group in the SEs molecules dissociated in alkaline media.

Figs. 8 and 9 represent the adsorption of E2 and EE2 on the surface of the catalyst without and in the presence of urea.

The presence of urea in commonly observed for municipal wastewaters concentration of 75 mg L^{-1} seemed to have negligible effect on the EE2 adsorption on TiO_2 . The effect of urea on E2 adsorption was more pronounced, the adsorption was deteriorated at all pH values except pH 7, although the adsorption in presence of urea was of the same order of magnitude as without the co-pollutant. The difference in behaviour of the two

substances may be explained by the difference in hydrophilic properties of two molecules: the presence of urea as an additional pollutant may have stronger effect on adsorption of more hydrophilic E2 molecule than of EE2 having more hydrophobic character.

The presence of ethanol seemed to have also negligible effect on the adsorption of SEs (see Figs. 6 and 8).

The results of the PCO experiments in absence of ethanol are shown in Figs. 10 and 11. One can compare these results with the ones containing ethanol (Figs. 2 and 4) and see that the PCO in absence of ethanol proceeds much faster, although the dependence of the PCO efficiency on pH saved the previously observed pattern: the higher the pH, the faster the PCO. The authors would like to point to the circumstance that the PCO of SEs exhibited much stronger sensitivity towards the presence of ethanol than their adsorption on TiO_2 . This could be explained by the role of OH-radicals in oxidation: radicals may be scavenged by ethanol molecules thus decreasing the PCO rate of SEs.

One can see that the presence of urea had negligible effect on the PCO of EE2. The effect on the PCO of E2 also was moderate, although the oxidation rate showed the behaviour opposite to the one of adsorption: the PCO in the presence of urea proceeded

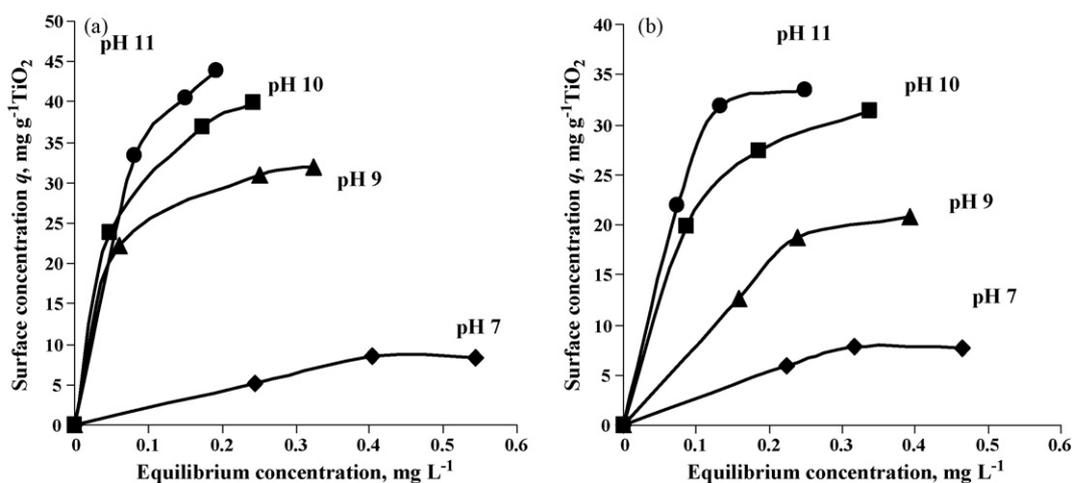


Fig. 8. Adsorption isotherms for E2 (a) and EE2 (b) on TiO_2 catalyst surface at different pH without urea (no organic solvent used).

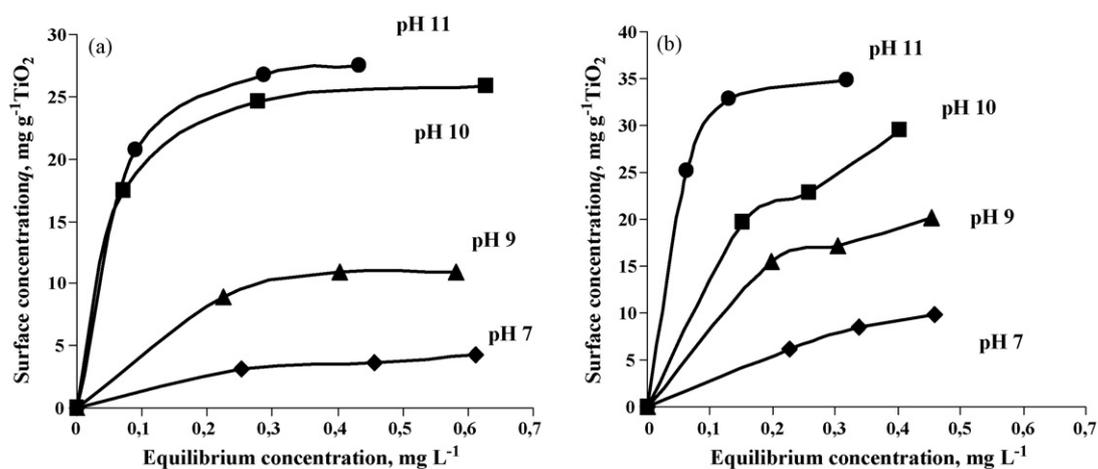


Fig. 9. Adsorption isotherms for E2 (a) and EE2 (b) on TiO₂ catalyst surface at different pH in the presence of urea (75 mg L⁻¹) (no organic solvent used).

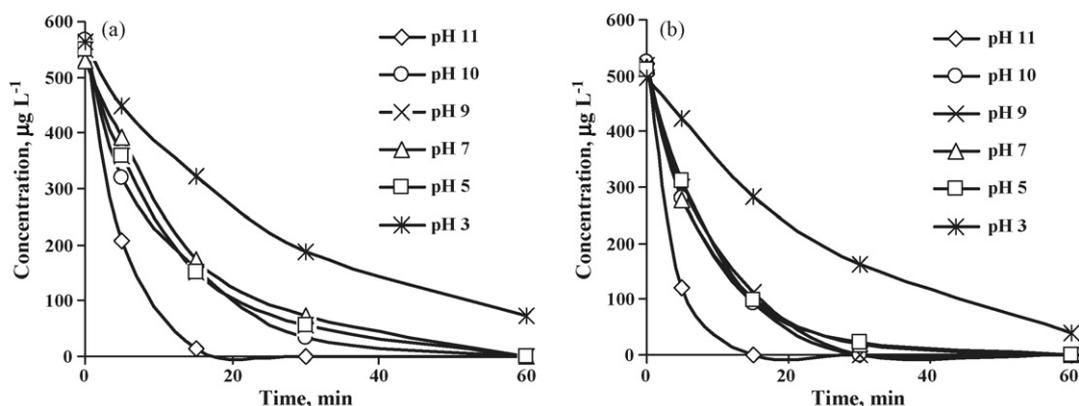


Fig. 10. The rate of PCO of E2 (a) and EE2 (b) at different pH without urea (no organic solvent used).

even a little faster than in absence of that at pH 7–10. The explanation of this phenomenon may require more knowledge in the PCO of SEs acquired with additional experiments at higher precision level. The dependence of the PCO rate on pH preserved the same pattern: the PCO rate increased with increasing pH.

The characteristics of the reaction kinetics for PCO of E2 and EE2 without and in the presence of urea at different pH were calculated using Langmuir–Hinshelwood equation for the

monomolecular reaction:

$$r = \frac{k \times K \times C_e}{1 + K \times C_e} \quad (2)$$

where r is the rate of SE degradation, mg L⁻¹ min⁻¹; k , the reaction rate constant, mg L⁻¹ min⁻¹; K , the Langmuir equilibrium constant, L mg⁻¹; and C_e is the equilibrium SE concentration, mg L⁻¹.

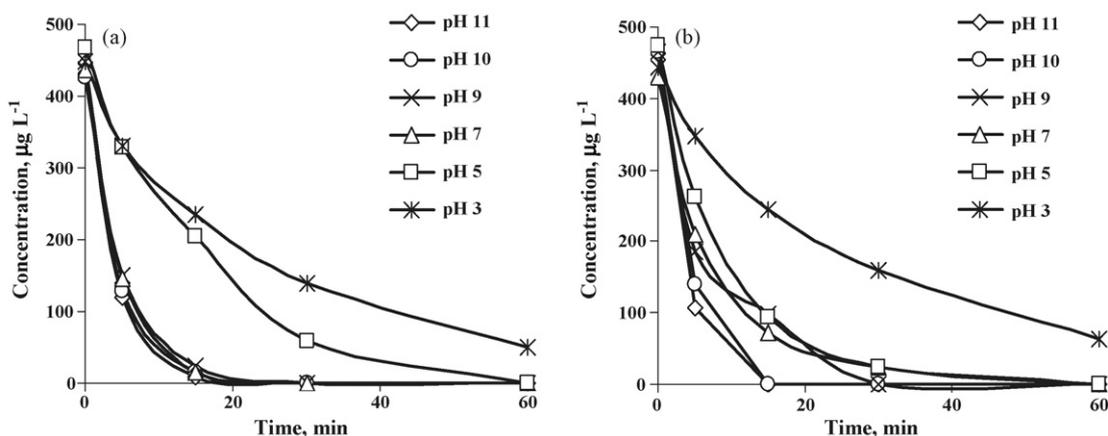


Fig. 11. The rate of PCO of E2 (a) and EE2 (b) at different pH in the presence of urea (75 mg L⁻¹) (no organic solvent used).

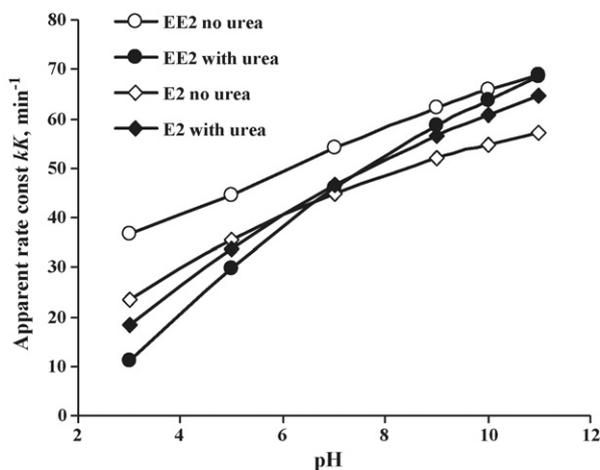


Fig. 12. The dependence of apparent reaction rate constant kK of PCO on pH for E2 and EE2 without and in the presence of urea (75 mg L^{-1}) (no organic solvent used).

The dependence of the apparent reaction rate constant of PCO on pH is given in Fig. 12. One can see the increased sensitivity of the PCO apparent reaction rate constant of both SEs towards pH in presence of urea, the slope of the curves ‘pH– kK ’ increased with the addition of urea. In the pH area of maximum oxidation rate, the alkaline one, the impact of urea seems to be insignificant, which indicates the selective character of PCO of SEs.

4. Conclusions

Steroid estrogens, natural β -estradiol (E2) and synthetic 17α -ethynylestradiol (EE2), are easily photocatalytically degraded on UV-irradiated TiO_2 surface at very small (10 mg L^{-1}) concentrations of the photocatalyst. No degradation of urea was observed on the TiO_2 surface under the experimental conditions due to its poor adsorption. The presence of urea did not interfere with the PCO of SEs. The alkaline media exhibited the highest efficiency in both PCO and adsorption of SEs.

The inhibiting effect of ethanol on the PCO rate of SEs occurred to be strong. The organic solvent-free dissolution techniques showed its feasibility for studies of the competitive adsorption on TiO_2 surface and PCO of SEs with other co-pollutants; the presence of organic solvents usually used for preparing stock solutions should be avoided.

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APPENDIX 4

Selective photocatalytic oxidation of steroid estrogens in presence of saccharose and ethanol as co-pollutants

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Selective photocatalytic oxidation of steroid estrogens in presence of saccharose and ethanol as co-pollutants

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Abstract The potential of the photocatalytic oxidation to selectively oxidise steroid estrogens, β -estradiol and 17 α -ethynylestradiol, in the presence of saccharose and ethanol as co-pollutants was clearly demonstrated. The alkaline media conditions remained the most beneficial for the PCO regardless the presence of co-pollutants under consideration. Saccharose appeared to be the more powerful competitor than ethanol. The influence of the co-pollutants is explained by their competition for the adsorption sites and also scavenging of the OH-radicals.

Keywords Endocrine disrupting compounds (EDCs) · β -Estradiol (E2) · 17 α -ethynylestradiol (EE2) · Titanium dioxide · Sucrose · Starch · Photocatalysis

Introduction

The detection of estrogens in the effluents of wastewater treatment plants (WWTPs) is a reason for concern about the contamination of the environment with endocrine-disrupting micropollutants. Estrogens are able to disrupt normal function of endocrine systems of living organisms even at concentrations of 0.1 ng L⁻¹ levels; the negative effects on the wildlife of aquatic environment, birds, mammals and even human have been reported (Mendes

2002). Steroid estrogens (SEs) are produced naturally by female organisms and also synthesised commercially mainly as components of the contraceptive pills, for hormone replacement therapy and for cattle hormonal growth promotion. β -Estradiol (E2) and 17 α -ethynylestradiol (EE2) are believed to be the most potent natural and synthetic estrogens. The conventional municipal WWTPs were found to be inefficient for the SEs removal (Carballa et al. 2004). Moreover, according to some authors the WWTPs even become the source of SEs pollution: the enzyme produced by faecal bacteria during the sewage treatment is believed to transform the inactive compounds to potentially more estrogenic ones (Johnson and Sumpter 2001; D'Ascenzo et al. 2003). These pollutants can then easily find their way to the aquatic environment.

Previously photocatalytic oxidation (PCO) was found to be an efficient water-treatment method for the removal of SEs (Ohko et al. 2002; Coleman et al. 2005; Malygina et al. 2005). However, the influence of other substances present in domestic sewage on the PCO of SEs and the PCO selectivity towards SEs were yet not sufficiently studied. Domestic sewage is a very complex mixture of organic and inorganic substances with the exact composition unknown. Boeije et al. (1999) reconstituted a synthetic sanitary fraction of domestic sewage based on an extensive literature analysis. Potato starch is considered to be one of the common constituents of domestic sewage. Its chromatographic analysis, however, is problematic due to the clogging of chromatography columns. Starch consists basically of poorly water-soluble amylase and insoluble amylopectin, polymers consisting of chains of mono- and disaccharide units. The authors therefore have chosen disaccharide saccharose as a completely water-soluble starch replacement in concentrations attributable to domestic sewage, which exceeds the ones of SEs by at least 100 times. PCO

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of saccharose has been studied previously (Vamathevan et al. 2001, 2002) as a model compound in the testing of Ag-doped titanium dioxide catalyst. It was noticed that saccharose's PCO is relatively slow when compared to other organic molecules. Nevertheless, it was assumed that saccharose could interfere with and possibly hinder the PCO rate of SEs via competition for the active sites of TiO₂ catalyst under conditions of saccharose concentrations considerably exceeding the SEs' ones. Ethanol is often used in SEs oxidation studies as a solvent; its role in PCO was also studied here.

Experimental

Target compounds

The natural β -estradiol (E2) and synthetic 17 α -ethynylestradiol (EE2) (Sigma–Aldrich) were used as target SEs. These compounds are hydrophobic and they were first dissolved using 99.5%-ethanol (Altia Oy, Finland) as a solvent followed by gradual dilution with Milli-Q water to prepare the stock aqueous solution of 10 mg L⁻¹ as described earlier (Malygina et al. 2005). This solution was constantly stirred at room temperature in a hermetically sealed flask to avoid re-crystallisation of the SEs. The solutions with required concentrations for the experiments were prepared by dilution of the stock solution with Milli-Q water under stirring for 30 min. The dissolution of SEs in a stock solution without using ethanol was conducted in similar manner, where ethanol was replaced with water with strong alkaline reaction (pH 12.4). The initial concentration of the solutions to be treated was 500 μ g L⁻¹. All PCO experiments were conducted at room temperature of 23 \pm 2°C. The pH value was adjusted with sulphuric acid or sodium hydroxide.

Saccharose, dried at 105°C, was dissolved in amount of 1 g in 1 L of Milli-Q water to make a stock solution. This solution was used in preparation of SE-containing samples to be treated. The concentration of saccharose of 50 mg L⁻¹ was used as equal to the medium potato starch concentration in the domestic sewage (Boeije et al. 1999). The PCO degradation of saccharose itself was also studied with the initial concentration of saccharose of 150 mg L⁻¹; TiO₂ concentration of 500 mg L⁻¹ was used in experiments with saccharose.

Photocatalyst

Titanium dioxide (TiO₂, Degussa P25) under near-UV irradiation was used as a photocatalyst. In general, the use of different TiO₂ loadings affects the adsorption and degradation rate of SEs, as was shown earlier. Its concentra-

tions in PCO-treated suspensions in experiments with SEs were 10 mg L⁻¹ as was thoroughly selected in the previous study (Malygina et al. 2005). The reason for such a low concentration of the catalyst was the good adsorption of the target compounds onto the TiO₂ surface. Greater amounts of the catalysts reduced the residual concentration of SEs below the detection limit. In experiments with saccharose higher concentrations of TiO₂ were used (see below); experiments with saccharose required higher catalyst concentration due to its slow oxidation.

Experimental methods

Centrifugation at 10,000 rpm was applied to separate TiO₂ from the samples before the analysis. The PCO experiments were performed in 0.25-L capacity thermostatted batch glass reactors with an inner diameter of 100 mm, supplied with a magnetic stirrer. The agitation intensity was maintained with a standard 25-mm Teflon stirrer at 300 rpm. A 365-nm UV-lamp (Sylvania F15W) was positioned horizontally over the reactor; the irradiance was about 1.1 mW cm⁻² measured by UVX Radiometer (UVX, USA). All PCO experiments were compared with reference samples, treated under identical conditions except UV-radiation.

The adsorption experiments with saccharose solutions of 250 mg L⁻¹ were performed in 0.50-L capacity flasks, where the solutions of various pH were mixed with 1 g L⁻¹ of TiO₂ at a stirring frequency of 900 rpm for 1 h at 25°C. Each flask was handled separately as a single-point sample, and each experiment was repeated three times. The concentration of compounds adsorbed on the surface of the catalyst q , mg g⁻¹ TiO₂, was calculated from the mass balance of the liquid phase.

Analysis

The concentrations of SEs were determined by means of high-performance liquid chromatograph (HPLC) supplied with 150-mm ZORBAX Eclipse XDB-C18 column (Agilent) and UV-detector at the wavelength 278 nm; mobile phase acetonitrile/water 1:1 at a flow rate of 1.0 mL min⁻¹. Chemical oxygen demand (COD) and total organic carbon (TOC) were determined after PCO and adsorption of saccharose. The COD was measured by standard procedure (Standard Methods 1995). The TOC analyses were carried out using TOC analyser Shimadzu 5050-A.

Results and discussion

The PCO efficiency relative to the catalyst concentration was calculated as the decrease in the concentration of the target compound divided by the amount of energy reaching

the surface of the sample and by the concentration of the catalyst used:

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

where E PCO process efficiency, $\text{mg W}^{-1} \text{h}^{-1}/(\text{g L}^{-1} \text{TiO}_2)$; Δc decrease in the compound concentration, mg L^{-1} ; V the volume of treated sample, L; I irradiation intensity, mW cm^{-2} ; s -solution irradiated surface area, cm^2 ; t treatment time, h; m concentration of TiO_2 , g L^{-1} .

Since the PCO kinetics at low concentration of substrate often is described by the pseudo-first order model, the parameters of that were determined to compare the results with data obtained by others. To obtain the kinetic parameters for the PCO of SEs the results were plotted as time in minutes against $\ln(C/C_0)$, where C_0 is the SE's initial concentration and C -the concentration at time t . The equation and correlation coefficient, R^2 , were obtained from the best-fit line. The plots indicated that PCO of SEs fitted well to the pseudo-first order equations, which is in agreement with previously published results (Ohko et al. 2002; Coleman et al. 2005). The rate constant k was obtained from the slope and the initial rate was calculated by multiplying k by C_0 . Following this the half-life was calculated. The results are presented in Table 1.

The influence of pH

Figure 1 presents the results of the SEs' PCO efficiency dependent on pH with and without admixtures. One can see that the efficiency of PCO steadily grows with the increasing pH having alkaline media as the most beneficial one. This pattern remained the governing one for both SEs despite the presence of admixtures. This result is consistent with the previous observations (Malygina et al. 2005).

Both the surface concentration of SEs on the TiO_2 and the PCO efficiency behave along the similar pattern: both the adsorption and the PCO exhibit simple linear dependence on OH-ions concentration (Malygina et al. 2005). The fact that both E2 and EE2 molecules are adsorbed well in strong alkaline medium in combination with the knowledge about a poor adsorption of phenolic compounds under similar conditions (Robert et al. 2000) indirectly indicates that the adsorption takes place with the molecule attached to its alcohol group and not the phenolic moiety. In addition, the observed difference in the adsorption of the two SEs due to the difference in the molecular structure indicates the key role played by the alcohol group in adsorption under alkaline media conditions (Malygina et al. 2006). Phenolic compounds, on the other hand, yield well to PCO under alkaline-media conditions (Preis et al. 1997). This indicates the radical mechanism prevailing in their

PCO. The influence of ethanol (see below) also indicates the radical oxidation of SEs.

The influence of ethanol

Ethanol in amount of approximately 4 g L^{-1} appears to be the most competitive substance in obstructing SEs' PCO under the experimental conditions. This is because of the competitive adsorption of ethanol at the active sites (Fig. 2, shown only for E2) and the possible OH-radical scavenging known for alcohols.

The last circumstance found a proof in the fact that the presence of ethanol affected SEs' PCO to a greater extent than adsorption of SEs by the TiO_2 surface in particular under strongly alkaline media conditions. Thus, if under moderately alkaline pH from 9 to 10 the PCO efficiency deterioration in presence of ethanol was consistent with the deterioration of adsorption, then at pH 11 the PCO efficiency decreased for about 2.3 times more than the adsorption did (Figs. 1, 2).

The influence of saccharose

The presence of saccharose also essentially hindered the PCO efficiency of SEs for the entire pH range (Fig. 1). However, the dependence on pH looks somewhat different from the one without co-pollutants: the PCO rate in strongly acidic media was slightly higher than in neutral or slightly acidic ones. This can be also seen in Table 1 (see the rate values).

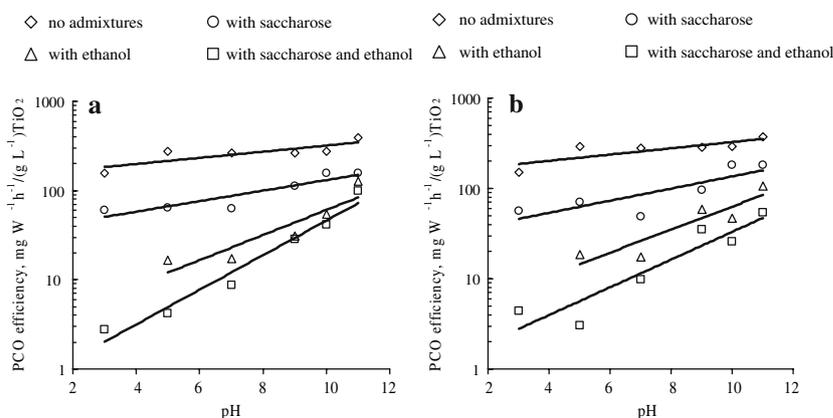
The PCO and adsorption of saccharose

To understand better the interactions between the SEs and saccharose the experiments for the PCO of saccharose were carried out under the similar experimental conditions as for the SEs. The experiments were carried out initially with 10 mg L^{-1} of TiO_2 and 50 mg L^{-1} of saccharose; however, no valuable results were obtained: no visible degradation of COD or TOC was observed within 4 h. After several experimental approximations towards increased concentrations of the catalyst with various concentrations of the pollutant, the TiO_2 concentration of 500 mg L^{-1} and the saccharose concentration of 150 mg L^{-1} were selected. Under these conditions, the results of a 2-h PCO showed some oxidation: in strongly alkaline medium (pH 11) the COD of the sample decreased by $20 \text{ mg O}_2 \text{ L}^{-1}$, i.e. about 10%. This is in agreement with the observations of other authors (Vamathevan et al. 2001, 2002) reporting that the saccharose's PCO rate is relatively slow when compared to other organic molecules. Therefore, the competitive oxidation of saccharose may not be a reason for the deterioration of the SEs' PCO efficiency. Also, the adsorption of

Table 1 The values of kinetic parameters for PCO of SEs in the presence of admixtures

| Substance | pH | k (min^{-1}) | Rate ($\mu\text{g L}^{-1} \text{min}^{-1}$) | Half-life (min) | R^2 | Substance | pH | k (min^{-1}) | Rate ($\mu\text{g L}^{-1} \text{min}^{-1}$) | Half-life (min) | R^2 |
|-----------------------------------|----|------------------------------|--|--------------------|-------|---------------------------------------|----|------------------------------|--|--------------------|-------|
| E2 | 11 | 0.254 | 143.86 | 2.8 | 0.995 | EE2 | 11 | 0.295 | 153.71 | 2.4 | 1 |
| | 10 | 0.091 | 51.68 | 7.4 | 0.995 | | 10 | 0.116 | 60.86 | 6.0 | 0.999 |
| | 9 | 0.070 | 38.14 | 9.7 | 0.990 | | 9 | 0.107 | 55.70 | 6.5 | 0.999 |
| | 7 | 0.068 | 35.94 | 10.4 | 0.991 | | 7 | 0.110 | 56.69 | 6.3 | 0.999 |
| | 5 | 0.072 | 39.70 | 9.6 | 0.990 | | 5 | 0.107 | 54.74 | 6.5 | 0.999 |
| | 3 | 0.034 | 19.14 | 20.2 | 0.998 | | 3 | 0.042 | 20.70 | 16.6 | 0.997 |
| E2 with saccharose | 11 | 0.049 | 22.56 | 13.7 | 0.992 | EE2 with saccharose | 11 | 0.058 | 26.99 | 11.8 | 0.996 |
| | 10 | 0.036 | 16.48 | 19.0 | 0.984 | | 10 | 0.050 | 22.66 | 13.7 | 0.997 |
| | 9 | 0.022 | 9.77 | 30.9 | 0.975 | | 9 | 0.018 | 9.11 | 36.3 | 0.975 |
| | 7 | 0.011 | 5.23 | 58.8 | 0.989 | | 7 | 0.009 | 4.40 | 72.6 | 0.984 |
| | 5 | 0.010 | 4.75 | 63.2 | 0.969 | | 5 | 0.011 | 4.99 | 60.1 | 0.983 |
| | 3 | 0.016 | 7.42 | 42.2 | 0.997 | | 3 | 0.015 | 6.46 | 48.0 | 0.995 |
| E2 with saccharose and ethanol | 11 | 0.021 | 11.79 | 32.9 | 0.997 | EE2 with saccharose and ethanol | 11 | 0.020 | 9.80 | 34.6 | 0.975 |
| | 10 | 0.012 | 5.86 | 58.7 | 0.994 | | 10 | 0.010 | 4.82 | 70.0 | 0.997 |
| | 9 | 0.010 | 4.95 | 66.2 | 0.997 | | 9 | 0.010 | 4.58 | 68.7 | 0.994 |
| | 7 | 0.003 | 1.31 | 245.7 | 0.980 | | 7 | 0.003 | 1.63 | 204.8 | 0.992 |
| | 5 | 0.001 | 0.48 | 623.3 | 0.773 | | 5 | 0.001 | 0.49 | 624.2 | 0.956 |
| | 3 | 0.001 | 0.36 | 918.7 | 0.972 | | 3 | 0.001 | 0.28 | 953.4 | 0.766 |

The PCO and adsorption of saccharose

Fig. 1 The dependence of PCO efficiency E on pH for E2 (a) and EE2 (b) solutions in the presence of admixtures in 15 min of treatment


saccharose on TiO_2 was studied to find out the reason of anomalous behaviour of SEs' PCO in acidic media (Fig. 3).

The maximum amount of saccharose adsorbed under the described experimental conditions was $9.9 \text{ mg g}^{-1} \text{ TiO}_2$ at pH 5. This indicates the poor saccharose adsorption compared to the SEs' one, which was up to $35 \text{ mg g}^{-1} \text{ TiO}_2$ even in the presence of ethanol under the much lower SEs' liquid-phase concentration (Malygina et al. 2005). The highest adsorption of saccharose on TiO_2 occurred in slightly acidic and alkaline media. This phenomenon can be easily explained in the part of slightly acidic media by the TiO_2 zero point charge, close to which the absence of electrostatic forces between TiO_2 and saccharose may result in better adsorption. It can explain the fact that the

PCO rate of SEs in the presence of saccharose was better in acidic media at pH 3 (Table 1), i.e., the poorest adsorption of the competing saccharose resulted in better adsorption and oxidation of SEs. The PCO rate at pH 7 close to the one at pH 5 may be explained by the difficulties in precisely maintaining pH in the neutral range: having no problem in adsorption experiments, the pH in PCO experiments at pH 7 showed the tendency to rapidly shift downwards due to, most probably, the formation of acidic PCO by-products. The increased adsorption of saccharose in alkaline media is more difficult to explain, although the difference in the absolute surface concentrations is not that big. In spite of the difficulties in explaining some phenomena, the objective of the adsorption study was

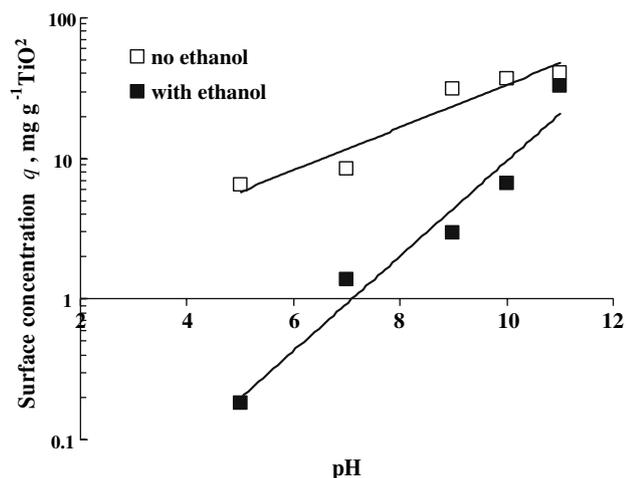


Fig. 2 The E2 (initial concentration $500 \mu\text{g L}^{-1}$) surface concentration on TiO_2 versus pH with and without ethanol

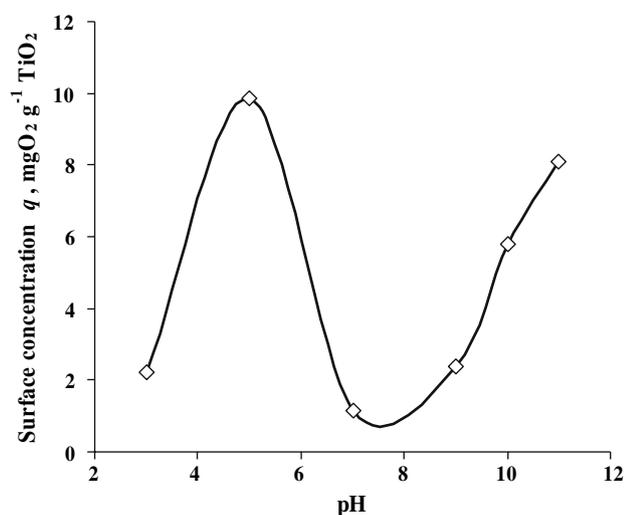


Fig. 3 Saccharose surface concentration on TiO_2 versus pH: initial concentration of saccharose 250mg L^{-1}

sufficiently achieved: the adsorption of saccharose is poor, thus indicating the reason for poor PCO. Therefore, the poor adsorption of saccharose and, thus, its poor PCO appears to be the reason for its minor, although noticeable, influence on the PCO of SEs under experimental conditions.

The simultaneous influence of ethanol and saccharose

The results of the experiments (Fig. 1, Table 1) also show that saccharose is a more powerful competitor for the PCO of SEs: the concentration of ethanol as big as 4g L^{-1} was not able to mask the effect of saccharose in concentrations of only 50mg L^{-1} . Therefore, the ability of the PCO to oxidise SEs in a selective manner should be verified in agreement with the experimental conditions; bigger

concentrations of co-pollutants may effectively slow down the PCO of the SEs.

The difference in PCO of SEs

One can see (Table 1) that in absence of any admixtures the PCO of EE2 proceeds a little faster than the one of E2's. This result is in consistency with the data of other authors (Coleman et al. 2005). However, in the presence of saccharose only under alkaline conditions EE2 exhibited similar behaviour, whereas in neutral and acidic media there was no more noticeable difference in PCO rates between two SEs. In presence of ethanol together with saccharose the picture was changed to the opposite one although to a little extent: the PCO of E2 under alkaline conditions proceeded even somewhat faster than the one of EE2. This could be because of the suppressed OH-radical actions in presence of ethanol and the different sensitivity of the SEs under consideration towards the adsorption competitors and the radical oxidation due to the difference in molecular structure (the ethynyl group in EE2).

Conclusions

The dependence of the PCO efficiency on pH exhibited the fastest oxidation under alkaline media conditions regardless the presence of co-pollutants under consideration. The experiments showed the drastic influence of the admixtures, saccharose and ethanol, to the PCO efficiency of SEs for the entire pH range. The influence may be explained by the competition of admixtures for the adsorption sites at the photocatalyst surface and also by the scavenging of the OH-radicals. Saccharose appears to be the more powerful competitor for the SEs in PCO reactions than ethanol. The interference of saccharose and ethanol, nevertheless, is far weaker in respect to the SEs' PCO than it could be expected from the concentrations of admixtures: 100-times higher saccharose concentration reduced the SEs' PCO efficiency three times and the thousands-times ethanol content reduced it six times only. This indicates the potential of the PCO to be a selective oxidation method for the SEs' removal from wastewaters. The influence of ethanol on the efficiency of PCO indicates the necessity of using organic solvent-free solutions for the studies of SEs behaviour.

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APPENDIX 5

Selective photocatalytic oxidation of steroid estrogens in the presence of copollutants in the sanitary fraction of domestic sewage

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Research Article

Selective Photocatalytic Oxidation of Steroid Estrogens in the Presence of Copollutants in the Sanitary Fraction of Domestic Sewage

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The photocatalytic oxidation (PCO) of the steroid estrogens (SEs), β -estradiol, and 17α -ethynylestradiol, competitive with some constituent compounds of the sanitary fraction of domestic sewage, was studied. The copollutants, urea, and saccharose, present in concentrations exceeding those of the SEs by a factor of a hundred to thousands, appeared to exert a weaker influence to the photocatalytic degradation of the SEs than was expected. The removal of the SEs from diluted urine proceeded, selectively, demonstrating the potential of PCO in the treatment of the separate sanitary fraction of domestic sewage.

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1. INTRODUCTION

In recent years, the observation of hermaphrodite fish in sewage treatment plant (STP) lagoons, reproductive abnormalities in reptiles, and decreased fertility of fish, mammals, and birds has made the question of the pollution of the aquatic environment with endocrine disrupting compounds (EDCs) one of great concern. These substances can interact with and disrupt the endocrine systems of living organisms. For humans, EDCs affect the male reproductive tract, both male and female fertilities, the central nervous system, and may cause several types of cancers [1]. Along with other EDCs, steroid estrogens (SEs) are believed to be major contributors to the observed estrogenic effects [2, 3]. Steroid estrogens are already potent at the fraction of ng L^{-1} concentrations, while most other EDCs are active at the $\mu\text{g L}^{-1}$ level [2].

The main source of SEs in domestic sewage is human waste that contains natural and also synthetic SEs originating from pharmaceuticals such as birth control pills and hormone replacement therapy. The SEs entering the STP in less active conjugated forms [4, 5] are, however, transferred in domestic sewage into the more potent active forms, presumably due to the presence of enzymes produced by faecal bacteria *E. Coli* [6]. Steroid estrogens have been detected in various concentrations in the discharge waters of STPs across

Europe [3, 7, 8], depending on the type of STP process used, the density of population in the area, and various other factors. These data indicate that the inadequate removal of SEs in conventional STPs can lead to the penetration of these pollutants to the potable water. Various suggestions for improvements such as the increased size of sewage treatment tanks to prolong biodegradation or the removal of SEs with increased sludge concentration have not provided a solution to the problem [8, 9]. An effective and economical treatment technique able to eliminate SEs from sewage is thus needed.

Several treatment strategies to eliminate SEs from aqueous media have been studied, all showing certain characteristic drawbacks. Simple redistribution of SEs between aqueous and solid phases by separation methods does not allow safe and complete elimination of SEs; further safe handling of the separated SEs is necessary [10]. Advanced oxidation processes such as ozone applications are able to remove SEs, although residual estrogenic activity at doses of ozone normally applied in potable water treatment has been observed [11]. Photocatalytic oxidation (PCO) has been confirmed to effectively eliminate SEs without the formation of estrogenic intermediates and is considered a potential approach [12–14].

In PCO, the excitation of a photocatalyst occurs as a result of the absorption of UV radiation at a wavelength sufficient to displace electrons from the valence band; for

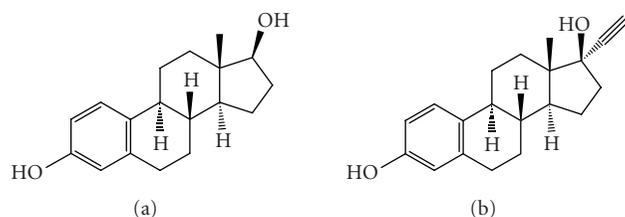


FIGURE 1: Molecular structures of E2 (a) and EE2 (b).

titanium dioxide, this is below 387.5 nm. The PCO often proceeds via adsorption of the pollutant on the surface of the catalyst, followed by direct subtraction of the pollutant's electrons, that is, oxidation, with positively charged holes. Another possible way is oxidation with OH-radicals that takes place at the catalyst surface or in its vicinity [15]. Both reactions may proceed simultaneously, and which mechanism dominates depend on the chemical and adsorption properties of the pollutant.

The elimination of SEs at the stage of the collection and separate treatment of the sanitary fraction of domestic sewage may appear beneficial compared to the treatment of large volumes of biologically treated municipal wastewaters. Sanitary sewage represents a complex mixture of organic and inorganic substances and the concentrations of copollutants are much higher than those of SEs and their presence may decrease the PCO rate of SEs. Thus, the objective of the present research was to establish the possibility of selective PCO of SEs in the presence of possible copollutants. Boeije et al. [16] have reconstituted a synthetic sanitary fraction of domestic sewage based on an extensive literature analysis, indicating urea and potato starch as the most common copollutants. However, chromatographic analysis in the presence of potato starch may be problematic due to clogging of chromatography columns. Therefore, the authors have chosen saccharose as a completely water-soluble starch replacement. To approximate the research results obtained in experiments with synthetic solutions of urea and saccharose to more realistic conditions, the authors studied the PCO of SEs in the presence of human urine.

2. EXPERIMENTAL

2.1. Material

Natural β -estradiol (E2) and synthetic 17α -ethynylestradiol (EE2) were chosen as target SEs (Figure 1). To prepare the aqueous solution of SEs, they are usually dissolved first in an organic solvent due to their hydrophobic character. However, this can affect the experimental results, as the solvent acts, as an additional copollutant and can interfere with the PCO of the SEs. In a previous research, the authors used ethanol as an organic solvent for the preparation of the stock solution of SEs. It was observed, however, that ethanol as an OH radical scavenger competes with SEs for adsorption sites, interfering with the PCO of SEs [17]. In the present research, the SEs,

which contain phenolic moieties, were successfully dissolved in water with a strongly alkaline reaction (pH 12.4) making the stock solutions free of the organic solvent. These stock solutions were constantly stirred in a hermetically sealed flask to avoid recrystallization of the SEs. The solutions with the required concentrations for the experiments were prepared by dilution of the stock solution with Milli-Q water under stirring for 30 minutes. The initial concentration of the PCO-treated solutions was around $500 \mu\text{g L}^{-1}$. All the PCO experiments were conducted at a room temperature of $23 \pm 2^\circ\text{C}$. The pH value was adjusted with sulphuric acid or sodium hydroxide.

Titanium dioxide (TiO_2 , Degussa P25) under near-UV irradiation was used as a photocatalyst. If not otherwise specified, its concentration in the PCO-treated suspensions was 10 mg L^{-1} as was thoroughly selected in previous studies [14]. This concentration of photocatalyst allows observation of the adsorption and oxidation results within the measurable SE concentration range: higher concentrations of TiO_2 result in complete adsorption and rapid elimination of SEs from the solution. Centrifugation at 10,000 rpm was applied to separate the TiO_2 from the samples before the analysis.

The copollutants were added to the solutions to be treated simultaneously with the SEs. Urea and saccharose, dried at 105°C , in concentrations, respectively, of 75 and 50 mg L^{-1} , broadly reflecting normal values in domestic sewage [16], were used in the experiments. The urine-water ratio was chosen from the average human excretion of 0.06 to 0.27 L of urine per each use to a dual flush system toilet utility of 3 to 6 L of water per flush. Both the maximum of 90 mL L^{-1} and minimum of 10 mL L^{-1} concentrations of urine in water were tested for SEs removal. Diluted urine did not show a noticeable UV-absorption at 365 nm.

2.2. Methods

The PCO experiments were performed in 0.25 L capacity thermostatted batch glass reactors with an inner diameter of 100 mm supplied with a magnetic stirrer. The agitation intensity was maintained with a standard 25 mm Teflon stirrer at 300 rpm. A 365 nm UV-lamp (Sylvania F15W) was positioned horizontally over the reactor; the irradiance was about 1.1 mW cm^{-2} measured by UVX radiometer (UVX, USA). All PCO experiments were compared with reference samples treated under identical conditions except UV-radiation.

The adsorption experiments with the SEs and urea under various pH conditions were performed in 0.50 L capacity flasks, where the solutions were mixed with TiO_2 at a stirring frequency of 900 rpm for 24 hours at 25°C . Each flask was handled separately as a single-point sample. The equilibrium concentration of compounds adsorbed on the surface of the catalyst q , $\text{mg g}^{-1} \text{TiO}_2$, was calculated from the mass balance of the sample. The experiments to determine the adsorption properties of saccharose from the solution containing 250 mg L^{-1} of saccharose on 1 g L^{-1} of TiO_2 were performed for 1 hour in a similar manner.

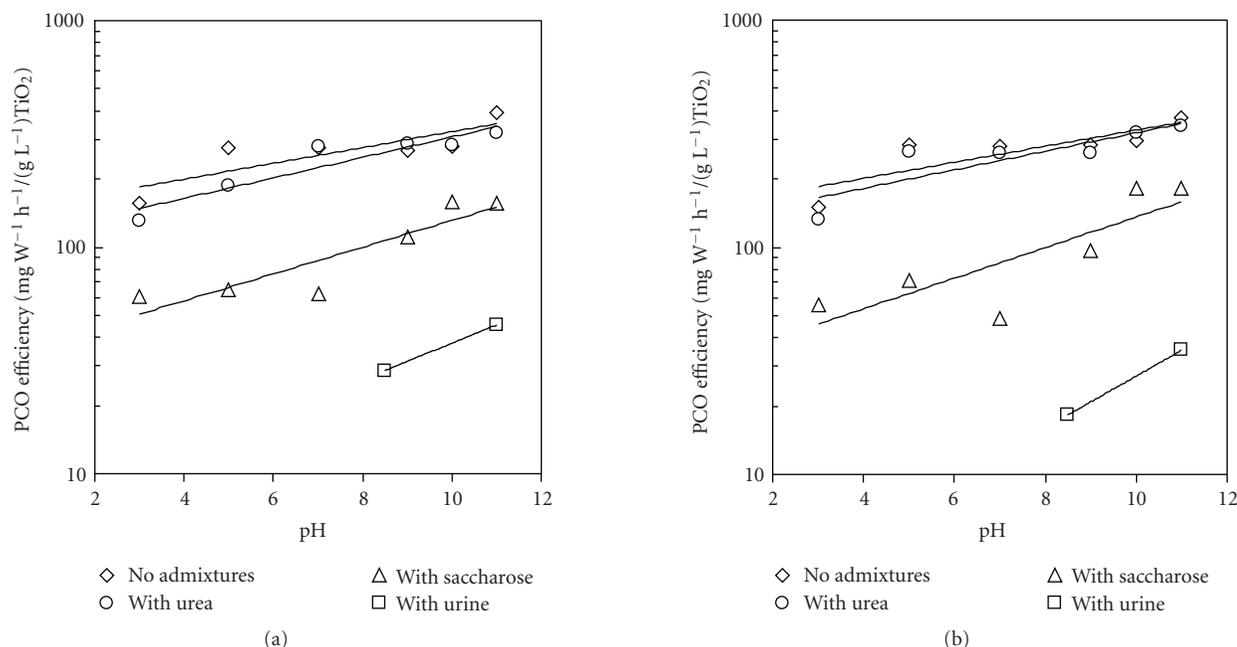


FIGURE 2: The dependence of the PCO efficiency of E2 (a) and EE2 (b) pH: treatment time 15 minutes and $10 \text{ mg L}^{-1} \text{ TiO}_2$ except urine-120 minutes and 1 g L^{-1} , respectively.

2.3. Analysis

The concentrations of SEs were measured by means of HPLC with a UV-detector using a 150 mm ZORBAX Eclipse XDB-C18 column (Agilent) at the wavelength 278 nm, mobile phase was acetonitrile-water (1 : 1) at a flow rate of 1.0 mL min^{-1} . The urea concentrations were measured according to the method described in [18], developed in [19], and modified in the present research. The 10 mL test tubes were filled with 3.5 mL of the 35-fold diluted sample, 0.25 mL of the reagent A, and stirred. The 0.8 mL of reagent B was then immediately added with subsequent stirring. The test tubes were stored at room temperature for 72 hours in the dark. The light absorbance was then measured at 520 nm. Reagent A was made of 8.5 g diacetylmonoxime in 250 mL of water together with 10 mL of solution containing 0.95 g of thiosemicarbazide in 100 mL of water (all chemicals Sigma-Aldrich). Reagent B was prepared by dissolving 300 mL of concentrated sulphuric acid in 535 mL of water with the addition of 0.5 mL of a solution containing 0.15 g of ferric chloride in 10 mL of water.

Chemical oxygen demand (COD), measured by a standard procedure [20], and total organic carbon (TOC) were determined after PCO and adsorption of saccharose. COD was also measured to observe the changes in the concentration of urine. The TOC analyses were carried out using the TOC analyzer Shimadzu 5050-A.

3. RESULTS AND DISCUSSION

The PCO was characterized by the process efficiency relative to the TiO_2 concentration calculated as the decrease in

the concentration of the SE divided by the amount of energy reaching the surface of the sample and by the concentration of the catalyst used:

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

E ($\text{mg W}^{-1} \text{ h}^{-1}$ per $\text{g L}^{-1} \text{ TiO}_2$) represents the PCO process efficiency relative to the catalyst concentration; Δc ($\mu\text{g L}^{-1}$)—decrease in the target compound concentration; V (L)—volume of treated sample; I (mW cm^{-2})—irradiation intensity; s (cm^2)—solution irradiated surface area; t (h)—treatment time; m (g L^{-1})—concentration of TiO_2 .

The dependence of the PCO efficiency of the SEs, related to the TiO_2 concentration, on pH with and without copolymers added can be seen in Figure 2. One can see that the strongly alkaline medium was the most efficient for the PCO of both natural and synthetic SEs despite the presence of admixtures.

The adsorption characteristics of the SEs on TiO_2 were carefully studied for various pH values (Figure 3). The results indicate that the adsorption of SEs increases with the increasing pH making the strongly alkaline medium beneficial.

The PCO efficiency and adsorption consistently improve with the increasing pH indicating that the PCO rate is determined by the adsorption properties of the SEs on the TiO_2 surface.

3.1. The influence of urea

Little influence of urea on the PCO efficiency of both SEs was observed; the beneficial character of the increasing pH remained (Figure 2). The observed indifference of the PCO

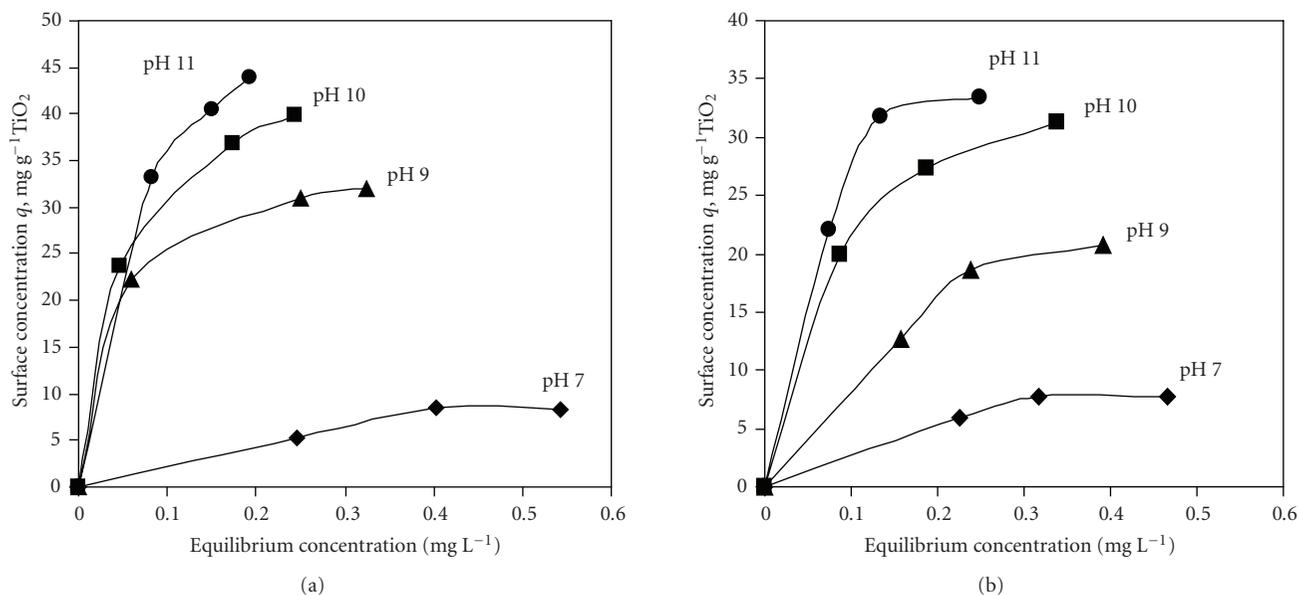


FIGURE 3: Adsorption isotherms for E2 (a) and EE2 (b) on TiO_2 catalyst surface at different pH values without co-pollutant.

of the SEs towards the presence of urea may be explained by the poor adsorption of urea at the TiO_2 surface. No detectable oxidation of urea was found within 2 hours of PCO at any of the pH values tested at the TiO_2 concentration of 10 mg L^{-1} . No changes in urea concentration were observed within the experimental time even with the catalyst concentration increase to 1 g L^{-1} .

Figure 4 shows that the presence of urea seemed to have an insignificant effect on the EE2 adsorption on TiO_2 . The effect of urea on E2 adsorption was more evident: the adsorption in presence of urea decreased although it was still of the same order of magnitude as without urea. The dependence of adsorption on pH remained similar to the previously obtained one (Figure 3), which confirmed that the PCO of the SEs depends on the adsorption properties. The difference in behavior of the two SEs may be explained by the difference in the hydrophilic properties of the two molecules: the presence of urea may have a stronger impact on the adsorption of the more hydrophilic E2 molecule than the more hydrophobic EE2. The slope of the lines of the logarithmic dependence of the surface concentrations on pH was somewhat greater in the presence of urea for both SEs, which indicates a higher sensitivity of adsorption towards pH in the presence of the admixture.

3.2. The influence of saccharose

The presence of saccharose essentially hindered the PCO efficiency of SEs for the entire pH range (Figure 2). Although the strongly alkaline medium remained the most efficient for the process, the dependence on pH appears to differ somewhat from that without copollutants: the PCO rate in strongly acidic media at pH 3, was slightly higher than in neutral

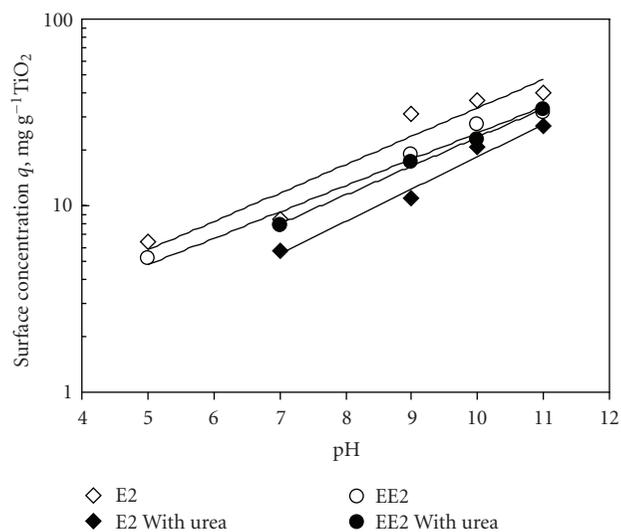


FIGURE 4: The SEs equilibrium surface concentrations on TiO_2 versus pH with and without the presence of urea (75 mg L^{-1}).

or slightly acidic ones. Since the adsorption is a prerequisite of PCO, the adsorptive properties of saccharose on TiO_2 were also studied to try to explain this deviation. The equilibrium surface concentrations versus pH for saccharose are presented in Figure 5. The best adsorption, although rather poor, was observed at pH 5, explained by the proximity to the zero charge point of TiO_2 . At pH 3, the adsorption was significantly smaller, which accounts for the better adsorption and PCO of SEs at this point. The difficulties in maintaining pH 7 in the PCO experiments may explain why the PCO

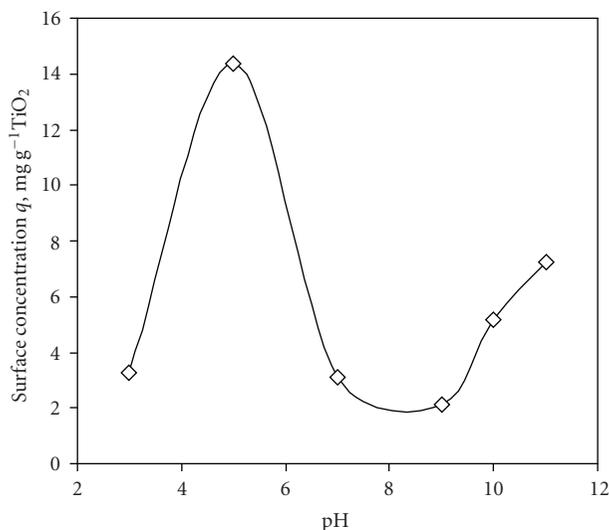


FIGURE 5: Saccharose equilibrium surface concentration on TiO_2 catalyst versus pH: initial concentration of saccharose 250 mg L^{-1} .

rates were similar at pH 5 and 7. PCO of an aqueous solution of 50 mg L^{-1} of saccharose with 10 mg L^{-1} of TiO_2 was carried out to gain the better understanding of the interactions between the SEs and saccharose. The results showed no visible degradation of COD or TOC within 4 hours. Both the catalyst and pollutant concentrations were then increased to 0.5 g L^{-1} and 150 mg L^{-1} , respectively, but only minor, around 10%, oxidation of saccharose was observed at pH 11 in 2 hours of PCO.

One can see that poor saccharose adsorption and, therefore, PCO cannot explain the interference exhibited by the saccharose in SEs' oxidation. The reduction in the PCO efficiency of SEs may thus be explained by radical scavenging properties of saccharose.

3.3. The influence of urine

The effect of urine as a copollutant on the PCO of SEs was studied under two pH conditions: pH 11 (the most beneficial for the process) and pH 8.5 (natural pH of urine diluted with the Milli-Q water). The photocatalyst concentration of 1 g L^{-1} was applied. The degradation of oxidisable substances in urine was tracked by the decrease in COD. The substances seemed not to undergo significant oxidation under the experimental conditions: the COD of the urine sample diluted 100-fold was initially around $200 \text{ mg O}_2 \text{ L}^{-1}$ and decreased by only 20 to $40 \text{ mg O}_2 \text{ L}^{-1}$ at pH 8.5 while at pH 11 remained practically unchanged within 2 hours. A more concentrated urine solution had an initial COD of $1400 \text{ mg O}_2 \text{ L}^{-1}$ and the COD did not change with PCO under the same conditions.

Initially, a urine solution with COD of $1400 \text{ mg O}_2 \text{ L}^{-1}$ was used in the experiments. Besides the negligible decrease in COD, no significant oxidation of SEs was observed within

2 hours of PCO. Presumably, the constituent compounds of urine, being resistant towards PCO, occupied the adsorption sites of the catalyst and did not allow the SEs to adsorb and oxidize under competitive adsorption conditions. The PCO degradation of SEs was clearly exhibited with the more diluted urine concentration with an initial COD of $200 \text{ mg O}_2 \text{ L}^{-1}$; the target compounds were eliminated dependent on pH as in Figure 2. Complete oxidation of E2 and 95% oxidation of EE2 were observed at pH 11 in the 2-hour experiment; around 75% of both SEs were oxidized under natural pH conditions. This result was observed with a negligible decrease in COD, which indicates that the SEs can be degraded in a selective manner by PCO in a strong alkaline medium. Greater concentrations of copollutants from urine may, however, dramatically slow down the PCO of the SEs.

3.4. The kinetic studies

The PCO of various organic compounds using UV-illuminated TiO_2 can be formally described by the monomolecular Langmuir-Hinshelwood kinetic model

$$-\frac{dc}{dt} = \frac{k \cdot K \cdot c}{1 + K \cdot c}, \quad (2)$$

dc/dt is the rate of oxidation, k is the apparent reaction rate constant, K —the adsorption coefficient of the compound to be oxidized, and c is its concentration at time t . If the concentration of the compound is very low, that is, $K \cdot c \ll 1$, which is the case in this research, the Langmuir-Hinshelwood model can be simplified to a pseudo-first-order kinetic reaction

$$-\frac{dc}{dt} = k' \cdot c, \quad (3)$$

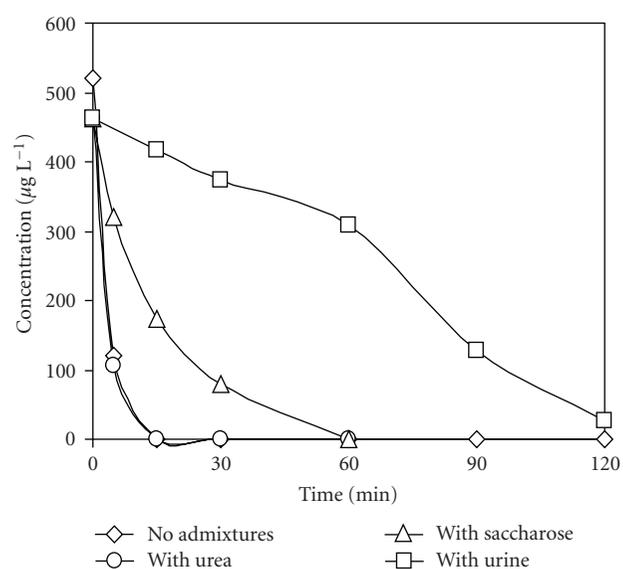
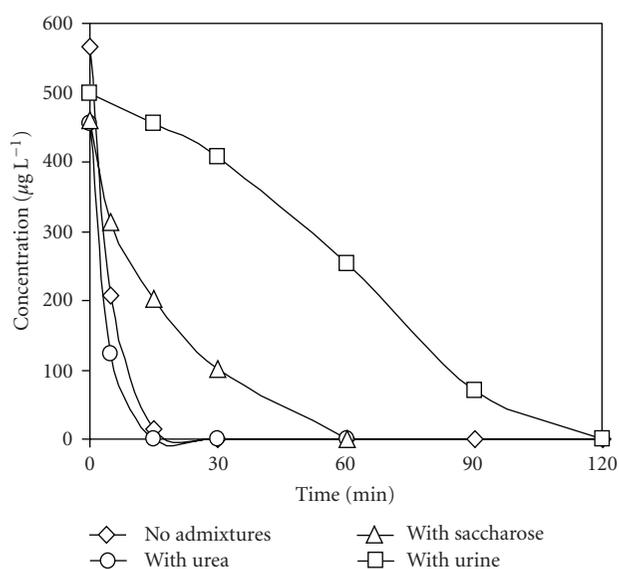
k' is the pseudo-first-order reaction rate constant ($k' = k \cdot K$).

The results of the PCO experiments of SEs solutions with and without copollutants were plotted as time in minutes against $\ln(c/c_0)$, where c_0 represents the initial concentration of the SEs. The best fit line was drawn and the equation and correlation coefficient, R^2 , were obtained. The plots demonstrated that the PCO of the SEs fitted well to the pseudo-first-order equations, which is consistent with previously published results [12, 13]. The rate constant k' was obtained from the slope and the initial rate was calculated by multiplying k' by c_0 . The half-life was then calculated. The results are presented in Table 1.

The data reveal that in the absence of copollutants the PCO of EE2 proceeded a little faster than that of E2, except for pH 11 and pH 3, where the rates are almost equal. This result is in agreement with the data of other authors: Coleman et al. [13] reported PCO rate values for acidic media (pH 3.5–4) as big as $0.522 \mu\text{mol dm}^{-3} \text{ min}^{-1}$ for E2 and $0.694 \mu\text{mol dm}^{-3} \text{ min}^{-1}$ for EE2, which, although exceeding the results given in Table 1, are of the same order of magnitude. The difference is attributed to the significantly higher UV-light intensity used by Coleman et al. [13].

TABLE 1: Kinetic parameter value for PCO of SEs with and without copollutants.

| Substance | pH | k' (min^{-1}) | Rate ($\mu\text{mol dm}^{-3} \text{min}^{-1}$) | Half-life (min) | R^2 | Substance | pH | k' (min^{-1}) | Rate ($\mu\text{mol dm}^{-3} \text{min}^{-1}$) | Half-life (min) | R^2 |
|--------------------|-----|-------------------------------|---|--------------------|-------|---------------------|-----|-------------------------------|---|--------------------|-------|
| E2 | 11 | 0.254 | 0.528 | 2.8 | 0.995 | EE2 | 11 | 0.295 | 0.519 | 2.4 | 1.000 |
| | 10 | 0.091 | 0.190 | 7.4 | 0.995 | | 10 | 0.116 | 0.205 | 5.9 | 0.999 |
| | 9 | 0.070 | 0.140 | 9.7 | 0.988 | | 9 | 0.107 | 0.188 | 6.5 | 1.000 |
| | 7 | 0.068 | 0.132 | 10.4 | 0.984 | | 7 | 0.110 | 0.191 | 6.2 | 0.999 |
| | 5 | 0.072 | 0.148 | 9.6 | 0.990 | | 5 | 0.107 | 0.184 | 6.5 | 0.999 |
| | 3 | 0.034 | 0.070 | 20.2 | 0.998 | | 3 | 0.042 | 0.070 | 16.6 | 0.997 |
| E2 with urea | 11 | 0.263 | 0.441 | 2.6 | 1.000 | EE2 with urea | 11 | 0.293 | 0.458 | 2.4 | 1.000 |
| | 10 | 0.183 | 0.290 | 3.7 | 0.986 | | 10 | 0.241 | 0.378 | 2.9 | 1.000 |
| | 9 | 1.176 | 0.290 | 3.9 | 0.990 | | 9 | 0.100 | 0.159 | 6.6 | 0.917 |
| | 7 | 0.175 | 0.278 | 3.9 | 0.993 | | 7 | 0.094 | 0.138 | 7.2 | 0.978 |
| | 5 | 0.068 | 0.116 | 10.1 | 0.987 | | 5 | 0.088 | 0.141 | 7.8 | 0.989 |
| | 3 | 0.036 | 0.058 | 19.0 | 0.996 | | 3 | 0.032 | 0.048 | 21.2 | 0.997 |
| E2 with saccharose | 11 | 0.049 | 0.083 | 13.7 | 0.992 | EE2 with saccharose | 11 | 0.058 | 0.091 | 11.88 | 0.996 |
| | 10 | 0.036 | 0.061 | 19.0 | 0.984 | | 10 | 0.050 | 0.076 | 13.7 | 0.997 |
| | 9 | 0.022 | 0.036 | 30.9 | 0.975 | | 9 | 0.018 | 0.031 | 36.3 | 0.975 |
| | 7 | 0.011 | 0.019 | 58.8 | 0.989 | | 7 | 0.009 | 0.015 | 72.6 | 0.984 |
| | 5 | 0.010 | 0.017 | 63.2 | 0.969 | | 5 | 0.011 | 0.017 | 60.1 | 0.983 |
| | 3 | 0.016 | 0.027 | 42.2 | 0.997 | | 3 | 0.015 | 0.022 | 48.0 | 0.995 |
| E2 with urine | 11 | 0.021 | 0.039 | 31.8 | 0.883 | EE2 with urine | 11 | 0.022 | 0.035 | 29.0 | 0.850 |
| | 8.5 | 0.011 | 0.019 | 62.5 | 0.967 | | 8.5 | 0.012 | 0.019 | 60.3 | 0.979 |

FIGURE 6: The rate of PCO of E2 (a) and EE2 (b) at pH 11 under different admixture conditions: 75 mg L^{-1} of urea, 50 mg L^{-1} of saccharose, 10 mL L^{-1} of urine.

In the presence of urea and saccharose, however, the rate of PCO of E2 was faster in neutral and strongly acidic media. No noticeable difference in the PCO rates of the SEs could be seen when urine was present as a copollutant. The results clearly indicate that despite the presence of copollutants, the PCO of the SEs exhibited the fastest rate under strongly alkaline media conditions. The impact of copollutants is illustrated in Figure 6, where the degradation curves of SEs are plotted for pH 11, the most beneficial pH for the process, in the presence of the admixtures under consideration. The interference of the copollutants was, nevertheless, far weaker in respect to the PCO of the SEs than could be expected from the hundred to thousands times higher concentration of the admixtures. This indicates the potential of PCO to be a selective oxidation method for the removal of SEs from wastewaters.

4. CONCLUSIONS

A strongly alkaline medium was found to be the most beneficial for the adsorption of SEs on the TiO₂ photocatalyst, which explains the most efficient PCO at high pH. The same result was observed also in the presence of urea, saccharose, and human urine.

The PCO of SEs was seen to be indifferent towards the presence of urea in concentrations commonly found in domestic sewage. Saccharose interferes with the PCO of the target compounds hindering the oxidation rate of SEs: saccharose, poorly adsorbed and oxidized photocatalytically itself, most likely acts as an OH-radical scavenger. Urine significantly decreased the PCO rate of SEs at concentrations above 1 : 100. Nevertheless, the effect of the copollutants on the PCO of SEs is far weaker than could be expected from the concentrations of the admixtures, which are from one hundred to a few thousands times higher than that of the SEs. Although higher concentrations of copollutants can dramatically slow down the PCO of SEs, realistic concentrations of urea and saccharose characteristic for the sanitary fraction of domestic sewage allowed selective removal of SEs.

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